

ELECTROCHEMICAL REDUCTION OF INDIUM OVER INDIUM TIN OXIDE
COATED GLASS BY USING RELINE AND ETHALINE DEEP EUTECTIC
SOLVENTS AS ELECTROLYTES

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BURCU KOÇ HASKILIÇ

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EUTECTIC SOLVENTS AS ELECTROLYTES**

submitted by **BURCU KOÇ HASKILIÇ** in partial fulfillment of the requirements
for the degree of **Doctor of Philosophy** in **Micro and Nanotechnology, Middle
East Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Deniz Üner
Head of the Department **Micro and Nanotechnology**

Prof. Dr. Gürkan Karakaş
Supervisor, **Micro and Nanotechnology, METU**

Prof. Dr. Ayşen Yılmaz
Co-Supervisor, **Chemistry, METU**

Examining Committee Members:

Prof. Dr. Naime Aslı Sezgi
Chemical Engineering, METU

Prof. Dr. Gürkan Karakaş
Chemical Engineering, METU

Prof. Dr. Almıla Güvenç Yazıcıoğlu
Mechanical Engineering, METU

Prof. Dr. Niyazi Alper Tapan
Chemical Engineering, Gazi University

Prof. Dr. Ayşe Bayrakçeken Yurtcan
Chemical Engineering, Atatürk University

Date: 03.08.2023



I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name Last name : Burcu Koç Haskılıç

Signature :

ABSTRACT

ELECTROCHEMICAL REDUCTION OF INDIUM OVER INDIUM TIN OXIDE COATED GLASS BY USING RELINE AND ETHALINE DEEP EUTECTIC SOLVENTS AS ELECTROLYTES

Koç Haskılıç, Burcu
Doctor of Philosophy, Micro Nanotechnology
Supervisor: Prof. Dr. Gürkan Karakaş
Co-Supervisor: Prof. Dr. Ayşen Yılmaz

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Indium tin oxide (ITO) is a common material used in many optical and electronic applications because of its high conductivity and transparency. ITO coated glass preferred as a substrate to deposit metal oxide films for photocatalytic applications. In this study, zinc and zinc oxide were aimed to electrodeposited on ITO substrate using different compositions of deep eutectic solvent (DES) electrolytes. The surfaces were then characterized using various techniques. The influence of the electrolyte's ionic structure, concentration, and pH on the ITO cathode's deposition mechanism was discussed. Zinc deposits were observed in aqueous solutions, while indium reduction occurred using DES as electrolytes. This observation is significant as indium is expensive and limited in resources, making recovery from secondary products crucial for sustainability.

It was found that using cathodic electrochemical treatment of ITO electrodes at -1.6 V deposition voltage and 80°C temperature in pure reline, pure ethaline, and their aqueous solutions with ZnCl_2 as a supporting electrolyte resulted in the separation of indium metal from ITO. Another finding is that the zinc deposition depends on both the water and ZnCl_2 concentrations of the reline solution. This study significant

for understanding the electronic structure between the cathode and electrolyte interface, which is suggested more complicated than the one in traditional aqueous electrolytes explained by classical double layer theory. The reduction of indium in ITO occurs in one step ($\text{In}^{+3} \rightarrow \text{In}^0$), which was oxidized in two steps ($\text{In}^0 \rightarrow \text{In}^+ \rightarrow \text{In}^{+3}$). This one-step method offers an economical and efficient approach for recovering valuable indium from secondary ITO products.

Keywords: Electrochemical Reduction, Indium Tin Oxide, Indium Recovery, Deep Eutectic Solution Electrolytes



ÖZ

ELEKTROLİT OLARAK RELİN VE ETALİN DERİN ÖTEKTİK ÇÖZÜCÜLER KULLANILARAK İNDİYUM KALAY OKSİT KAPLI CAM ÜZERİNDEKİ İNDİYUMUN ELEKTROKİMYASAL İNDİRGENMESİ

Koç Haskılıç, Burcu
Doktora, Mikro ve Nanoteknoloji
Tez Yöneticisi: Prof. Dr. Gürkan Karakaş
Ortak Tez Yöneticisi: Prof. Dr. Ayşen Yılmaz

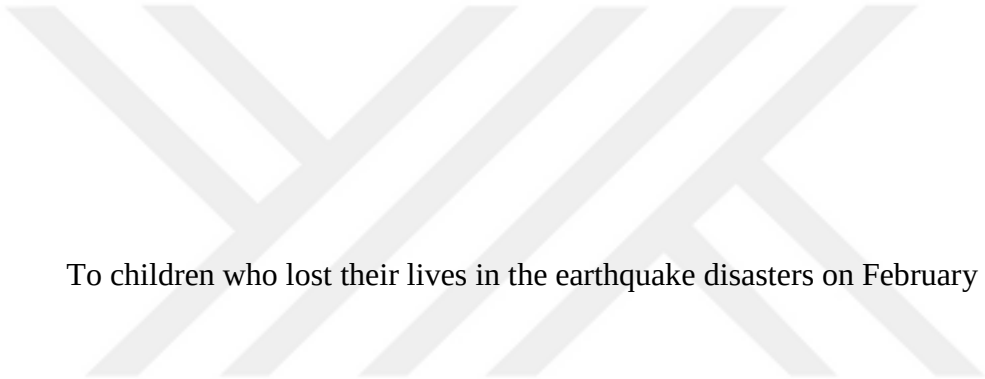
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İndiyum kalay oksit (ITO), yüksek iletkenliği ve şeffaf yapısı nedeniyle birçok optik ve elektronik uygulamada kullanılan yaygın bir malzemedir. ITO kaplı cam, fotokatalitik uygulamalar için metal oksit film biriktirmede altlık olarak tercih edilmektedir. Bu çalışma kapsamında, çinko ve çinko oksit yapılarının farklı derin ötektik çözücü (DES) elektrolit bileşimleri kullanılarak ITO kaplı cam numuneleri üzerinde elektrokimyasal olarak çökeltilmesi hedeflenmiştir. Yüzeyler daha sonra çeşitli teknikler kullanılarak karakterize edilmiştir. Elektrolitin iyonik yapısının, konsantrasyonunun ve pH'ının ITO katodunun biriktirme mekanizması üzerindeki etkisi tartışılmıştır. Sulu çözeltilerde çinko birikintileri gözlenirken, elektrolit olarak DES kullanılarak indiyum indirgenmesi meydana gelmiştir. Bu gözlem indiyum metalinin pahalı olması ve kaynaklarının sınırlı olması nedeniyle, bu metalin ikincil ürünlerden geri kazanımı sürdürülebilirlik için çok önemli hale getirmektedir.

Çalışmanın sonucunda ITO elektrotlarının 1,6 V biriktirme voltajında ve 80°C sıcaklıkta saf relin, saf etalin ve bunların destekleyici elektrolit olarak $ZnCl_2$ ile sulu çözeltilerinde katodik elektrokimyasal işleme tabi tutulmasının, indiyum metalinin

ITO'dan ayrılmasıyla sonuçlandırıldı deęerlendirilmiřtir. Dięer bir bulgu ise, inko birikimi ve indiyum indirgenmesinin elektrolit özeltisi ierisindeki su ve ZnCl_2 konsantrasyonlarına baęlı olmasıdır. Bu alıřma, klasik ift tabaka teorisi ile aıklanan geleneksel sulu elektrolitlerdekinden farklı olarak daha karmařık olduęu gözlemlenen katot ve elektrolit arayüzü arasındaki elektronik yapının anlařılması aısından önem arz etmektedir. Döngüsel voltametri alıřmaları indirgeme tepkimesinin tek reaksiyon adımımda ($\text{In}^{+3} \rightarrow \text{In}^0$), metalik indiyum oksidasyonunun ise iki adımda ($\text{In}^0 \rightarrow \text{In}^+ \rightarrow \text{In}^{+3}$) gerekleřtięini göstermektedir. Bu tek basamaklı yöntem, ikincil ITO ürünlerinden deęerli indiyumun geri kazanılması iin ekonomik ve verimli bir yaklařım sunmaktadır.

Anahtar Kelimeler: Elektrokimyasal İndirgeme, İndiyum Kalay Oksit, İndiyum Geri Kazanımı, Derin Ötektik özelti Elektrolitleri



To children who lost their lives in the earthquake disasters on February 6, 2023

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LIST OF ABBREVIATIONS

BE	Binding energy
CB	Conduction band
CE	Counter electrode
ChCl	Cholibe chloride
CIGS	Copper indium gallium selenide
CV	Cyclic voltammetry
D	Grain size
DC	Direct current
DES	Deep eutectic solvent
DSSC	Dye-sensitized solar cells
EDL	Electrical double layer
EDS	Energy dispersive X-ray spectrometry
EEE	Electric and Electronic Equipment
EG	Ethylene glycol
EPSR	Empirical potential structure refinement
eV	Electron volt
FTO	Fluorine doped tin oxide
GCS	Gouy-Chapman-Stern
HBA	Hydrogen-bond acceptor
HBD	Hydrogen bond donor

HBD	Hydrogen-bond donor
HRTEM	High resolution transmission electron microscope
IL	Ionic liquid
ITO	Indium doped tin oxide
K	Kelvin
LCD	Liquid-crystal display
M	Molar
mM	Milimolar
MR	Molar ratio
nm	nanometer
OLED	Organic light-emitting diode
OPD	Overpotential deposition
PEG	Poly ethylene glycol
R&D	Research and development
RE	Reference electrode
Rpm	Revolutions per minute
RTIL	Room temperature ionic liquids
SAED	Selected area (electron) diffraction
SEM	Scanning electron microscope
SPR	Surface plasmon resonance
SHE	Standard hydrogen electrode
TCO	Transparent conducting oxides

TEM	Transmission electron microscope
u	Internal parameter
U	Urea
UPD	Underpotential deposition
UV	Ultraviolet
V	Volt
VB	Valence band
WE	Working electrode
WEEE	Waste Electric and Electronic Equipment
XPS	X ray photoelectron spectroscopy
XRD	X ray diffractometer

LIST OF SYMBOLS

SYMBOLS

μA	Mikroampere
a_0	Crystallite width along the a-axis
c_0	Crystallite width along the c-axis
Cat^+	Cation
E^{eq}	Equilibrium potential
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
Mn^+	Metal ions
v_{scan}	Sweep rate
β	Broadening of diffraction line measured at the half of its maximum intensity
θ	Angle of diffraction
κ	Scherrer constant
λ	X-ray wavelength

CHAPTER 1

INTRODUCTION

Zinc oxide (ZnO) is a semiconducting metal oxide widely used as a photocatalyst. It can generate electron-hole pairs necessary for redox reactions based on the absorption of sunlight. ZnO has a wide bandgap of 3.37 eV and a large exciton binding energy of about 60 meV at room temperature (Hwang et al., 2007). However, the large bandgap only allows it to benefit from a small part of the sunlight, and very high electron-hole recombination rates limits its photon efficiency on photocatalytic activity.

There are several different methods for manufacturing ZnO nanostructures from 1D to 3D; such as chemical vapor deposition (Bae et al., 2004), molecular beam epitaxy (Peterson et al., 2004), and RF magnetron sputtering (Kuo et al., 2009). Different wet chemical techniques are also employed for zinc oxide synthesis to obtain different morphologies. Among them, electrochemical deposition stands out as being very appealing due to its affordability and excellent control over ZnO particle morphology (Sanchez et al., 2012).

ZnO-coated transparent materials, such as glass, are more preferred for photocatalytic materials than suspended catalyst reactors. One major disadvantage of using ZnO nanoparticles in suspension is the difficulty of separation and recovery of the particles from liquid phase. Additionally, suspensions have a low quantum efficiency due to the high recombination rate of the hole-electron pairs and photon accessibility (Lai & Lee, 2008). Thin films of ZnO are superior photocatalyst because they have several advantages, such as quick electron transport and homogeneous exposure of the photocatalyst, the ability to deposit the photocatalyst over varied substrates, efficient solar energy absorption, and a high surface area (Cruz et al.,

2018). Therefore, ZnO thin films typically deposited on transparent substrates have been extensively studied, primarily for waste water treatment.

The electrodeposition method is a promising technique to prepare ZnO thin films on an ITO-coated glass substrate due to its simplicity and economic affordability. Electrodeposition of ZnO onto transparent conducting oxide (TCO) substrates, such as glass plates covered with indium-tin oxide (ITO) or F-doped SnO₂ (FTO) surfaces are widely used as a cathode and electrodeposition is applied by using aqueous electrolytes (Xu et al., 2009; Maleki-Ghaleh et al., 2016; Skompska & Zarebska, 2014). By this way, indium tin oxide (ITO) coated glasses are both served as substrates for electrodeposition of thin films and working electrode for electrodeposition. The electrochemical and chemical stability of the interfaces between electrolyte and ITO surface is important for determining the final deposit.

Researchers have noted that the photocatalytic activity of thin films depends on the morphology, crystal composition, crystallinity, and surface area of the zinc oxide layer. Among these factors, surface morphology appears to be more important than surface area in achieving higher photocatalytic activity (Ali et al., 2010; Li & Haneda, 2003). Among its low cost and ease of application, electrodeposition also allows precise control over the morphology, size, and density of the ZnO nanoparticles onto the substrate. This might be performed by experimenting with various electrodeposition parameters such as electrolyte composition, precursor concentration, bath temperature, applied current density, and potential. Typically, ZnO is electrodeposited from an aqueous salt solution and an oxygen precursor at temperatures below 100°C (Sanchez et al., 2012). Hydrogen peroxide (Pauporté & Lincot, 2001), zinc nitrate (Izaki & Omi, 1996), or molecular oxygen might be used as an oxygen source (Peulon, & Lincot, 1998). The starting point of this work was to show that shape- and size controlled ZnO nanoparticles can be deposited by using nonaqueous electrolyte solutions.

Ionic liquids (ILs) can be used as electrolytes in electrodeposition to accelerate nucleation, surface diffusion, and crystallization, providing a prominent alternative

to traditional aqueous electrolytes. Ionic liquids have several advantages over aqueous media, including higher electrochemical stability, lower vapor pressure, and wider electrochemical potential windows which is also investigated mostly as electrolyte (Endres et al., 2017). ILs also allow for the formation of different crystal structures and provide more homogeneous, crack-free, and mechanically stable depositions without hydrogen evolution.

Deep eutectic solvents (DESs) are analogs of ILs that are gaining popularity for electrochemical applications for zinc metal and its oxide (Dumitru et al., 2016 and Abbott et al., 2007). Although DESs have physical characteristics that are similar to those of other ILs, their chemical characteristics have very different application areas (Abbott et al., 2007). DESs are made up of carefully chosen combinations of two or more components, specifically hydrogen-bond acceptors (HBA) and hydrogen-bond donors (HBD), that can combine to form eutectic mixtures (Amoroso et al., 2021). The large, nonsymmetric ions in DESs have low lattice energy and hence, low melting points. In addition to their nontoxic, biodegradable structure and ease of synthesis compared to other ILs, their strong network of intermolecular forces plays an important role on the mechanism electrochemical reactions. The hydrogen bondings between the constituents of DES serve as an electrolyte source for shape and size directing influence during electrochemical treatment. In this study, reline and ethaline, both choline chloride-based DESs, were studied as electrolytes in zinc electrochemical deposition.

The established electrodeposition techniques rely on zinc salts as a source of zinc ions and other salts as supporting electrolytes to grow ZnO nanostructures. The identity of the anion can strongly influence the electrochemical pathway via changing the morphology, dimension of the final deposit and deposition rate (Smith et al., 2014). Salts that contain chloride (Peulon & Lincot, 1998) and nitrate (Izaki & Omi, 1996) are typically used in literature. Anions may either adsorb onto the electrode or penetrate between the electrode-electrolyte interphase and bond to the cations in the electrolyte, making it difficult for the target ions to reach the surface.

In this study, ZnCl_2 was used as the zinc precursor in a ChCl based DES, where both have the same Cl^- anion in order to eliminate other anions and their counter effects.

The electrochemical treatment of ITO electrodes in DES-based solutions is a highly complex process that requires a thorough understanding of the underlying electrochemical mechanisms and kinetic processes. In order to investigate size and shape controlled ZnO electrodeposition on an ITO-coated glass substrate, deposition parameters were carefully selected. To reduce the viscosity of the DES and resolve mass transfer problems, a relatively high temperature is preferred for electrodeposition (Zhang et al., 2012). The investigation was done in either an aqueous solution or in ChCl -based DES solutions containing ZnCl_2 precursor at 80°C with a -1.6 V applied potential. After electrodeposition for 30 minutes, sample surfaces were characterized with X-Ray Diffractometer, Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The characterization results were examined comparatively that are obtained both in aqueous solution and in DES under applied deposition conditions.

According to the characterization studies, very dense zinc metal and zinc oxide deposition was obtained in aqueous solution in line with literature. However, no zinc metal or any zinc compound was achieved on the cathode in electrochemical studies in both DES, reline and ethaline, under same deposition parameters. This finding demonstrated that hydrogen bond donors (HBDs) in the DES structure adsorbed on the ITO surface thus blocked the adhesion of zinc ions onto the substrate surface.

More interesting finding of this study is that under the applied electrochemical process conditions, phase separation of ITO on the surface of the working electrode observed and indium metal was reduced in both reline and ethaline. The results of the investigations were also made into another focus of this study in addition to zinc oxide deposition because indium is a critical raw material with economic importance and a high supply risk (Pereira et al., 2018). Electrochemical reduction of indium from ITO has also been studied in various electrolytes in literature since indium is

reported as at a bottleneck in the supply and demand. Metal recovery using electrolysis from aqueous solutions involves hydrogen gas formation, causing unstable deposits and structures like dendritic growth and hydrogen embrittlement (Walsh & Gabe, 1979). In addition, molten salt electrolysis is an excellent electrolyte for extracting and refining metals and alloys, but CO₂ generation and high-temperature operation require resolution (Su et al., 2022).

The electrochemical treatment of ITO electrodes in DES based solutions is a highly complex phenomenon that requires a thorough understanding of the underlying electrochemical mechanism and kinetic processes. To that end, this research aimed to provide a comprehensive analysis of the chemical composition changes that occur on ITO working electrodes, as well as the deposition of zinc and reduction of indium mechanisms under comparable conditions in hydrated DES with its pure form was also investigated.

Mixing controlled amounts of water with DES may be a practical way of modifying and designing electrolyte properties so as to adjust electrostatic interactions between DESs and electrode surfaces (Shah & Mjalli, 2014). Reline is hygroscopic material and literature suggests that the presence of water significantly affects its hydrogen bonding interactions, providing an opportunity to tune reactions in an electrodeposition systems. This study also focuses on fundamental aspects of zinc oxide nucleation and growth mechanisms on ITO, as well as indium reduction mechanism from the ITO surface in hydrated reline electrolytes and the results are compared with pure reline. The results showed that the presence of water in reline can significantly effect on hydrogen hydrogen bonding interactions of reline and indium reduction. By controlling the amount of water added, it is possible to manipulate the zinc deposition and indium reduction.

The electrochemical reactions occurred on the ITO cathode in pure and aqueous reline electrolytes were investigated by using cyclic voltammetry (CV). Chemical compositional analysis of the surface, morphological effect, and recovery rate were also studied for the same purpose. Therefore, relative surface analysis was performed

for the samples treated in aqueous solution, reline, and hydrated/aqueous reline solution to determine the elemental composition of the outermost atomic layer of the sample surface by means of X-ray photoelectron spectroscopy (XPS).

Another innovative aspect involves not only comparing different types of electrolytes but also conducting a systematic review of the effects of various other parameters on indium reduction. These parameters include the quantity of ZnCl_2 and water in the electrolyte, the pH value of the electrolyte, and the duration of the electrochemical experiment. Furthermore, the study investigates the changes in the electrode-electrolyte interface and their effects on zinc electrodeposition on the surface, in addition to changes in the ITO structure during electrochemical application. Finally, change in optical and electrical properties were discussed for the electrochemically processed ITO film in various reline solutions were discussed.

The results of this comprehensive analysis on various electrochemical parameters, including electrolyte type such as aqueous electrolyte, DES, and hydrated DES under comparable conditions, post heat treatment effect on electrodeposited films, electrolyte pH, deposition time, and ZnCl_2 concentration effect on chemical composition changes that occur on ITO working electrodes, as well as the deposition of zinc and their results, were discussed in the related section in this order in view of both zinc deposition and indium reduction.

This study is significant because this is the first publication that discusses the concentrated modification or change of ITO film during electrodeposition of ZnO in deep eutectic solvent by discussing electrochemical mechanisms in accordance with electrochemical parameters. According to the best of our knowledge, this is the first study reporting a thorough and systematic experimental study of electrochemistry with the aim of developing guidelines for appropriate DES type electrolyte selection for efficient indium recovery.

1.1 Motivation and Objective

Zinc oxide is a popular photocatalyst that creates electron-hole pairs when exposed to sunlight, which are necessary for redox reactions. However, its wide bandgap and high electron-hole recombination rates limit its photon efficiency in photocatalytic activity.

Recent research suggests that the surface morphology of ZnO plays a crucial role in determining its photocatalytic activity. Therefore, the main objective of this study is to control the shape, size, and arrangement of ZnO particles. For this purpose, the electrodeposition method was selected as it allows for precise control of particle morphology by adjusting deposition parameters. In this study, choline chloride-based deep eutectic solvents (DESs) were used as electrolytes due to their strong hydrogen bonding network, which can serve as a shape and size directing agent.

However, unexpected results were obtained during the study. Characterization studies revealed that no zinc was achieved on the cathode in reline and ethaline. Instead, the study discovered that indium was reduced from ITO on the working electrode. The recovery of indium, which is an economically important raw material with a high supply risk, was also investigated in this research.

This study is significant because, to our knowledge, it is the first publication on the modification of ITO film during the electrodeposition of ZnO in a deep eutectic solvent by systematically observing either zinc deposition or indium reduction with various electrochemical parameters.

CHAPTER 2

LITERATURE REVIEW

As outlined in the introduction, this study has made significant contributions to the existing literature on both zinc oxide coatings and indium reduction using deep eutectic solvents. This chapter of the thesis will delve deeper into these topics, examining the research conducted under the broad headings of zinc oxide semiconductor coatings, the use of ILs and DESs as electrolytes, and the reduction of indium from indium tin oxide (ITO).

Zinc oxide semiconductor coatings have been found to have a diverse range of uses in various fields, including solar cells, sensors, and optoelectronics. This chapter will explore the various methods used to produce these coatings and investigate their properties and potential applications.

In addition, the use of ILs and DESs as electrolytes has been studied extensively in recent years because of the fact that their special properties, such as low toxicity and high conductivity. This chapter will discuss the research conducted on the use of these solvents in electrochemical experiments related to zinc oxide coatings and indium reduction.

Lastly, the reduction of indium from ITO is an important research topic due to the high demand for indium in various industries. This chapter will examine the various methods used to reduce indium, including the use of DES, and investigate the properties of the resulting samples.

Overall, this chapter will provide a comprehensive overview of the research conducted on zinc oxide coatings and indium reduction using deep eutectic solvents, and their potential applications in various fields.

2.1 Zinc Oxide (ZnO) Thin Films

Zinc oxide (ZnO) is a significant material for semiconductor application areas because to its direct and broad band gap in the near-UV spectral region, as well as its strong free-exciton binding energy, which enables excitonic emission processes to continue at or even above room temperature. In the visible range of the spectrum, single crystals of ZnO can be fully transparent. Moreover, it exhibits significant absorption in the near ultraviolet, which is related to the photoconduction feature of single crystal ZnO (Thomas, 1960).

Zinc oxide has three crystallographic phase structures: hexagonal wurtzite, cubic Zn mixture, and cubic rock salt. Among these phases, zinc oxide commonly crystallizes in wurtzite-type structure ($a = 3.25 \text{ \AA}$, $c = 5.12 \text{ \AA}$) that is most thermodynamically stable at ambient conditions. The hexagonal space groups generate ZnO crystals, which may be characterized as a series of alternating planes made of tetrahedrally linked O^{2-} and Zn^{+2} settling along the c-axis. ZnO crystal is formed by hexagonal space groups that can be described as a number of alternating planes composed of tetrahedrally coordinated settled along the c-axis. The d-orbital electrons of the zinc atoms hybridize with the p-orbital electrons of oxygen atoms.

Because of its unusual physical and chemical characteristics, zinc oxide has become an established metal oxide material with remarkable biodegradable, semiconducting, optical, photocatalytic, resistant switching, and piezoelectric capabilities (Laurenti Cauda, 2018). Table 2.1 (Pearson et al., 2005) gives a brief overview of basic physical parameters for ZnO. ZnO is indeed an n-type semiconductor with a substantial exciton binding energy and a broad bandgap of 3.37 eV at ambient temperature. ZnO is a white powder with an odorless molecular mass of 81.38 g/mol.

ZnO has been studied as a semiconductor in electrical devices since antiquity. Yet, the inability to regulate its electrical properties has presented difficulties for researchers in this sector. Many investigations on the performance of ZnO single crystal substrates and multilayer films have been carried out to resolve these issues.

The goal of these investigations is to expand the usage of ZnO as an optoelectronic or electronic component. In addition, scientists have been attempting to get a greater awareness of the significance of lattice defects and impurities within ZnO semiconductor materials. This is critical for regulating n-type conductivity and acquiring p-type conductivity, both of which are required for a variety of applications. The Janotti & Van de Walle (2009) study sheds light on these issues and provides insights into how ZnO can be optimized for use in electronic devices.

ZnO is a semiconductor material with a high exciton binding energy of approximately 60 meV (Wang et al., 2021). Unlike other semiconductor materials with small exciton binding energies, ZnO is capable of ensuring efficient excitonic emission and exciton stability even at high temperatures. These features make ZnO a suitable material for excitonic device applications at room temperature, as noted by Sun et al. in their study published in 2002.

ZnO also exhibits outstanding chemical stability, which favors photocorrosion resistance. Additionally, ZnO has a high thermal stability due to its melting point of 1975°C, as shown in Table 2.1. Because of its low cost, abundance in nature, environmental friendliness, and simple fabrication process, ZnO thin film is commercially preferred in most nanotechnology applications. All of these favorable properties make ZnO an excellent candidate for photocatalysts (Saravanan & Dubey, 2022), UV detectors (Boruah, 2019), light-emitting diodes (Hwang et al., 2007), and dye-sensitized solar cells (DSSC) (Anta et al., 2012).

Table 2.1 Physical parameters of ZnO (Pearson et al., 2005)

Physical Parameters	Values
Lattice parameters at 300 K	
a_0	0.32495 nm
c_0	0.52069 nm
a_0/c_0	1602 (ideal hexagonal structure shows 1.633)
Density	5.606 g/cm ³
Stable phase at 300 K	Wurtzite
Melting point	1975 °C
Thermal conductivity	0.6, 1–1.2 Wm ⁻¹ °C ⁻¹
Linear expansion coefficient (/°C)	a_0 : $6.5 \text{ cm}^3 \times 10^{-6}$
	c_0 : $3.0 \text{ cm}^3 \times 10^{-6}$
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap (RT)	3.37 eV, direct
Exciton binding energy	60 meV
Electron Hall mobility at 300 K for low n-type conductivity	200 cm ² /V s
Hole Hall mobility at 300 K for low p-type conductivity	5–50 cm ² /V s

2.1.1 Zinc Oxide Application Areas

Together with the physical features listed above, ZnO has a wide variety of applications and uses for several commercially essential reasons including such thermo-mechanical durability, availability of doping, non-toxicity, ease of supply, and low cost. Because of its electrical sensitivity to particular gases, it is a promising

candidate for chemical or gas sensor applications (O'Brien et al., 2010). Single crystals, sintered pellets, nanoparticles, nanorods, thick and thin films, and other materials are appropriate for use as gas sensors. Infact, ZnO thin films are the favored form for usage in sensors due to their simplicity of production.

Even at high temperatures, ZnO has a large band gap and robust emission processes. The biggest difficulty in developing ZnO-based TCOs is determining the appropriate metal dopants and optimal content for optimum electrical conductivity (Jayathilake & Peiris, 2018). By incorporating group III elements inside the ZnO structure, resistivity may be greatly reduced, making it a viable low-cost TCO for electrical and optoelectronic purposes (Liu et al., 2013).

In addition to their optical properties, ZnO nanoparticles are also used as a powerful photocatalytic and photo-oxide compound against chemical and biological species due to their chemical properties. Additionally, zinc ions throughout the kind of Zn^{+2} are a vital trace element present in human body components such as muscle, bone, skin, and dental hard tissues (Pushpalatha, 2022). Similarly, it is known that ZnO-based structures in the form of bulk phase and nanoparticles are biodegradable in the body. Because of these features, zinc oxide in the field of health therapeutic carriers, biological detection, gene transfer, nanomedicic discovery, biological labeling, medical implant coatings, electronic sensors, waste water treatment. (Mandal, et al.,2022)

Zinc oxide is used in the makeup business as a sunblock because of its broad-spectrum UV protection and chalky white appearance. Sunscreens contain ultraviolet blocking agents, such as TiO_2 and ZnO nanoscale particulates, which provide broad-spectrum UV protection, seamless application, and a transparent look. Even a 100-nm decrease in particle size improved cosmesis, there are raising concerns about systemic toxins and oxidative stress (Adler et al., 2020).

The current situation's dramatically rising energy demand has sparked a lot of interest in the creation and improvement of more effective energy production and storing technologies. Supercapacitors and ultracapacitors have developed over the

past few decades, and they have the ability to lead to significant improvements in energy storage. Supercapacitors are a hopeful technology with possible uses in space or defense equipment, hybrid cars, backup energy systems, and portable gadgets (Dhanemozhi, et al., 2017). ZnO based composites are the favourable material for supercapacitor applications due to an excellent capacitance behavior, low equivalent series resistance and easy ionic diffusion into the composite.

Zinc oxide has been a topic of interest due to its luminescence properties and its potential applications in the electrical and optoelectronic fields. Its unique properties have led to its use in ultraviolet light-emitting diodes, laser diodes, and dye-sensitized solar cells (Pawar et al., 2009). Researchers have made significant advances in the field of Dye-sensitized Solar Cells (DSSCs) since ZnO was first used as a photoanode. One of the key reasons for this is ZnO's large excitation binding energy, which makes it an ideal material to be used in DSSCs. Another important factor is that ZnO is relatively inexpensive, which has made it an attractive option for researchers. Furthermore, ZnO is stable against photocorrosion, making it a reliable choice for use in DSSCs (Tsubomura et al., 1976).

ZnO, or zinc oxide, has long been a subject of study in the scientific community. In 2012, Anta et al. discovered that organic molecules were able to inject electrons into the conduction band of the wide band gap semiconductor. This discovery opened up a world of possibilities for the development of new photoanode designs for dye-sensitized solar cells (DSSCs). Due to its diverse range of morphologies, ZnO is a versatile material that can be used to create a variety of photoanodes. Furthermore, ZnO has been identified as a promising candidate for ultraviolet light-emitting devices thanks to its wide band gap and exciton binding energy (Pawar et al., 2009).

Since the 1990s, researchers have been exploring the use of optically pumped random lasers in a range of ZnO structures, including thin films, nanoparticles, and nanowires. These structures have been produced on a wide variety of substrates, such as Al₂O₃, SiC, GaN, and metal, expanding the potential applications for ZnO even further (Liu et al., 2014).

It is necessary to address the environmental pollution and energy shortage brought on by the continued expansion of the world's people and economy. As a result, photocatalysis is recognized as a key enabling technology for uses such as energy storage and pollutant degradation. Zinc oxide is favored in photocatalytic studies over alternative semiconductors such as TiO_2 , WO_3 , Bi_2O_3 , and Fe_2O_3 due to its low cost, good mechanical-thermal capacity, elevated photosensitivity, moderate redox potential, broad bandgap providing an outstanding driving force to induce redox reactions, and high quantum efficiency (Kumar & Rao, 2015). Moreover, it is non-toxic, readily crystallizes, and may be produced in a variety of forms from diverse precursors.

The photocatalytic mechanism, which is an important process in environmental remediation, is initiated by the excitation of ZnO with photons. This creates excited electron-hole pairs in the CB and VB, respectively. The positive-hole then disrupts the water molecule to form a proton and a hydroxyl radical. This hydroxyl radical is then responsible for directly trapping the organic pollutant for further oxidation. In addition to this, the photogenerated electrons react with adsorbed oxygen molecules at the surface to form super oxide anion ($\cdot\text{O}_2^-$), hydroperoxy ($\cdot\text{OH}_2$), and hydroxyl ($\cdot\text{OH}$) radicals. These radicals are also strong oxidizing agents that can aid in the decomposition of organic pollutants as well as the cell walls of microorganisms. As Adhikari et al. (2014) have noted, this process has been shown to be effective in environmental remediation efforts and has the potential to be a major tool in addressing environmental concerns.

Although ZnO is widely used in photocatalytic degradation, it is important to consider its limitations in such studies (Yadav et al., 2022). ZnO is only able to absorb UV light, so it cannot absorb the visible portion of the solar spectrum due to its wide band gap. As a result, a very limited portion of solar energy can be utilized for photocatalytic reactions, as only around 3 to 5% of UV light is able to reach the earth. This restricts the efficiency of photocatalytic reactions and lowers the degradation rate. Another drawback is that ZnO has a high recombination rate of charge carriers, which also decreases the degradation rate. Furthermore, the low

surface area of ZnO poses a problem due to its tendency to aggregate during catalytic reactions, further reducing its effectiveness. Finally, ZnO is also unstable in acidic conditions, which can limit its practical applications in certain contexts.

To address the challenges associated with ZnO nanostructures, researchers have explored various strategies. One approach is to exert control over the morphology, shape, and crystal size of the structures, as demonstrated by studies such as those conducted by Shinde et al. (2011) and Casey et al. (2006). Another avenue of exploration involves combining ZnO with other semiconductors, as seen in the work of Tian et al. (2009). Additionally, doping ZnO with metals or heteroatoms has been shown to be effective in overcoming these drawbacks, as demonstrated by Zheng et al. (2008). Finally, researchers have also sought to increase oxygen vacancies or defects through the use of different synthesis techniques or by changing synthesis parameters, as demonstrated by Zheng et al. (2008) and other studies.

Mclaren and coworkers (2009) investigate the shape, orientation and size effects on photocatalytic activity of ZnO nanostructures. The researchers discovered that hexagonal plate-like nanoparticles with polar faces demonstrated a higher photocatalytic decomposition of methylene blue dye compared to rod-shaped particles with non-polar faces. Interestingly, the study also focused on the size effect and revealed that particle size had only a minor impact on the activity, while the shape factor was considerably more dominant. The mechanism behind the shape effect can be explained by the higher positive energy of the (001) polar face that absorbs OH^- ions, thus triggering the production of $\cdot\text{OH}^-$ radicals for degrading the organic pollutants or dye in the system. This means that the polar face of hexagonal nanoparticles is more reactive and efficient in the photocatalytic reaction, which is an important finding that can be applied to the development of more effective photocatalytic systems.

In conclusion, the use of ZnO as photocatalysis offers great potential for resolving many of today's environmental and energy-related issues in a variety of applications. A good photocatalyst should make efficient use of light, be secure, and be reasonably

priced. One benefit of using ZnO as a photocatalyst is its versatility in different applications. For instance, ZnO nanoparticles have been used in wastewater treatment, air purification, and solar cell technology. Additionally, researchers have found that ZnO's performance can be improved by altering its particulate size, morphology, and porosity during synthesis. By controlling these variables, the photocatalytic activity of ZnO can be optimized for a specific application. Furthermore, it is worth noting that the properties of ZnO nanoparticles are largely determined by their morphology. Therefore, choosing the appropriate manufacturing method is crucial for tailoring the morphology and properties of ZnO nanoparticles.

2.1.2 Synthesis Approaches for Zinc Oxide Thin Film

Photocatalytic and semiconductor thin film technology is a versatile and adaptable solution for a wide range of applications. One of its key advantages is its flexibility, which makes it an ideal choice for industries that require a versatile material. This technology is used for water treatment, self-cleaning surfaces, and air purification. In fact, its ability to purify air is particularly important given the increasing concerns about air pollution worldwide.

Another advantage of thin film technology is its low production cost, which makes it a cost-effective solution for many industries. This cost efficiency is achieved through the use of advanced manufacturing techniques that are optimized to reduce the amount of material and energy required to produce the films. As a result, thin film technology is often the preferred choice for companies that are looking to reduce their costs without compromising on quality.

Within this context, ZnO thin films are an attractive option for a wide range of photocatalytic applications. These films are known for their exceptional photocatalytic properties, which make them ideal for use in applications that require high levels of efficiency. Moreover, they are easy to produce and can be tailored to meet the specific requirements of different applications. This versatility and

flexibility make ZnO thin films a popular choice for companies looking to improve their products and processes while keeping costs low.

The various ZnO thin film synthesis techniques are discussed in this section. The synthesis techniques are broadly divided into three categories: physical, chemical, and biological routes. Magnetron sputtering, pulsed laser deposition, electrochemical methods, and electron beam evaporation are examples of physical procedures (Droepenu, 2022). According to Hessien (2022) and Droepenu (2022), chemical synthesis comprises hydrothermal, solvothermal, sol-gel, chemical bath deposition, wet chemical process, spray pyrolysis, microemulsion, and precipitation processes. In addition, it is worth mentioning that metal oxide nanomaterials can be synthesized through a green or biogenic method that involves the use of plants or microbes, as highlighted by Kalpana and Devi Rajeswari (2018).

Sputtering and chemical vapor deposition enable big area depositions which making them the commercially most efficient ZnO deposition methods (Ellmer et al., 2007). ZnO films readily consolidate, in contrast, for example, to ITO films, which can be produced as amorphous films (Uchino et al., 2000). The primary structure of ZnO sheets is (0001), which denotes that the c-axes of the crystallites are parallel to the surrounding surface (Ellmer et al., 2007). Obviously, each approach has advantages and disadvantages. It is essential to thoroughly examine the particular application and desired ZnO characteristics before choosing a synthesis method. Additionally, factors like expense, scalability, and environmental effect need to be taken into account.

Magnetron sputtering is a widely used high-vacuum deposition process in the thin film industry. It is used to create ZnO layers for a variety of applications, such as solar cells (Kluth et al., 2006). One of the primary benefits of this process is the low-pressure plasma environment, which allows for the efficient transportation of atoms to the substrate. The resulting nucleation, complex formation, and film growth on the substrate are encouraged by the simultaneous bombardment of energy species from the plasma on the consolidation of mostly neutral atoms (Kaiser et al., 2002).

Magnetron sputtering also enables large-area layer formation at relatively low substrate temperatures, making it a highly desirable process for thin film applications (Ellmer et al., 2007). However, there are some drawbacks to the process. One of the primary issues is plasma instability, which can lead to a significant decrease in ion substrate current as the substrate-to-target distance increases (Arnell & Bates, 1992). This drop in ion substrate current can result in reduced film quality and non-uniform film deposition. To get around this limitation, numerous adjustments have been made to the magnetron sputtering process. However, these adjustments can come at an increased cost. Despite these challenges, magnetron sputtering remains a widely used and highly effective method for creating ZnO layers in thin film applications.

ZnO thin-film deposition technique called chemical vapor deposition (CVD) is used to provide uniform deposition over sophisticated geometries which was preferred in the industrial sector as well (Purica et al., 2002). Adsorption onto the surface, desorption from the surface, diffusion of gaseous byproducts into the stream, and diffusion of reactants to the substrate make up its five key steps. Numerous reactor process types, including atmospheric pressure, low pressure, and plasma-enhanced chemical vapor deposition, are covered by CVD. Besides the benefits offered by this technique there are several drawbacks of CVD, including the need for volatile precursors to be volatile at close to room temperature, the potential toxicity or corrosiveness of metal-organic precursors, and potentially dangerous byproducts of CVD reactions. Another significant drawback is that the films are typically deposited at high temperatures, which limits the types of substrates that can be coated and may result in mechanical instability in the deposited films. (Creighton & Ho, 2001).

Another method for depositing ZnO is called physical vapor deposition (PVD). This process involves extracting atoms and/or molecules from a solid source material and condensing them into a vapor phase, which is then deposited onto a substrate surface under vacuum conditions. PVD is a scalable route for synthesizing ZnO nanoparticles with controlled orientation and high aspect ratios, making them useful for various applications such as sensors, solar cells, and optoelectronics (Wang et al., 2005).

The extraction process used to create the vapor phase can be carried out using different energy sources, each with specific characteristics tailored to the deposition method. For example, ion beam sputtering, pulse laser deposition, and electron beam physical vapor deposition (Gomez & Tigli, 2013) are all PVD techniques that use different energy sources. Ion beam sputtering involves using high-energy ions to sputter atoms from a target material, which are then condensed onto the substrate. Pulse laser deposition uses high-energy laser pulses to vaporize the target material, which then condenses onto the substrate. Electron beam physical vapor deposition uses an electron beam to vaporize the target material, which is then condensed onto the substrate (Singh & Wolfe, 2005).

Adsorption of atoms and/or molecules on a substrate surface triggers the formation of thin films. Islands are created as a result of the steps of nucleation and coalescence that follow adsorption. Depending on the specific deposition settings, each of the aforementioned phases can be efficiently modified to promote the formation of an island individually, preventing the production of a compact film (Laurenti & Cauda, 2018). As a result of this approach, a porous film with specific micro/nanoscale structures and morphologies would be the final product, which is significant for a variety of applications (Laurenti & Cauda, 2018).

Conventional PVD techniques, on the other hand, have limitations such as high investment costs and poor deposition rates (Von Niessen et al., 2010). Because of this, this technology is primarily used to produce rather thick coatings on top of precious components like turbine vanes for aircraft engines or thin film applications that are mass produced. In addition, the coating source can only be seen by surfaces that are directly in its line of sight which cause difficulty in coating components uniformly when they have complex features (Von Niessen & Gindrat, 2011).

Spray pyrolysis is a method for quickly, affordably, and easily producing dense ZnO films. A metal salt precursor solution is atomized, the resulting vapors are transported, the vapors condense into drops, and the drops are then thermally decomposed on a heated substrate. The thin film network is then formed by stacking

and overlaying the metal salt droplets on the surface of the substrate and heating the substrate to generate oxides to form (Laurenti & Cauda, 2018). The key elements influencing the resulting thin-film structure and performance are the solvent, salt amount and type, and additions in the feed solution (Laurenti & Cauda, 2018). The main drawbacks of spray pyrolysis for the production of oxide thin films are obtaining hollow and/or porous particles, strong grain size dependence of film thickness, and low deposition efficiency for large substrates (Korotcenkov & Cho, 2017).

The selection of deposition method is influenced by several factors such as the material being deposited and the desired properties of the finished product. One key factor that needs to be considered is the overall quantum efficiency for interfacial charge transfer, which can be improved through enhanced charge separation and the suppression of charge carrier recombination (Wang et al., 2018). Additionally, controlling the dimension and shape of the particles can also play a crucial role in enhancing their photochemical properties.

While there are several deposition methods available, electrochemical deposition stands out due to its instant synthesis time, cost-effectiveness, absence of chemical reductants or oxidants, and ability to eliminate unwanted byproducts. Furthermore, it offers the added benefit of precise particle size control and shape directing of the final product through modifying deposition parameters like current density, applied potential, electrolysis time, and electrolyte (Tonelli et al., 2019). This makes electrochemical deposition an ideal choice for achieving size and shape controlled ZnO deposition on ITO coated film, which aligns with the objectives of this study. Therefore, after careful consideration and analysis of the advantages offered by the electrodeposition technique and how it aligns with the objectives of this study, it was concluded that the electrodeposition method would be the best-suited for this particular research.

2.1.3 Electrodeposition of Zinc Oxide Thin Film

Numerous methods, including chemical vapor deposition (CVD), sputtering, hydrothermal methods, electrochemical deposition etc. can be used to apply ZnO thin film as discussed in the previous part. Thin-film electrodeposition was identified as a potential technology due to its ability to regulate thickness, large-area deposition, easy procedure, good adhesion, and a cost-effective manufacturing process (Henni et al., 2015). There are various studies in literature for the deposition of ZnO on conducting substrates through electrodeposition in aqueous electrolyte solution at different morphologies from a compact film to nanowires in literature for various applications (Yoshida et al., 2004). Morphology of the deposited film depends both on chemical and electrochemical parameters such as precursor concentration, polarization potential or temperature (Skompska & Zarębska et al., 2014).

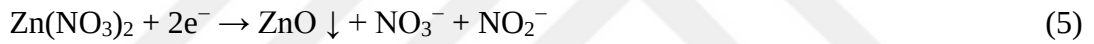
In the electrochemical synthesis of zinc oxide, the hydroxide precursor is first reduced, then Zn(OH)_2 is precipitated, and finally ZnO is produced by dehydrating Zn(OH)_2 (Skompska & Zarębska, 2014). The first report of this process was by Izaki and Omi in 1996, where an aqueous solution including Zn^{2+} ions and a source of OH^- was used. Since then, oxide layers have been formed by electrodeposition as well, through the use of either completely dissolved precursors in the growing process or by oxidizing metallic surfaces. The mechanism behind the formation of oxide layers relies on the electrochemical release of hydroxide ions in an oxygen-containing environment to precipitate oxide or hydroxide at the electrode. Typically, water or nitrate ion reduction is used to accomplish this. The process has been studied extensively due to its potential in various applications such as in the fields of electronics, solar cells, and sensors. Furthermore, recent studies have shown that the use of additives or complexing agents in the electrolyte solution can significantly affect the morphology and properties of the resulting oxide layers (He et al., 2022).

Efficient electrodeposition of ZnO employing aqueous and non-aqueous electrolytes has been documented in the literature, with various advantages and disadvantages

(Henni et al., 2015). In general, electrodeposition of ZnO in aqueous media occurs by reduction of different precursors to OH⁻ ions, such as nitrate ions (NO⁻³), molecular oxygen (O₂) and solution of H₂O₂ that are mostly reported precursors in literature. Unlike nitrate ions and molecular oxygen, H₂O₂ precursor generally indicate porous films rather than vertically aligned nanorods to the substrate (Skompska & Zarębska, 2014). Chemical reactions take place on the cathode surface as a result of ZnO electrodeposition from nitrate baths are as follows:



or



According to the electrodeposition mechanism performed in zinc nitrate bath, hydroxyl (OH⁻) ions react with Zn²⁺ ions to create Zn(OH)₂, which then transforms into ZnO. It is possible to deposit metallic zinc at the cathode where Zn²⁺ ions may be present at the cathode surface and cause a layer of metallic zinc to develop. The use of oxygen reduction to prepare zinc oxide films has varying degrees of complexity depending on the effects of the substrate and solution due to the parallel reactions, i.e. the formation of hydrogen peroxide. However, this route has advantages over those involving water or nitrate ions in terms of the simplicity, controllability, and lack of by-products. (Peulon & Lincot, 1998).

Furthermore, it is worth noting that the use of dissolved oxygen as a precursor, instead of Zn(NO₃)₂, allows for the modulation of the [OH⁻]/[Zn²⁺] ratio in the electrolyte solution through varying deposition parameters such as temperature. In fact, the process of oxygen reduction leads to the formation of OH⁻, followed by zinc

hydroxide precipitation and its subsequent dehydration, as has been demonstrated by Gautier et al. in 2016:



Notably, this method presents unique opportunities for researchers to explore the interplay between deposition parameters and chemical properties of the resulting material, which could have important implications for a wide range of applications in materials science. Zinc chloride is generally preferred as a source of zinc in molecular oxygen-based electrodeposition methods. When ZnCl_2 is used as a zinc precursor, the OH^- ions produced at the electrode being supplied during the precipitation of ZnO , yielding in a practically constant interfacial pH (Skompska & Zarębska, 2014).

Goux and colleagues presented a thermochemical investigation of ZnCl_2 breakdown (Goux et al., 2005). They discovered that the primary soluble species at temperatures over 50°C is ZnCl^+ , yielding in a Zn^{2+} level over less than 20% by 90°C (Goux et al., 2005). When this happens, the bulk of the Zn^{2+} ions that contact with the cathode bond with the OH^- ions that are deposited on the substrate, driving growth down the longitudinal axis. As a result, Zn^{2+} diffusion in aqueous ZnCl_2 mixture is lower when compared to molecular oxygen.

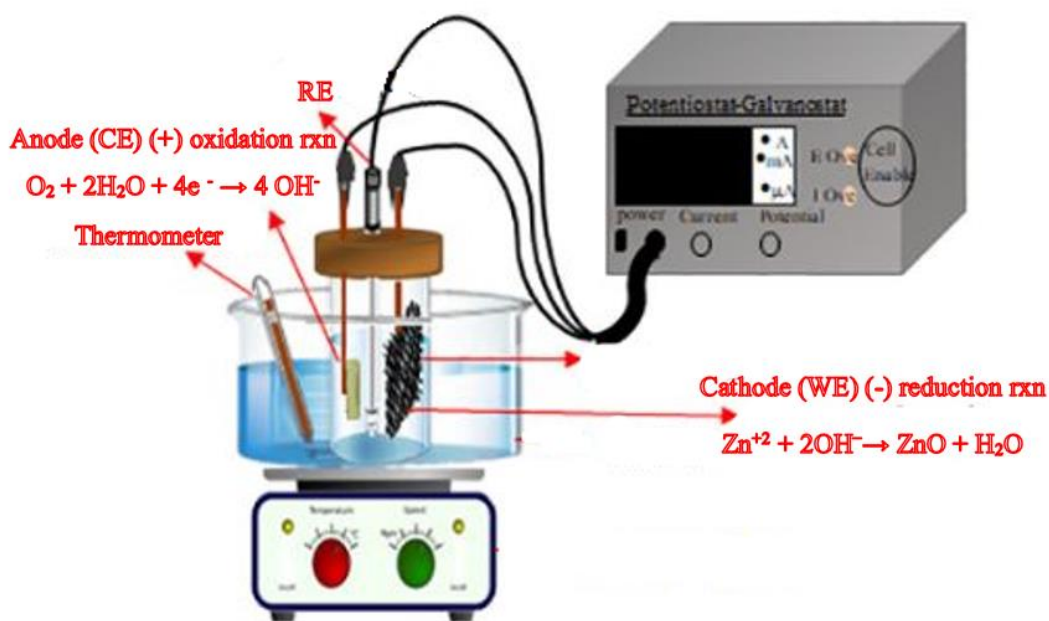


Figure 2.1. Zinc oxide electrodeposition mechanism from oxygen precursor and $ZnCl_2$ zinc source in aqueous electrolyte (Saidi et al., 2020).

Zinc oxide electrodeposition mechanism from oxygen precursor and $ZnCl_2$ zinc source in aqueous electrolyte has been depicted in Figure 2.1. While Goux et al. (2005) investigated the effects of electrodeposition temperature on the morphology and crystalline structure of zinc oxide deposits, Tena-Zaera et al. (2008) claimed that increasing $ZnCl_2$ concentration or decreasing electrodeposition current density can enhance overall deposition rate of zinc oxide deposits. Specifically, Goux et al. found that the electrodeposition temperature affects the density and thickness of the zinc oxide films. Meanwhile, Tena-Zaera et al. also suggested that the increase of $ZnCl_2$ concentration can lead to the synthesis of denser and larger zinc oxide particles, while the decrease of electrodeposition current density can result in a more uniform distribution of the particles. Overall, these findings provide important insights into the factors that affect the morphology, crystalline structure, and deposition efficiency of zinc oxide deposits.

2.1.4 Shape and Size Effect of Electrodeposition Parameters on ZnO Nanostructures in Aqueous Electrolyte

Photocatalytic activity is greatly influenced by the surface area and porosity of semiconducting metal oxide complexes (Zhang et al., 2014). Researchers have focused on expanding the surface area of metal oxides to improve their photocatalytic activity. However, recent studies suggest that surface morphology is another crucial factor for photocatalytic activity. According to several researchers, size and shape effects on the surface morphology are more important than the surface area (Wang et al, 2007) (Li et al., 2007). Therefore, in recent years, many researchers have shifted their attention to the fabrication of hierarchical metal oxide nanostructures with intricate surface morphologies, which are expected to exhibit improved photocatalytic activity due to their unique structural designs.

To achieve the desired surface morphology, the deposition of ZnO nanostructures with controllable size, external and interior morphology, and orientation is of utmost importance. The functional properties of these structures are strongly dependent on their structural parameters. The film growth is achieved by surface reactions, particularly electron transfer for the generation of OH^- , and crystal growth of ZnO, which is significantly affected by the presence of surface adsorptive chemicals that directly affect the deposition parameters (Jung et al., 2008). Therefore, researchers have been exploring various methods to optimize the deposition process and control the surface adsorption of these chemicals to achieve the desired functional properties of the ZnO nanostructures. This is a critical area of research that has the potential to revolutionize the field of photocatalysis.

Achieving the desired surface morphology is crucial for the deposition of ZnO nanostructures with controllable size, external and interior morphology, and orientation. The functional properties of these structures depend strongly on their structural parameters. Surface reactions, particularly electron transfer for the generation of OH^- , and crystal growth of ZnO are the mechanisms behind film growth. These mechanisms are influenced by the presence of surface adsorptive

chemicals that directly affect the deposition parameters. Researchers are exploring various methods to optimize the deposition process and control the surface adsorption of these chemicals to achieve the desired functional properties of the ZnO nanostructures. Due to the fact that the morphology of the nanostructured materials obtained by electrodeposition differs considerably with the content of electrolyte and deposit conditions, in this part of the thesis literature studies are exemplified about various deposition parameters that contribute to the shape and size controlling of ZnO thin film.

For electrodepositing ZnO from solutions containing oxygen precursors, ZnCl_2 salt is employed; the chloride ion is a naturally occurring part of the deposition bath (Skompska & Zarębska, 2014). Electrolytes like KCl or NaCl that are added to the deposition bath to increase the solution's conductivity at low concentrations of Zn^{+2} and change the deposit rate are another source of Cl^- ions (Skompska & Zarębska, 2014). These molecules added to increase conductivity of the solution cause an increase in the chlorine ion in the electrolyte bath. The strong adsorption properties of Cl^- ions on ZnO crystal, however, cause them to act as a capping agent above the limit, blocking some faces and promoting the growth of other facets. (Xu et al., 2005).

In other words, the concentration of Cl^- ions in the bath solution is another crucial electrolyte parameter that affects morphological factors such as deposit shape and size. For example, greater Cl^- concentrations, i.e. $[\text{KCl}] > 1 \text{ M}$, stimulate c-axis development, resulting in a considerable increase in nanoparticle thickness from 80 nm to 300 nm (Skompska & Zarębska, 2014). This behavior is explained by the selective adsorption of Cl^- on the (0001) plane of ZnO, thus controls the (0001) face and promotes lateral development in nanowire form (Xu et al., 2005). Additionally, the effect of Cl^- concentration on the surface morphology and crystal structure of ZnO nanowires has been extensively studied in recent years. Studies have shown that lower Cl^- concentrations lead to the formation of hexagonal-shaped nanowires, while higher concentrations promote the growth of triangular-shaped nanowires.

Therefore, it is important to carefully consider the Cl^- concentration when attempting to control the morphology of ZnO nanowires.

In a same manner, Xu et al. (2009) studied the crystallographic orientation of the ZnO deposit in nano/microscale. With altering the electrodeposition settings, Cl^- preferentially binds to the (0001) planes, causing ZnO crystals to obstruct the formation of crystals along the c-axis. As a consequence, ZnO may be electrodeposited as compact films in the form of hexagon shaped nanowire arrays, rods, plates or particles (Skompska & Zarębska, 2014).

Apart from salts like KCl and NaCl, chemicals like amines (Xu et al., 2009) or eosin Y (Ichinose et al., 2014) were investigated for the electrodeposition of ZnO nanostructures to modify the morphology of ZnO crystals. Ichinose and coworkers (2014) added citric acid and eosin Y as a structure directing agent to the electrolytic bath. The crystal orientation of ZnO nanostructures was parallel with c-axis obtained for the ZnO-Citric Acid hybrid thin film and contrasting pattern was obtained for the ZnO-Eosin Y hybrid films. Structure-directing agent utilizes crystal through changing orientation by 90° . During the electrolysis, depending on the choice of the agent, selection of nuclei and also controlled crystal growth can be achieved. For instance, it was suggested that eosin Y show catalytic activity to the reduction of O_2 enhances formation of ZnO unlike citric acid (Ichinose et al., 2014).

Henni and coworkers (2016) studied the effect of addition of the Al dopant and H_2O_2 at various concentrations which is another investigation on electrolyte effect effect on nucleation and growth mechanism of electrodeposited ZnO nanostructures. Cyclic voltammetric studies show that at very low H_2O_2 concentration (2 mM) dissolution of zinc metal observed rather than its oxide form. The rise in number density of nucleation is explored when the concentration of H_2O_2 in electrolytic solution reaches 7 mM. With larger concentrations of H_2O_2 , however, a drop in nucleation density is seen, which is most likely due to a decrease in the number of active sites (Henni et al., 2016).

There are studies in the literature on the contribution of other deposition parameters to the shape control of ZnO onto the surface, in addition to electrolyte content and concentration. These parameters include the pH of the electrolyte solution, deposition temperature, and applied potential. Understanding the effects of these parameters can lead to improved control over the growth and properties of ZnO coatings. Goux et al. (2005) investigated the chronoamperometric results of a FTO electrode at 300 rpm under deposition conditions (at -0.75V) in aqueous ZnCl₂ solution, saturated with molecular oxygen, at various electrodeposition temperatures. The results revealed that at temperatures under 34 °C, the electrode became nonfunctional and polarized as a Zn(OH)₂ thin layer, but at higher temperatures, the transition of Zn(OH)₂ to ZnO occurred owing to delayed drying of the hydroxide layer that had initially created on the electrode (Goux et al., 2005).

Other variables, such as applied voltage, can also significantly influence the growth of ZnO nanostructures, necessitating a thorough understanding for the controlled synthesis of desired properties. Henni et al. (2015) studied the impact of different potentials during electrodeposition in the range of -0.8 V to 1.2 V on the nucleation of ZnO seeds. The intensity of the (0 0 2) reflection is larger where ZnO is deposited at potentials between 1.0 and 1.1 V relative to potentials greater than 1.1 V, according to XRD measurements (Henni et al., 2015). Additionally, the sample produced at 0.8 V has an inhomogeneous layer, while those synthesized at higher potentials have more densely packed hexagonal grains. These findings indicate that growth rates increase more rapidly as potential increases.

Because of its beneficial features, also including high solubility for metal complexes, high electrical conductivity, and low viscosity, electrodeposition in aqueous medium is an extensively utilized method (Maniam & Paul, 2020). Unfortunately, aqueous media have significant drawbacks that prevent the deposition of some strategically essential metals, alloys, and semiconductors with quite negative redox potentials (Zhang et al., 2016). Water, for example, has a rather small potential window with just 1.23 V, limiting the materials that may be deposited with desirable characteristics (Zheng et al., 2018).

To elaborate on this further, the oxygen and/or hydrogen evolution reactions require specific overpotentials, which broaden the potential apertures of aqueous solutions (Yokoyama et al., 2018). The hydrogen evolution reaction, which is the simplest electrocatalytic reaction, is mainly provoked in acidic or alkaline aqueous electrolytes ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) (Saidi et al., 2020). Unfortunately, the electrolytic evolution of hydrogen on the cathode can cause non-uniform and cracked deposits, which ultimately lead to mechanical and corrosion instability of the surface (Zhao et al., 2019).

These limitations have driven researchers to search for alternative solvents with broader potential windows, such as ionic liquids (IL) and organic solvents. These solvents have shown promising results in electrochemical applications, and their use could potentially overcome the limitations associated with aqueous solutions. For instance, ILs are known for their wide potential windows, low vapor pressure, and high thermal stability, making them ideal for electrodeposition processes (Zhang et al., 2016). Similarly, organic solvents have been shown to improve the quality and uniformity of deposits due to their lower hydrogen evolution overpotentials compared to water. Overall, while aqueous solutions have several advantages, their limitations have driven researchers to look towards alternative solvents that could potentially broaden the range of materials that can be deposited with desired properties.

2.2 Ionic Liquids (IL) and Deep Eutectic Solvents (DES)

Ionic liquids (ILs) are gaining popularity due to the potential of chemically modifying the cationic moiety and the wide variety of IL design with a very big selection of anions. This variety comprising physical attributes includes melting point, miscibility, viscosity, density, resistivity, and refractivity (Zhang et al., 2012). ILs become a new class of promising solvents, especially in the fields of physical chemistry, chemical engineering, material science. ILs have also find a place in catalysis, electrochemistry, material chemistry, medicinal chemistry, energy, fuels

etc. both industrial and laboratory scales (Singh & Savoy, 2020). Furthermore, because of their low vapor pressure along with a high boiling point, which enable recycling, metal-free ionic liquids have grown in popularity with the rising importance of green chemistry (Rogers & Seddon, 2003).

The choice of cation and anion can significantly affect the properties of ILs, like their melting point, viscosity, and conductivity. The mostly investigated cations for ILs are imidazolium, pyridinium, ammonium, and phosphonium which are associated with anions such as halides, tetrafluoroborate, hexafluorophosphate, carboxylates, alkyl sulfates, and sulfonates (Prodius & Mudring, 2018) (Hayes et al., 2015).

Although the physical characteristics of DESs are comparable to those of room temperature ionic liquids (RTIL), their physicochemical characteristics indicate that their application areas are drastically different. DESs have significant benefits over ILs. To begin with, DES may be simply created by combining two safe components capable of producing a eutectic combination, so avoiding the purification and waste disposal stages commonly seen with ILs. Second, they are less expensive than regular ILs. Finally, they are chemically stable to water, making storage easier. Lastly, the vast majority are biodegradable, biocompatible, and non-toxic (Zhang et al., 2012). Deep Eutectic Solvents are defined by the following general formula (Kumar & Sharma, 2017):



where Cat^+ is any ammonium, phosphonium, or sulfonium cation and X is a Lewis base, usually a halide anion. Between X and Y, sophisticated anionic species are produced, which can be Lewis or Brnsted acids. Moreover, z denotes the quantity of Y molecules that link with the X anion (Smith et al., 2014). Deep eutectic solvents (DESs), which fall under the IL category, are eutectic mixtures of at least two components that are a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD), which can be any number of species (Ma et al., 2018).

DESs have been found to have potential applications in the fields of catalysis, electrochemistry, and green chemistry due to their unique properties. Because of the fact that DESs retain similar features and properties with ionic liquids (ILs), they are specified as a new class of ILs in literature. DESs were developed as an alternative to ILs in order to address their limitations (Satlewal et al., 2018). Despite the fact that ILs and DESs exhibit several similarities, such as the fact that both are generated by mixing two or more solid parts to generate a liquid with ionic characteristics, these are two separate classes of substances in terms of physical properties. ILs are often composed of organic cations with either organic or inorganic anions, whereas DESs are composed of a donor and acceptor of chemical bonds (Płotka-Wasyłka et al., 2020).

In other words, DESs are created from a eutectic mixture of Lewis or Brnsted acids and bases that includes different anionic and/or cationic species, whereas ILs are made up of a single type of individual anion and cation (Smith et al., 2014). Furthermore, DESs have been discovered to have novel applications in fields such as green chemistry and biotechnology. If the advantages of DESs have been evaluated within the framework of electrochemistry, even though DESs have relatively smaller electrochemical windows compared with some ionic liquids like the imidazolium salt based ILs, it is feasible to get high current efficiency in the deposition of metals including Zn. (Smith et al., 2014). Under separate cover, DESs are simple to prepare, do not easily react with water, are biodegradable, and are reasonably inexpensive, all of which are relevant qualities of these solvents in the scope of this study.

DESs were classified into four types by Abbott et al. (2007): Type I (quaternary salt + metal halide), Type II (quaternary salt + hydrated metal halide), Type III (quaternary salt + hydrogen bond donor), and Type IV (metal halide + hydrogen bond donor). Among these DES types, Type III display a considerable importance since its components are largely available and cheaper. Therefore, Type III DESs have been mainly used as green solvents in a variety of applications such as catalysis, extraction, and electrochemistry.

According to Mjalli et. al. (2016), the physical properties of Type III DES, such as melting point, density, viscosity conductivity, pH and refractive indices, are mainly determined by the strength of hydrogen bonding between its components. However, there are ways to modify these properties for specific applications by altering the hydrogen bond donor component. Glycerol, ethylene glycol, urea, oxalic acid, malonic acid, and benzamide are the most frequent hydrogen bond donors for Type III DES (Maniam & Paul, 2020).

On the other hand, halide salt components, which act as hydrogen bond acceptors, are required to synthesize Type III DES. Some examples of these components are di/tri methylethanaminium chloride and choline chloride (Smith et al., 2014). Interestingly, choline chloride can be combined with inexpensive and biodegradable hydrogen bond sources to create eutectic solvents that are not only less expensive but also more environmentally friendly. As a result, choline chloride-based DESs have been extensively researched both experimentally and theoretically for possible uses.

It is important to also mentioned that despite their potential benefits, more research is still needed to fully understand the properties and limitations of Type III DES. Nonetheless, the development of these solvents and their potential applications in various industries show promising prospects for the future.

2.2.1 ChCl Based Deep Eutectic Solvent

Choline chloride (ChCl), also known as 2-hydroxyethyl-trimethylammonium chloride, is a bifunctional molecule found in nature that contains both a quaternary ammonium salt and an alcohol functional group (Amoroso et al., 2021). These versatile compounds have become the focus of extensive research, as they have been shown to be highly effective as deep eutectic solvents (DESs), which are organic molecules that are environmentally benign, non-toxic, and biodegradable. ChCl-based DESs have showed considerable potential in a variety of applications ranging

from cleaning agents towards drug delivery systems. They are of particular interest in the health-related sector, as they are widely used in pharmaceutical, cosmetic, and food production. In fact, ChCl is a frequently preferred nutrient for metabolism, anti-carcinogenesis, and lipid transport utilization, as it is able to connect with other complex vitamins and enhance their beneficial effects.

In DESs, urea, sugars, alcohols, hydroxyacids, and aminoacids act as HBA, allowing for modulation of viscosity, pH, and polarity (Amoroso et al., 2021). Within this content, ChCl-based deep eutectic solvents are categorised as alcohol/sugar-based, acid-based, amide-based, water-based, and ternary combinations depending on the structure of HBD (Amoroso et al., 2021). The majority of these combinations can be used as solvents in a variety of uses because they are liquid at ambient temperature (Amoroso et al., 2021). Moreover, the benefit of being able to adjust viscosity, pH, and polarity for utilization in health-related industries such as medicines, foods, and cosmetics is perhaps what makes ChCl-based DES so intriguing. The primary disadvantages of these solvents are typically much greater viscosities and densities over water as well as other organic solutions, which can impede mass and energy transfer during chemical processes. Mild heating and the addition of water or glycerol can also reduce intermolecular interactions while preserving the solvent's supramolecular structure (Amoroso et al., 2021).

ChCl:ethylene glycol, commercially named as ethaline and ChCl:glycerol commercially named as glyceline is a kind of alcohol/sugar-based DES. Perkins and coworkers (2014) study hydrogen bonds in ChCl:ethylene glycol (ethaline) and ChCl:glycerol (glyceline) revealed on chloride hydroxyl anion group of HBD forms the majority of intermolecular hydrogen bonds, with cation choline interactions contributing the least to the complex web of molecular interactions (Amoroso et al., 2021).

Reline is a 1:2 molar mixture of ChCl and urea, and it is the most widely used amide-based DES. Abbott et al. first suggested the interesting solvent characteristics of reline in 2003. For instance, when combined, the freezing points of urea and choline

chloride drop dramatically from 133 and 302 degrees Celsius, respectively, to as low as 12 degrees Celsius (Amoroso et al., 2021). The hydrogen bonding structure, which includes urea-urea, chloride-urea, and choline-urea, as well as ChCl ion pairs, is the source of these and many other unique characteristics. The chemical structures of reline and ethaline components are referred in Figure 2.2.

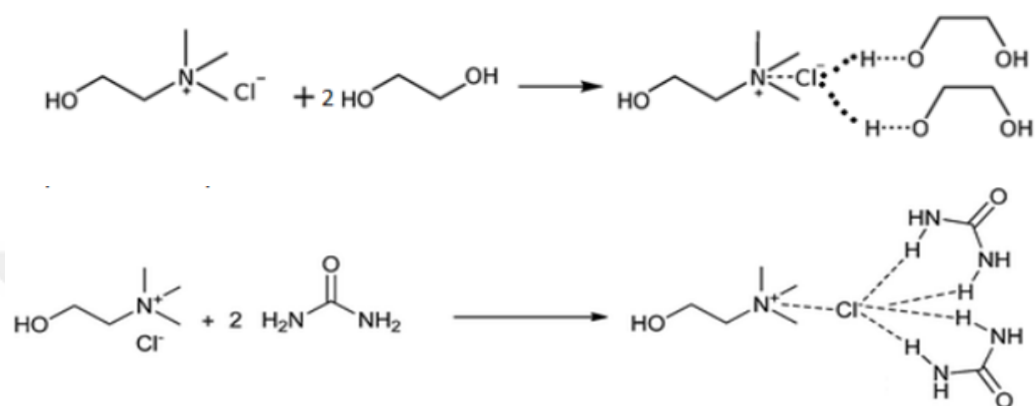


Figure 2.2. ChCl:urea DES structure with a eutectic point of 1:2 ratio, at the top ethaline including choline chloride binding to two ethylene glycol molecules and at the bottom reline choline chloride together with two urea molecules (MIHĂILĂ et al., 2021).

In the case of reline, each chloride anion (Cl) is anchored by two urea compounds via an H-bonding relationship (Kumari et al., 2018). This implies that the Cl anions are close to the hydroxyl group in choline cations (Ch⁺), allowing urea to be accommodated more effectively inside the H-bonded complex (Kumari et al., 2018). The hydroxyl group of Ch⁺ is able to interact with the chloride anion (Cl⁻) via hydrogen bonding, further stabilizing the complex. This interaction is essential for the formation of the H-bonded complex between urea and chloride anion (Cl⁻).

In other words, choline and urea form a mutual binding with the chloride anion, forming a sandwich-type layered structure that allows for the greatest possible charge allocation between each component while simultaneously increasing the system's entropy and lowering the melting point (Hammond et al., 2016).

Additionally, reline has a high specific solubility for many metal compounds and a very high dissolving capacity (Zhang et al., 2012).

In spite of favorable solvent properties, similar to the common feature of the DESs, reline display some drawbacks compared with aqueous and common organic solutions such as high viscosity and density which restricts mass and heat transfer rate during chemical and physical processes which are strategically important for electrochemical deposition (Liu et al., 2019). On the other hand, addition of water to DES can cause a drastic change of chemical and physical properties that is found critical for many applications (Shah & Mjalli, 2014).

Water addition disrupts the hydrogen-bond network and weakens intermolecular interactions while maintaining the solvent's supramolecular structure (Liu et al., 2019); (Amoroso et al., 2021). As a result, the characteristics of DES-water combinations are widely variable. Moreover, adding regulated amounts of water to DESs may result in a straightforward and practical method of modifying and designing their characteristics (Vilková et al., 2020).

Reline, a type of polymer, has an interesting property: it is hygroscopic, meaning that it can absorb moisture from the environment. The presence of a certain amount of water in reline can significantly affect its hydrogen bonding interactions, which can be controlled in order to shape the particles and enhance their surface properties during electrodeposition. This unique property has been studied by Liao et al. (2008), who found that the introduction of water can provide a new way to manipulate the properties of reline. By understanding the effects of water on this polymer, we can explore new possibilities for its use in various applications, such as coatings and adhesives.

2.2.2 Deep Eutectic Solvent (DES)-Water Mixtures

Even noteworthy chemical, physical, biological and thermal properties with non-toxic, sustainable and eco-friendly characteristics which make them promising

solvents in many applications of DESs, they need further development and implementation as mentioned above because of unfavorable characteristics like high viscosity and density (Perdizio et al., 2017). When electrochemical applications are considered, besides desired properties such as wide electrochemical potential window, high thermal stability, tunable solubility, DESs have good ionic conductivity based on free charge ions and ion mobility. Moreover DESs are generally highly viscous due to very large and complex cations in their structure which are enlarged further reacting with anions. (Singh & Savoy, 2020)

On the other hand, it may be necessary to investigate the development of conductivity, viscosity, or pH for the electrolyte due to their significant impact on the DES/electrode interface during electrodeposition. Conductivity is particularly important because it affects the ability of the electrolyte to conduct electric current, which is crucial for electrodeposition. Viscosity, on the other hand, determines the flow characteristics of the electrolyte during electrodeposition, which in turn affects the uniformity and thickness of the resulting coatings. pH, meanwhile, affects the chemical properties of the electrolyte and can influence the morphology and structure of the coatings.

To address these concerns, a mixture of suitable co-solvents can be used as an alternative to pure DES. For instance, a mixture of eco-friendly and low viscous water with DES has been found to be one of the preferred alternatives (Kuddushi et al., 2019). By combining these co-solvents, the properties of the electrolyte can be fine-tuned to optimize the electrodeposition process and improve the quality of the resulting coatings. Understanding the behavior of these electrolytes is therefore critical for designing more efficient and long-lasting electrochemical systems. With this knowledge, researchers can develop new strategies for improving the performance of existing electrochemical systems and can design new systems with enhanced capabilities.

Several studies have gone into great detail into the nonideal performance of liquid binary DES solutions by means of various solvents (Zhang et al., 2022). Nonideality

is often represented as an imbalance among experimental data for large macroscopic quantities and data gained from the combination of the corresponding amounts of the specific components (for example, volume, enthalpy, or internal energy) for any liquid binary combination (Zhang et al., 2022).

According to the study on binary DES mixtures, in contrast to DMSO, MeOH, and EtOH, water as a co-solvent in reline achieves less deviation from the ideal structure, according to Zhang and colleagues (Zhang et al., 2021). The deviation from ideality increase in the sequence $\text{H}_2\text{O} < \text{DMSO} < \text{MeOH} < \text{EtOH}$ which is ascribed to the strength of the particular interaction between solvent molecules as well as the compactness of the eutectic solvent framework structure (Zhang et al., 2021). In fact, H_2O molecule can interact with four contiguous H_2O molecules via hydrogen bonds (HB), whereas MeOH and EtOH contain simultaneously proton donor and acceptor regions that also can generate two HBs in the form of a long range HB network structure, causing departures from ideality. In addition, the hygroscopic nature of ChCl can lead to the absorption of moisture, which can affect the stability and performance of DESs during long-term storage (Chen et al., 2019). Therefore, it is essential to create practical techniques for ensuring proper storage conditions for ChCl based DES , kind of ethaline and reline.

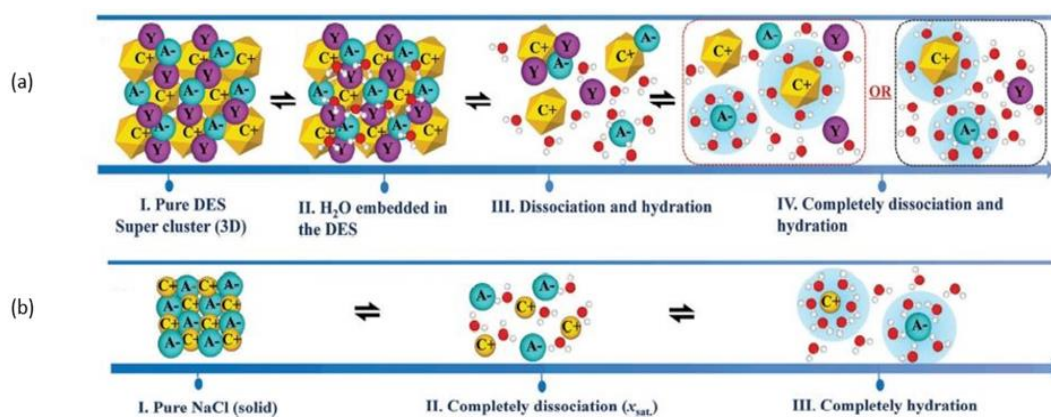


Figure 2.3 Schematic mechanism for (a) the typical aqueous DES system (b) aqueous NaCl system where the yellow, blue spheres, red spheres and purple spheres ones represent cation, anion, water and HBD, respectively (Ma et al., 2018).

DESs have become designable solvents for a variety of processes, including catalysis and separation engineering, but their high viscosity may make them less useful for the electrodeposition. The physico-chemical characteristics of DESs are significantly affected, no matter how minute, any traces have an impact small traces of water or any other organic solvent as an impurity. Infact, It has been demonstrated that some DES- H_2O systems perform better and are more affordable (López-Salas et al., 2019). However, studying the entire system is crucial because the internal structure can differ significantly. Ma and colleagues compare the results of conventional DES- H_2O systems with the NaCl- H_2O system to illustrate a behavioral model for DES and NaCl response to water. Simplified mechanism for the aqueous DES and NaCl system are compared in Figure 2.3 (a) and (b) (Ma et al., 2018).

Cations are represented in yellow color signed as C^+ , whereas anions are illustrated in blue color with A^- symbol for both NaCl molecule and DES which can be described as $CA.nY$ (Y refer to the HBD interacting with the anion and n associated to the number of HBDs) (Ma et al., 2018). In the case of small amount of water addition, water molecules totally mix with DES throughout strong interactions like hydrogen bonds. In addition, water molecules assimilate inside the system. When the amount of water increases, the dissociation of DES clusters into single ions or ion

pairs begins as can be seen from the third part of Figure 2.3 (a). The NaCl-water system, on the other hand, has a more conventional design, making it more prone to complete dissolution with even a small amount of water (Ma et al., 2018). The delicate equilibrium of these properties is upset by the addition of water, resulting in total dissolution and subsequent hydration in the NaCl-water system. This happens when the amount of water in the DES reaches extremely high levels, whereas in the NaCl-water system, even a small addition of water causes complete dissolution.

This major difference in attitude towards the solution can be attributed to the distinct properties of pure DES as a solvent. Specifically, pure DES contains much larger and asymmetric ions compared to those found in pure NaCl, which only contains Na^+ and Cl^- ions. In dilute DES solutions, the structural features of the solution may result in partial hydration of some larger ions (Ma et al., 2018). However, upon considering the entire solution, hydration appears to be the dominating factor. Contrary to what is seen in aqueous NaCl solutions, the anions in DES are more pronouncedly hydrated than the cations in the solution. As more water is added to the solution, DES ions are completely dissociated (as seen in Figure 2.3 (a), part IV), and the rate at which the ions in DES are hydrated depends on the size of the ions. At this stage, all the cations and anions in the solution are totally hydrated, making aqueous DES similar to aqueous NaCl solution (as shown in Figure 2.3 (b)) (Ma et al., 2018). It is also worth noting that, according to Choi et al. (2011), water is an integral part of the complex DES structure and is strongly retained in the solvent, making it difficult to evaporate.

The characteristics of the resulting films are influenced by a number of factors during the electrodeposition procedure such as electrode settling, substrate direction, electrolyte content, pH, deposition potentials, temperatures (Bijani et al., 2009). It may be feasible to regulate and improve the structural, mechanical, and magnetic characteristics of electrodeposited films and multilayers by modifying these deposition factors. One of the most important factors in achieving the required structural and functional characteristics is the electrolyte selection. The electrolyte in the electrochemical cell creates the electrical connection between the electrodes

and serves as a conduit for electron flow. Important factors for an electrodeposition device include electrolyte current density, conductivity, pH, and others (Mahapatro & Suggu, 2018).

It is possible to adjust the properties such as pH, viscosity and conductivity of electrolytes we use in this study by diluting these solutions with water (kumari et al., 2018). The hydration effect on deep eutectic solvents with a choline chloride HBA was reported in numerous papers mainly justified through modelling approaches (Ma et al., 2018). Likewise theoretical works, suggested that water influences DES properties and modifies the DES molecular network according to its percentage in the mixture (Shah & Mjalli, 2014).

In this study, it is clear that there is a need for more experimental studies on the effect of water on reline and ethaline solutions. While there have been some modeling studies, they do not provide the same level of insight as experimental studies. For example, Shah and Mjalli (2014) conducted an experimental study on the physical properties of reline water mixtures at 30°C. Their findings, which can be seen in Table 2.4, show that there were moderate changes in density and pH with increasing water content. Additionally, viscosity and conductivity were found to be strongly dependent on the amount of water present. However, this study only scratches the surface of the potential effects that water can have on these solutions, and further experimental investigations are needed to fully understand the impact of water on reline and ethaline solutions.

Table 2.2 Physical characteristics of reline-water mixtures at 30 °C (Shah & Mjalli, 2014).

Molar ratio (reline:water)						
Property	1:0	9:1	7:3	1:1	3:7	1:9
Melting point	12	8.39	−3.04	−18.14	−27.00	−41.88
Density (g cc ^{−1})	1.216	1.214	1.21	1.202	1.186	1.136
Viscosity (cP)	552	444	131.1	66.7	19.6	3.2
pH	10.072	10.245	10.206	10.133	9.882	9.682
Conductivity (mS cm ^{−1})	2.31	4.17	6.85	9.36	21.6	59.7
Refractive Index	1.5044	1.5011	1.4984	1.4917	1.4792	1.4499
Speed of sound (m s ^{−1})	2140	2067	2023	1988	1912	1696
Water weight (%)	0	2.2	8.2	17.2	32.7	65.2

Likewise, the impact of water on the hydrogen bonding structure of reline was assessed. Shah and Mjalli (2014) demonstrated how the proportion of water affected the number of urea-urea, urea-anion (urea-chloride), as well as urea-cation (urea-choline) hydrogen bonds. Their findings show that the concentration of hydrogen bonds among urea-urea decreases as the water fraction increases, indicating a strong interaction between water and hydrogen bonding moieties. According to the study, there are fewer hydrogen bonds among both urea-anion and urea-cation as water fraction rises, indicating weaker interactions between these species when water is present. On the other hand, when the water amount is increased the number of hydrogen bonds in reline, indicating a disruption in its structure. This information is important for understanding the behavior of reline as electrolyte and can aid in the development of electrodeposition applications.

Furthermore, Hammond et al. (2017) conducted a comprehensive analysis of the impact of water on the nanostructure of ChCl/urea (1:2) by utilizing empirical potential structure refinement (EPSR) and neutron scattering studies in the presence of Pt (111) electrode as a function of electric potential. The researchers examined the

water's impact on the coordination number (N_{coord}) of the ChCl-based DESs at various concentrations. The coordination number provides vital information on the number of molecules with the closest neighbors that are in direct contact with a given atom or molecule in a crystal structure or solution and is an important parameter for understanding the structure and properties of the solution (Hammond et al., 2017).

The results of the study showed a change in coordination numbers between various hydrogen bonding moieties with the weight fraction of water in reline-water mixtures (Hammond et al., 2017). The researchers found that the presence of water altered the structure of the ChCl-based DESs and affected the coordination numbers of the hydrogen bonding moieties. Additionally, the study examined the effects of water on the nanostructure of the ChCl/urea (1:2) system. The results indicated that the presence of water resulted in a change in the nanostructure of the system, which was observed through EPSR and neutron scattering. Overall, the findings of the study provide valuable insights into the effects of water on the structure and characteristics of ChCl-based DESs, which can have implications in various fields such as materials science and electrochemistry.

The change of N_{coord} values is likely to occur in all aqueous mixtures of common hydrogen bond donors and acceptors which indicate important structural interactions. With the exception of the choline-urea hydrogen-bonding interaction (OH-NH_2), which retains its coordination number even in the presence of water, at about 1 weight percent H_2O addition, this finding suggests that the coordination number of components weakens when water is added (Hammond et al., 2017).

It is important to note that choline and urea molecules have a high affinity for one another, which explains the peculiar behavior of their hydrogen-bonding interaction. Although this increase in intermolecular interaction strength suggests that aqueous reline containing up to 1 weight % water has different physicochemical properties from pure correlate, more research is required to fully comprehend this phenomenon and its potential applications in various fields. Additionally, this research could be

extended to other similar hydrogen bond donors and acceptors to determine whether the same phenomenon occurs in other aqueous mixtures

Hammond and colleagues (2017) also noted that as water content raised, the strength of the hydrogen link between choline and urea decreased. The solution still retains the properties of pure-DES even at up to 40.95 weight percent water because the water also functions as a hydrogen bond donor and is absorbed into the reline network, strengthening the hydrogen bonds that are arranged between both HBA and HBD. Complete reline component solvation occurs when the water quantity hits the overcrowding limit (at about 51 wt% H₂O). A new phase is created as a consequence of this total solvation, and this new phase differs from pure DES in terms of its characteristics. Consequently, the addition of water to DES can result in the creation of a new solution with distinct characteristics.

2.2.3 Ionic Liquid based Electrolytes for Electrodeposition of Size and Shape Controlled ZnO Nanostructures

Ionic liquids (ILs) are widely utilized for electrodeposition of metals and metal oxides owing to their unique properties. These liquids have a wider electrochemical window, enabling the deposition of metals with extremely low redox potentials (Wei & Ivaska, 2008). This is particularly useful when attempting to deposit metals that are typically difficult to deposit using conventional methods. In addition, either the good thermal stability or low vapor pressure of ILs make them well-suited for deposition of especially metals at high-temperature (Zhang et al., 2016). This is especially useful when high-temperature deposition is required.

Furthermore, ILs provide tunable properties that allow for appropriate modification or strategic selection of both the cations and anions present in the liquid. This allows researchers to control deposit properties and alter nucleation rates and growth mechanisms (Zhang et al., 2016). Because of their advantageous features and

adaptability, ionic liquids are increasingly being used in electrochemical deposition investigations. These properties will be explored in detail in this section.

As explained in various parts of this study, the complex hierarchical ZnO structures has been gained attention recently to provide potential areas for functional applications including photocatalysts, sensors and drug release systems. In this framework, for the ZnO electrodeposition alongwith electrodeposition parameters, the addition of organic agents or inorganic additives into the electrolyte solution, employing templates or perform electrodeposition in IL/DES that are used as a versatile source of anions are the foremost investigated methods.

As a result of their unique features and possible uses, ionic liquids (ILs) are increasingly being used as electrolytes. It has been observed that air- and water-stable ILs, halometallate ILs, ionic liquids with metal containing cations, protic ILs, and deep eutectic solvents (DESS) are the most often utilized electrolytes for electrodeposition (Zhang et al., 2016). Among them imidazolium based room temperature ionic liquids which is a kind of ILs that contain metal cations, have been investigated due to the highly structured character, broad hydrogen bond network, and the ability of ions to form ion aggregate (Azaceta, 2011) (Tulodziecki, 2012) (Azeceta, 2013).

Tulodziecki and colleagues (2012) investigated the electrodeposition of ZnO on platinum, stainless steel, and ITO substrates under oxygen saturation using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), 1-Butyl-1-Methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmImTf) as electrolytes. They investigated the effect of temperature and zinc cation concentration on oxygen reduction and discovered that cation content and temperature improve oxygen reduction using CV analysis. The fundamental disadvantage of these metal-containing cations type imidazolium-based ILs is that they are typically more viscous than most molecular solvents. Moreover, because to anions' weak coordinating

power, mass transport and metal salt solubility in these ILs are fairly restricted (Zhang et al., 2016).

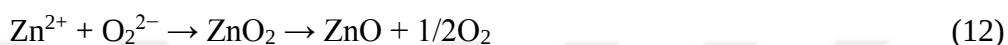
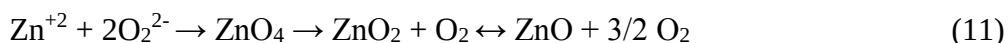
Several methods such as ionothermal (Cun et al., 2016), hydrothermal precipitation (Adhyapak, 2014) or antisolvent method (Dong et al., 2010) by using IL/DES have been developed to fabricate nanostructured ZnO with modified photocatalytic efficiencies. The final product in these studies are generally nano-sheets, nano-rods or nano-particles. Numerous studies have shown that electrodeposition from ionic liquids is a novel technique for growing ZnO films because it has a number of advantages over other approaches, including low reaction temperatures (below 100 °C), gentle material processing, and ease in depositing films on a variety of substrate shapes with controllable thickness. In addition, ZnO grain size can be changed by adjusting the electrochemical parameters overpotential, current density, pulse parameters, and bath temperature (Tulodziecki et al., 2012) (Azaceta et al., 2009) (Azaceta et al., 2011) (Dumitru et al., 2016).

As previously mentioned, deep eutectic solvents (DESs) are another type of IL that is frequently used because they have melting points lower than room temperature, reasonable solubility for a variety of metal salts, are affordable, may be recyclable without endangering human health, are well-tolerated by water and air, are relatively biocompatible, and are less expensive than their counterparts. There are only a few reports on the electrodeposition of ZnO thin films that concentrate on the sample morphology and use deep eutectic solvent as the electrolyte. (Costovici et al., 2014) (Dumitru, 2016) (Harati, 2012).

The electrochemical synthesis of ZnO nanopowders was examined using reduction process of Zn metal in ChCl based DES with the addition of H₂O₂, which raised the OH⁻ ion concentration, resulting in a greater yield and crystallinity of ZnO nanodeposits (Dumitru, 2016). It is presented that the addition of H₂O₂ to the electrolyte solution prevents producing univalent Zn⁺ cations. Therefore the only Zn⁺² source is electrochemical dissolution of Zn atoms from metallic anode rather

than oxidation of Zn^+ intermediate cations in the presence of H_2O_2 that favors the film growth.

Costovici and coworkers (2016) are described the mechanism for the reaction process in ChCl based DES that is through oxide route rather than hydroxide unlike aqueous media. As an alternative, the oxidation of metallic zinc deposits into ZnO using peroxide and superoxide ions produced by oxygen reduction reactions is taken into consideration (Costovici et al, 2016):



In other words, Costovici and colleagues (2016) found that the mechanism for the reaction process in ChCl based DES is through the oxide route, as depicted in the above reactions. This is in contrast to the hydroxide route observed in aqueous media, as also discussed in the related section in which traditional electrodeposition studies in aqueous media are detailed. This suggests that the reaction process in ChCl based DES may follow a different mechanism than in aqueous media. Furthermore, this finding sheds light on the unique properties of ChCl based DES as a solvent and opens up possibilities for exploring its potential applications in various fields.

As particularly described at the electrodeposition of ZnO from aqueous solution part of this thesis, while the deposition mechanism in aqueous electrolyte is triggered with the formation of OH^- ions, in ChCl-based DES the nucleation mechanism is initiated by the formation of oxide ions. In either case ZnO electrodeposited onto the substrate through following a different pathway for reactions. Costovici et al. (2014) also reported an effective electrochemical production of ZnO nanopowders via anodic dissolution of Zn metal in DES-based electrolytes, in a similar way. Zinc acetate dihydrate was the precursor for Zn^{2+} and ChCl-urea and ChCl-ethylene glycol were used as eutectic mixtures with addition of hydrogen peroxide (H_2O_2). According to XRD investigations hexagonal wurzite ZnO nano powders

electrochemically synthesized by using platinum cathode and zinc anode. Consistent with the above reaction summarizing the electrodeposition of ZnO in anhydrous medium, the cyclic voltammogram shown in the research results reveals the current increases associated with the dissolution of Zn^{2+} and oxidation of O^{2-} at the same time to synthesize precipitated ZnO in anodic scanning.

Dumitru and co-workers (2016) studied deposition of ZnO onto glassy carbon cathodically by using choline chloride based DES as electrolyte namely, ChCl-urea and ChCl-ethylene glycol. At various scanning rates, cyclic voltammograms (CV) were recorded at 70 °C. During electrodeposition $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was selected as zinc precursor. Aside from zinc metal deposition, ZnO can be formed via electrochemical mechanism in the more negative potential range by joining zinc ions with peroxide and superoxide produced by the oxygen reduction reaction, as shown in the preceding reactions (Dumitru et al., 2016). This process is referred as the oxygen reduction reaction (ORR) and is a crucial step in the formation of ZnO under nonaqueous conditions. In fact, the Zn^{2+} ions played the role of an electrocatalyst for the reduction of nitrate ions in both reline and ethaline solutions by either reducing to Zn metal or remaining adsorbed on the electrode surface.

In conclusion, the available literature on the electrodeposition of ZnO thin films is limited, especially in regards to sample morphology and the use of DES as electrolytes. It has been depicted that DES are a more effective option for electrodeposition compared to conventional aqueous solutions. This method of deposition may offer a unique opportunity to gain further insight into the morphology of ZnO thin films, leading to potential applications in diverse industries. Additionally, there is no existing study that compares the photocatalytic activity of ZnO obtained through electrochemical processes with DES and aqueous electrolytes under identical conditions, which is a unique aspect of this study. Further exploration into this area could provide valuable information for the development of new and improved photocatalytic materials.

2.3 Indium Recovery

2.3.1 Indium, Indium Oxide and Tin-doped Indium Oxide

Transparent conducting oxides (TCOs) are thin film materials that are crucial for technological applications and the focus of in-depth research due to their usage in photonic and electrical devices. The development of TCO has advanced significantly with the growth of technology, and several TCO films based on various metals have arisen. Films like indium oxide (InO_x), zinc oxide (ZnO), tin oxide (SnO_2), and tin-doped indium oxide are among them ($\text{In}_2\text{O}_3:\text{Sn}$) (Kőrösi et al, 2011).

TCOs are a group of thin film materials that have proven to be crucial for technological advancements in the fields of photonics and electronics (Hosono, 2007). These materials are in the focus of in-depth research due to their many potential applications, which range from the development of solar cells and touchscreens to the creation of transparent electrodes for organic light-emitting diodes (OLEDs) and liquid crystal displays (LCDs) (Hosono, 2007).

Over the years, the development of TCOs has witnessed significant progress, thanks to the growth of technology and the increasing demand for more efficient and cost-effective materials. Today, there are several TCO films based on various metals that have been developed, each with its unique set of properties and potential applications. The most often utilized transparent conducting oxides are tin-doped In_2O_3 , also known as indium-tin oxide (ITO) and fluorine-doped tin oxide (FTO) (González et al., 2004).

Indium oxide (stoichiometric form is indexed as In_2O_3 whereas non-stoichiometric form referred as InO_x) and tin-doped indium oxide ($\text{In}_2\text{O}_3:\text{Sn}$) are the most commonly used TCOs (Kiriakidis et al., 2003). With a broad bandgap of 3.7 eV, indium oxide ($\text{In}_2\text{O}_3 / \text{InO}_x$) is a frequently researched n-type semiconductor (Bender et al., 2001). Optoelectronics, especially in electrical devices incorporating indium titanium oxide (ITO), along with flat panel displays, smart windows, and light-

emitting diodes, have found usage for ITO (Lu et al., 2023). In_2O_3 (InO_x) and $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) films are very well investigated materials due to their valuable electro-optical properties. These materials are also suitable for potential technological applications in various fields.

Tin-doped indium oxide or indium tin oxide (ITO) is known as the degenerate n-type semiconductor material (Yu et al., 2016). This oxide film composed of mainly (90%) In_2O_3 with minor addition to SnO_2 by weight (Mammana et al., 2012). Bulk ITO is in yellowish grey color, however in the form of thin film, it is colorless and transparent. Thin film surfaces always have a presence of non-stoichiometric In_2O_3 and the generation of oxygen vacancies, such that the InO_x -related species (Plumley et al., 2018; Lu et al., 2023; Martin et al., 2016).

Indium oxide and ITO films are electrically conductive metal oxides, having wide band gaps with identical crystalline structure (Mammana et al., 2012). Because of their electrical conductivity and optical transparency, these materials are classified as TCO materials. Currently, ITO is widely used for electronics especially in LCD screens, touch control screens, antifogging glasses, mirrors etc.

In_2O_3 is a semiconducting oxide having an ionically bonded cubic bixbyite structure (Giusti, 2011). As compared to covalently bound materials, point defects occur rather quickly during synthesis (Giusti, 2011). These deficiencies are mostly made up of oxygen vacancies and interstitial indium atoms. Indium cations, for example, are found in two separate six-fold-coordinated locations in the ITO unit cell. One-quarter of the cations are trigonally compressed octahedral, while the other three-quarters are severely deformed octahedral, referred to as b and d sites, respectively (González et al., 2004); (Giusti, 2011).

The cubic In_2O_3 cell has 80 elements and a lattice parameter of 10.117 (Giusti, 2011). Cations occupy the 32 sites in two distinct nonequivalent positions, 8b and 24d. With six of the corners filled with oxygen atoms and the other two empty in either the b or d sites, the indium atoms are positioned in the middle of a distorted cube (Giusti, 2011). The distance between indium and oxygen atoms is 2.18, whereas in d-sites

with less symmetry, three distinct In-O distances are observed: 2.13, 2.19, and 2.23. The b sites have oxygen vacancies along the body diagonal, whereas the d sites have them along the facial diagonal (González et al., 2004) (Ma et al., 2015).

The inherent oxygen vacancies are another significant point defect. Because oxygen vacancies are electrically charged, they play an essential role in doping by forming neutral or charged complexes with dopant atoms. Interstitial oxygen atoms or/and oxygen vacancies can restore the charge imbalance created by the different valences of indium and tin in ITO (Ovadyahu et al., 1983).

Besides intrinsic dopants such as oxygen deficiencies, ITO also contains extrinsic dopants as tin (Sn). Because of the valence difference between tin and indium, charge imbalance occurs by doping process. This imbalance recovered by contribution of oxygen vacancies or interstitial oxygen atoms (Mizuhashi, 1980). Moreover, according to Mössbauer experiments only Sn^{4+} ions were detected whereas Sn^{2+} ions are absent in ITO content which provoke a model with oxygen interstitials (González et al., 2004). All these defects, depending on their stoichiometry, which might be generally positive, negative, or neutral, directly affect the conductivity of ITO (Frank and Köstlin, 1982) ; (Giusti, 2011).

2.3.2 Indium Recovery from Indium Tin Oxide (ITO)

ITO and ITO based products have been receiving significant attention due to their wide applications in both industry and research. ITO accounts for over 97% of the worldwide transparent conductive film industry and is widely employed in a variety of electronic devices requiring superior electrical and optical features (Swain et al., 2015).

ITO thin films' uses were heavily reliant on properties such as good optical transparency with in visual spectrum, reflectance in the infrared range, and superior electrical conductivity (Ghanizadeh et al., 2016). Because of their electrical and optical characteristics, these thin films may be employed in a variety of applications.

ITO films are mostly used in optoelectronic devices such as touchscreen displays, flat screen displays, electrochromic displays (ECDs), liquid crystal displays (LCDs), organic light emitting diodes, and solar cells (Ghanizadeh et al., 2016).

The electrical resistivity of ITO film is in the order of $1\text{--}2\times 10^{-4}\ \Omega\cdot\text{cm}$ (Gusti, 2011). Along with roughness, manufacturers aim to produce these optoelectronic devices with either high optical transparency or low resistivity. (Malik & de la Hidalga-Wade, 2017). Electric and electronic equipment (EEE) is the fastest-growing solid waste globally, and waste electric and electronic equipment (WEEE or e-waste) is indeed the extremely fast growing solid trash (Işıldar et al., 2018).

Işıldar et al. (2018) have been recently investigated global market data and growth capacity for WEEE. The WEEE increase from 2013 to 2020 was reported in India and China with the highest rates 145 and 98%, respectively. This increase in WEEE can be attributed to the rise in electronic devices consumption and the lack of proper disposal methods. Moreover, an increase in the demand for electronics and, consequently, WEEE generation, is anticipated for all developed and developing economies, including Türkiye (Işıldar et al., 2018; Dang et al., 2014).

This clearly illustrates the significance of rare metal recovery in WEEE equipment eventually of its economic life span. This demonstrates the need for strong laws and policies to encourage the recovery and recycling of rare metals from WEEE as well as the development of environmentally friendly extraction methods. Additionally, it highlights the potential financial gains that can result from recovering rare metals from WEEE.

Even though people are still looking for alternatives, ITO electrodes are still used in optoelectronic devices because there is no way to replace them with better performance. Since indium is a rare metal and its natural resources are running out, it is becoming more and more important to find ways to recycle it from other materials. In fact, the European Commission lists indium as one of the most important raw materials and a critical resource (European Commission, 2018).

Reprocessed waste materials are used instead of primary raw materials. These reprocessed materials are called secondary raw materials. In addition, the recovery of secondary raw materials instead of its ores considerably reduces the carbon and ecological footprints by maintaining these critical resources in the economy as long as possible (European Commission, 2018).

According to the Federal Strategy to Ensure Secure and Reliable Supplies of Critical Minerals executive order, indium is among the 35 crucial raw materials that should be vulnerable to interruption in the supply chain and perform an important function in product manufacture (USGS, 2020). Its departure would have serious ramifications for the economic and national security of the United States. (USGS, 2020). In addition to ITO, other indium components such as indium phosphide, indium arsenide, indium antimonide are critical semiconductors that are used in the electronic components and devices. Third- (3G), fourth- (4G), and fifth-generation (5G) wireless systems are connected by fiber-optic networks using InP lasers in the telecommunications industry (USGS, 2020). Consequently, there is a growing necessity to explore the optimal methods for recycling and reclaiming indium by means of suitable treatment of outdated electronic devices.

There is little information on the occurrence of indium minerals in environment. Indium is one of the least abundant minerals on Earth and it is most frequently saved from zinc-sulfide ore in sphalerite and chalcopyrite minerals in concentrations between fewer than 1 part to 100 parts per million (USGS, 2020). The global production of indium from refineries is presented in Table 2.3 for 2018 and 2019. Around 40 percent of the world's indium is produced in China, where the average price paid for the metal at New York City dealers in 2019 was calculated to be \$390 per kilogram (USGS, 2020).

Table 2.3 2018 and 2019 global indium refinery output (USGS, 2020).

Country	Indium refinery production	
	2018	2019
Belgium	3.0%	2.6%
Canada	7.8%	7.9%
China	40.5%	39.5%
France	5.4%	6.6%
Japan	9.4%	9.9%
Republic of Korea	31.7%	31.6%
Peru	1.5%	1.3%
Russia	0.7%	0.7%

Limited amount of information is available in literature about the recovery/recycle of In from ITO film/scraps (Chou and Huang, 2009; Wang, 2011). The electroconductive electrode in LCDs is made of ITO films, which are sandwiched among two glass planes (Dang et al., 2014). As previously mentioned, ITO is a mixture of mainly indium oxide ($\text{InO}_x/\text{In}_2\text{O}_3$), 80-90 % by weight, and remaining tin oxide (SnO_2). Based on this composition, LCD screens contains approximately 1400 g of indium per ton after removing organic materials in its structure. Similarly, one cellular phone embodies about 6.2 mg indium when the average weight of a cellular phone was taken into account (Takahashi et al., 2009).

The concentration of indium in zinc minerals is about 10 mg/kg which is much smaller than its content in the LCDs (Barrera, 2005). Additionally, in developed countries, the average lifespan of an LCD TV is between three to five years, and for

computers and smartphones, it is even less time (Schmidt, 2005). Therefore LCDs are one of the major electronic waste equipment.

To sum up, it is a big problem for the long-term health of the industry to collect and reprocess indium metal from used electronic devices. Indium is taken from used ITO circuit boards that are thrown away in Japan and the Republic of Korea (USGS, 2020). But there wasn't enough information about how much secondary indium could be recovered from waste. The rate of recycling indium metal is also very low, based on the "Report on Critical Raw Materials and the Circular Economy" published by the European Commission in 2018. On the other hand, some important raw materials, such as vanadium, tungsten, cobalt, etc., have a high rate of recycling (European Commission, 2018). The different ways that different critical metals contribute to the circular economy can be explained by the fact that there aren't enough cost-effective recycling paths or by the nature of the end product and the sector of the material that is used. So, it's important to come up with new recycling technologies for important raw materials that are efficient and have good recycling rates. It's also important to encourage the use of recycled materials in different industries to cut down on the need for new materials and make better use of resources, which can lead to a more sustainable and circular economy.

2.3.3 Indium Recovery Methods

Several methods for indium recovery have been reported for removal of indium from LCDs and ITO coated glasses in literature (Zhang et al., 2015); (Yang et al., 2013); (Lee et al., 2013); (Rocchetti et al., 2015). In these studies, first waste LCDs are pre-cleaned by removing several layers of polarizing film and liquid crystal components (Fontana et al., 2021). The interior LCD screen is made up of sandwich construction with numerous layers, including two refractive films, two glass layers covered via ITO thin film, and a layer of liquid crystals. Liquid crystal aligned between two transparent ITO electrodes which are also in contact with the thin film transistor

(TFT) and color filter (CF). While LCD shows two layers of ITO glass, accounting for 85 wt% of the screen, OLED displays just one layer (Fontana et al., 2021).

When an electric current is transmitted through the liquid crystals, they rearrange in a manner that either allows or prevents light from passing through the polarizing coatings. This is how images appear on the screen. This technology has altered the production of displays and is utilized in a variety of devices, including smartphones and televisions. The margins of the panel were cut with a cutting machine in order to obtain pristine CF and TFT glass. The polarizing coating from the glass substrate is frequently removed by performing thermal treatment, which involves heating the LCDs over 200 °C for around seven minutes (Savvilotidou et al., 2015). Moreover, liquid crystals can be physically separated from glass substrates by a washing step at room temperature using distilled water, sodium dodecylbenzenesulfonate, isopropyl alcohol, and ethyl alcohol (Rochetti et al., 2015). In conclusion, chemical/thermal treatment and rinsing eliminate the majority of organic components, including liquid crystals, polarizing coatings, etc. Glass containing oxidized metals, such as indium and tin, must be further processed to recover the valuable metals. As stated in the preceding sections, this process of metal recovery is significant for both environmental and economic reasons. From Table 2.4 the main metal recovering methods are shown.

Table 2.4 Indium recycling from end-of-life flat panel displays (Fontana et al., 2021).

Metal Recovery Technologies from ITO			
Thermal Processes	Hydrometallurgical Processes		Electrochemical Methods
Vacuum chlorination	1)Leaching	2)Separation and Purification	
Vacuum carbon reduction	Inorganic leaching agents	Solvent extraction	
	Organic leaching agents	Ion exchange	
	Complexing agents	Cementation	
	Bioleaching agents	Adsorption	
		Electrodeposition	

The ITO target is a 9:1 mass ratio mixture of In_2O_3 and SnO_2 (Nakashima & Kumahara, 2002). Other than the In, Sn, and O elements, the ITO target used contains less than 20 ppm of all other elements (Li et al, 2011). Therefore, recovering indium from secondary ITO targets is crucial. On the other hand, tin, which is not as

valuable and rare as indium, is also recovered with the same technologies, and its recovery from the same targets can support the long-term viability of the electronics industry, although it is not commonly investigated. There are two ways to get indium out of used ITO substrates: pyrometallurgy and hydrometallurgy.

Literature data shows that hydrometallurgical treatment which involves leaching, concentration, separation and electro refining steps, is the most-suitable and most-favorable approach for indium recycle from waste panels (Zhang et al., 2015). In order to recover indium from used ITO targets, Li and colleagues studied acid leaching-neutralization-precipitation-zinc cementation in 2011. Direct indium recovery was 78%–81% because indium bound to hydrous tin oxide (Li et al., 2011). Leaching from waste ITO scraps is carried out in strongly acidic or basic aqueous solutions (e.g. sulfuric acid, nitric acid, hydrochloric acid, as In_2O_3 is easily dissolved in acidic media, or sodium hydroxide and sodium hypochlorite. The most recommended solution for removing ITO was selected for both economic (quick kinetic and less expensive chemicals) and technical factors. (less caustic). Leaching also involves the application of complexing agents like cyanide and thiosulfate as well as oxidants like ferric iron and hydrogen peroxide (İşildar et al., 2018). Therefore, the current conventional recovery method requires the use of corrosive and hazardous chemicals which are not environmentally benign.

Another recycling route for indium is pyrometallurgical/pyrochemical processes which involves vacuum metallurgy and chlorination reaction. First SnO_2 containing In_2O_3 is reduced to obtain metallic In-Sn alloy by using carbon (C) or carbon monoxide (CO) as reducing agent under vacuum environment (Itoh and Maruyama, 2011). Molten Sn has lower vapor pressure than In. Therefore, the vaporization of indium in the In-Sn alloy is carried out under 1 Pa vacuum above 1100°C (Ebin and Isik, 2016). Indium vapor is finally created, cooled, and retrieved as metallic indium (He et al., 2014). The method's primary drawbacks are its high temperature, vacuum, and use of hazardous CO gas. Infact, the rate of reduction goes up to 90% and the time needed for reduction goes down at higher temperatures and when CO reducers are used. This means that operational costs go up (Itoh and Maruyama, 2011). So,

when choosing the right temperature and reducing agent for a given reduction process, it is important to think about the trade-off between reduction rate and cost.

Besides this feasibility issue, Sn recovery rate from LCD glass is low due to the low vapor pressure in the vacuum process temperatures which is another challenge of this method that should be improved (Ebin and Isik, 2016). In addition to this problem with viability, this approach also faces the obstacle of a poor Sn recovery efficiency from LCD glass due to low vapor pressure at the vacuum process conditions (Ebin and Isik, 2016). Tin recovery is also taken into account to increase the viability of high-cost recovery technologies like hydrometallurgy or pyrometallurgy. Nonetheless, there has been a rise in research into developing efficient and cost-effective methods for metal recovery from ITO in response to rising demand from a variety of industries.

In pyrometallurgy, thermal reduction or chlorination processes can be used to recover indium from waste ITO targets (Fan et al., 2021). Therefore, chlorination reaction or vacuum chlorinated separation processes is another pyrochemical approach that might be used in indium extraction (Ma & Xu, 2013) (Ma et al., 2012). In general, this method involves chlorination of In using chlorinating agent such as chlorine, carbon tetrachloride, hydrogen chloride, ammonium chloride, sodium chloride, calcium chloride, and other similar chlorinating agents. (Ebin and Isik, 2016). Metals can be separated and purified by preference due to the moderate evaporation temperature of metal chlorides (Ebin and Isik, 2016). Literature claims that sequential reduction and chlorination processes of indium oxide to indium chloride can occur with greater efficiency at 350 degrees Celsius than other indium chlorides and tin chlorides (Ma et al., 2012).

Indium chloride is the end product of the chlorination method that needed to be purified and separated; the product also incurs additional production costs. Chlorinated indium and tin can be evaporated and condensed. This process has the good effectiveness and usefulness because it has relative low temperature compared with conventional pyrochemical approaches. Since the cost of chlorinated separation

technique depends on indium recovery ratio, manufacturing purity, and chlorinating agent regeneration besides recovery of indium regeneration of excess chlorinating agent can lead to a considerable effect on the overall efficiency of the process. The recovery rate can be reached upto 99.48% at 400°C depending on atmosphere, residence time, and concentration of reducing/chlorination agent under vacuum environment (0.09 MPa) (Ma et al., 2012). Infact, the typical chloride metallurgy process takes place in air or in a nitrogen environment. Either have drawbacks sort of the indium recovery ratio in air is rather low while high nitrogen content raises the cost of manufacture. In addition, because hydrogen chloride and chlorine gases are extremely corrosive in nature, special attention must be paid to any reactor leaks in conjunction with special operating requirements such as vacuum conditions (Terakado et al., 2010).

For the recycling of indium metal from ITO, pyrometallurgical technology is being greatly enhanced. Scraps containing metals are burnt at a high temperature furnace, followed by the set apart of precious metals and impurities as slag in the metal recycling process (Zhang & Xu, 2016). The pyrometallurgical process involves multiple phases, beginning with the pretreatment and ending with the final extraction. All stages are performed at a high temperature, and the reaction environment is extremely specific. Maintaining the specific process condition complicates the entire procedure. Collectively, they result in a more expensive procedure, which raises the price of the products. In addition, the process is linked to the release of hazardous gases regardless the application of various cleansing techniques to control emissions.

Virtually, metal reduction and also tin-indium alloy separation are the two most important steps in the pyrometallurgical procedure for secondary ITO target (Chen et al., 2019). Also, metal reduction and indium-tin separation are the two most important steps in the pyrometallurgical recovery procedure for the ITO waste target (Itoh & Maruyama, 2011). In the first step, CO reduces ITO to In-Sn alloy at a relatively mild temperature. Due to the difference in vapor pressures between indium and tin, the indium in the In-Sn alloy selectively evaporates as the temperature

increases in the second stage. Indium is collected as metallic indium after cooling the resultant indium vapor. ITO's inability to separate indium metal from tin while recovering indium from trash is its biggest problem. Therefore, the complex and long process mentioned above actually aims to find a solution to this problem which is grounded on the reducing and evaporating properties of the In-Sn-O system.

The industrial indium recovery process of ITO refuse material has had significant progress, but still has room for development. In comparison to hydrometallurgy, the pyrometallurgical recovery technique for ITO waste target is now used less often in the industry because to its excessive use of energy, increased metal evaporation loss, and high pollutant emissions. Whereas, the hydrometallurgical process embraces the use of large amounts of caustic and volatile acids, which raises operational risks and generates waste acids. Furthermore, solvent extraction, in particular, can easily lead to environmental contamination and resource waste because of its dependence on a separate water phase during the extraction process. The ion-exchange technique has a number of drawbacks, including a high salt consumption rate, an inefficient analytical rate, a lack of discrimination, and corrosion risk. The electrolytic refining process has reached maturity, but it is limited from further growth due to the high energy required and the large amounts of acid and hydroxide required. To sum up recycling with hydrometallurgy is expensive because of the removal of leftover acid and the additional separation of indium and tin, which can lead to environmental contamination. (Chen et al., 2019).

Therefore more environmental friendly and cost-effective methods have been investigated instead of hydrometallurgical method. Biohydrometallurgical technique is based on similar principles however liquid medium contains biological molecules instead of leaching agents. Even with the negative effects of hazardous chemicals reduced, hydrometallurgical processes nevertheless tend to leach materials at a quicker pace than biohydrometallurgical ones (Işldar et al., 2018).

Moreover, several experiments have concentrated on recovering the ITO film from the glass substrate itself. On the line, up to 75% ITO removal has been reported

(Choi et al., 2014). However, it is not possible to reuse the recovered ITO directly since In/Sn ratio changed which lead to poor quality of the film. Even, the mechanism underlying the variation in the In–Sn proportion is unclear and currently being investigated further Choi and coworkers (2014) hypothesize that the In–Sn ratio altered due to a decrease in oxygen vacancies. To sum up, in order to directly recycle metallic indium from waste ITO scraps, environmentally friendly and high efficiently methods are desired and studied. Accordingly, electrochemical reduction of ITO is an alternative technique that should be considered.

2.3.4 Electrochemical Reduction of Indium

In brief, hydrometallurgical and pyrometallurgical retrieval methods are the main ways to recycle indium from ITO substrates (Su et al., 2022). The main technological step in hydrometallurgical recovery is crushing the ITO substrate, followed by leaching it along with sulfuric acid, and then recovery of indium/tin throughout a sequence of extraction and separation steps, as was covered in the previous section. The hydrometallurgical recovery method necessitates the use of significant quantities of acid and/or organic agents (Su et al., 2022). It is necessary to treat waste water in a series of subsequent steps, and the length of the recovery process flow makes it challenging to achieve industrialization. Pyrometallurgical recovery is performed at elevated temperatures, uses a lot of energy, and produces greenhouse gases despite having a simple flow chart and high recovery efficiency (Su et al., 2022). Consequently, an effective and environmentally friendly method is needed to recover indium straightforwardly from ITO.

Metals are currently produced on an industrial scale using electrochemical technologies. For the fabrication of thin-film semiconducting complexes like InSb, InAs, and Cu(In,Ga)Se₂, which are extensively used in devices for electronics and optics, electrodeposition of indium is of great interest (Traore et al., 2011). Cost, product purity, efficiency, sustainability, and other factors should be used to measure technological progress in industry. In addition, according to Song et al. (2021) and

Armstrong et al. (1996), electrodeposition has an increased operational capability due to the tunable potential of the electrode and the metal's adjustable electroreduction property by attempting to control the electrolyte, i.e. the including ligand, and has demonstrated superior performance throughout the extraction of metal from multimetallic spend in the case of ITO. Therefore, a variety of novel recycling and recovery technologies, including electrochemical approaches, have caught researchers' interest for strategic metals like indium.

ITO has durable electrical and optical properties over a wide potential range mainly due to its stability in both acidic and basic solutions. On the other hand, it may lose its conductivity and transparency under extreme anodic or cathodic environments which limits the potential window of ITO in applications such as transparent conductive electrode (Liu et al., 2015). Therefore, the electrochemical behavior and structural changes of ITO has been investigated under different electrochemical conditions.

Some underappreciated chemical and electrochemical restrictions apply to ITO (Ciocci et al., 2021). ITO surface flaws include different In:Sn ratios, grain boundary orientations, interstitial Sn^{4+} or interstitial In, and oxygen vacancies (Ciocci et al., 2021). Studies pointed out that, all these complex non-stoichiometric microstructure variations and defects may influence the ITO electrochemical answer. Therefore, the onset potential associated with the ITO reduction was investigated which showed that the onset potential shifted depending on surface heterogeneities (Gökçeli & Karatepe, 2021). From this point of view, it can be concluded that electrochemical reduction of ITO highly related to the electrode surface properties.

According to Liu et al (Liu et al, 2015), the solution media strongly influences the electrochemical behavior of ITO. This suggests that the characteristics of ITO may be designed for specific applications by selecting the appropriate electrolyte. In order to expand the electrochemical window of ITO, electrolyte conditions such as pH and various anions were studied in order to control them appropriately. According to the variation of electrodeposited ITO at various pH levels, the onset potential of ITO

decreases as the electrolyte's pH rises, indicating that reduction is more advantageous in acidic environments than in basic media (Liu et al., 2015).

In addition, it was discovered that the existence of specific anions within the electrolyte enhanced the electrochemical stability of ITO. Hence anion effect in electrolyte including different potassium salts (SO_4^{2-} , Br^- , Cl^- and NO_3^-) anions were studied (Liu et al., 2015). The reduction process of ITO is heavily reliant on the anions in the electrolyte, as NO_3^- ions greatly block reduction while SO_4^{2-} and Br^- are more relevant to potential than Cl^- (Liu et al., 2015). These findings were attributed to thermodynamic and kinetic variables during electrodeposition by Liu and colleagues (2015). Similarly according to Spada et al. (2013), various electrolytes, including AlCl_3 , GdCl_3 , Na_2SO_4 , and NaOH , have varying threshold potentials for the cathodic reduction of ITO. The threshold potential was determined to be greatest in the NaOH electrolyte and lowest in the AlCl_3 electrolyte by the authors (Spada et al., 2013). This indicated that the reduction potential of ITO can be considerably impacted by the electrolyte that is used.

Even though stability of ITO substrates in terms of electrochemistry and chemistry in acidic and basic electrolytes are underestimated mostly as discussed by Liu's group (2015), there are some researches discussed the corrosive effect of electrolyte on ITO. ITO and its electrochemical properties were investigated primarily in corrosive electrolytes. In such a medium, and particularly at pH values below 1, the ITO electrode is chemically dissolved and unstable (Senthilkumar et al., 2008). Recent research has demonstrated, however, that ITO exhibits excellent electrochemical stability in neutral and alkaline electrolytes, making it a viable material for a variety of applications under these conditions. This has prompted additional research into the electrochemical behavior of ITO in non-acidic environments.

Matveeva (2005) studied the electrochemical characteristic of ITO during both cathodic and anodic processes in 1 M NaOH solution by cyclic voltametry (CV). In this investigation, the fact that ITO dissolves in acidic solutions but performs better

in basic electrolyte solutions was explored. This is analogous to what was discussed about in other studies about the corrosion of ITO and tin oxide in acidic and basic electrolytes. Moreover, the electrochemical performance of ITO in acidic solution in the presence of HCl has been examined. Folcher et al. (1997) developed a two-step anodic ITO dissolving process using 0.04 M or 0.1 M HCl solutions. It was reported that first radical species, Cl° and OH° , may be formed in the electrolyte during electrochemical process following the corrosion of ITO due to breaking of In–O surface bonds via the radical species (Folcher et al., 1997). HCl solution at lower pH exhibited significantly higher dissolution rate for ITO (Virolainen et al., 2011). Moreover ITO demonstrated most stable performance in the pH-values close to 8.00.

When etching ITO with a wet chemical process required for the production of LCD, the dissolution of ITO in the presence of agents such as HCl was utilized and exhibited a similar reaction mechanism (Huang et al., 2004). This technique is preferred to dry etching techniques due to its lower cost and greater efficacy. However, the use of HCl as an etchant can raise safety and environmental concerns. Amorphous ITO film can be dissolved in dilute acids, besides polycrystalline ITO film can only be etched in a rather concentrated acid solution. The surface In-O bonds are damaged by undissociated HX molecules ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) all across the process, resulting in InX_3 and H_2O as the reaction product, which may be elucidated by the reaction below (Hernandez et al., 2020).



Spada et al. (2013) have found that the electrochemical response of ITO in electrolyte medium is strongly dependent. They showed that the limit potential for cathodic reduction of ITO differs in AlCl_3 , GdCl_3 , Na_2SO_4 , and NaOH electrolytes, indicating that various metal ions in buffer solutions including electrolytes (acidic and basic) enhance lateral diffusion by metal ion adsorption on ITO. During the reduction of ITO, the oxygen ion from the oxide lattice combines with H^+ ions from the water molecule, creating hydroxyl ion and In/Sn atoms on the substrate's surface.



The interaction between of substrate surface as well as the electrolyte is blocked by the development of metallic islands that resemble spheres made of indium or tin (Spada et al., 2013) . Yet, even when the electrolyte solution completely covers the substrate surface with metal droplets, the reduction process is still possible because the electrolyte still finds diffusion pathways across the porous metallic layer. Spada and coworkers (2013) suggested that this blocking effect increase the electrolyte resistance which trigger the sudden rise in voltage's absolute value with a view to keep a steady current.

Molten salt electrolysis is widely used for electrolytic reduction of metal oxides, as exemplifying above since molten salt electrolyte possesses high ionic conductivity and wide electrochemical windows. However, molten salt electrolysis causes CO₂ emission, due to the CO₂ generation from the carbon anode, and requires high-temperature operation. Using a molybdenum rod serving as the working electrode in melted LiCl-KCl at 450°C and a constant potential variation of 1.7 V, Cui and colleagues (2019) examined the electrochemical redox mechanisms of ITO. They observed reduction peaks at about -1.0 V and -1.2 V that are ascribed to In and Sn, respectively. Electrochemically anodic dissolution of indium occurs in two steps at the potentials around -0.8 V and -0.2 V attributed to oxidation of In to In⁺ and In⁺ to In³⁺, respectively. Meanwhile reduction of Sn to Sn²⁺ observed at -0.3 V according to the cyclic voltammograms with SnO₂ in molten salt.

Although recovering indium from waste panels has been the subject recent years' extensive research, industrial recycling plants remain to be developed (Virolainen et al., 2020). In the academic literature, new processes to enhance the technical, economic, and environmental viability of indium recycling have been proposed. In addition, the removal tin and indium's effectiveness is unavailable in the majority of studies. Using ionic liquids to dissolve indium and tin from LCD surfaces is one of the suggested procedures (Ebin & Isik, 2016). These processes require additional study to ascertain their efficacy and economic viability.

2.3.5 Non-Aqueous Electrolytes for Electrochemical Reduction of Indium Tin Oxide (ITO)

Because of its controllability, high conversion efficiency, and minimal equipment needs, electrochemical technology is a preferred technique for extracting metals (Song et al., 2020). In addition, less research was conducted in the field of selective separation of metals that are containing two or more metal cations. The process becomes more convoluted due to the prospect of simultaneous discharge of multiple cations, which causes the purity of the metals to decline. In order to develop efficient and cost-effective methods for the selective separation of metals from complex solutions or materials, additional research is required. It is possible to separate and recover indium and/or tin metal resources from ITO through electrochemical selective deposition or reduction, based on the difference in reduction potential of these different metals.

Metal recovery through electrodeposition from aqueous solutions trigger simultaneous hydrogen gas synthesis during electrodeposition at rather negative potentials, leading to H₂ evolution (Walsh & Gabe, 1979). The evolution of hydrogen gas reduces the effectiveness of electrodeposition and can result in unstable deposits or structures like hydrogen embrittlement, dendritic growth, and pinholes (Deferm et al., 2019). Since hydrogen is not generated in these media, ionic liquids or deep eutectic solvents may be employed as alternate electrolytes for electrochemical deposition. Just a few studies have been published on the electrodeposition of indium or indium alloys utilizing ILs or DESs (Deferm et al., 2019).

Non-aqueous electrolytes have demonstrated the benefits of broad electrochemical windows and high stability comparable to aqueous electrolytes (Rai et al., 2021). To illustrate that the electrolyte stability window for pure water is 1.23 V, this value is 2.5 V for reline (Popescu et al., 2013). This means that reline is more stable than pure water in terms of electrolyte stability, making it a better option for certain applications that require higher stability and because of their greater breakdown voltage, they are used in precise metal electrodeposition (Rai et al., 2021).

Non-aqueous electrolytes contain traditional organic solvents such as dimethylformamide or -sulfoxide, molten salts like LiF-CaF₂ or LiCl-KCl, ionic liquids (e.g. [P₂₂₂₅][NTf₂], chloro aluminate ILs) and DESs such as ChCl based DES (Rai et al., 2021). Conventional organic solvents contain impurities that necessitate purification processes that negatively impact the electrodeposition of metal ions. Xianwei and coworkers (Su et al., 2022) recover and reuse ITO by following multi steps at high temperature, voltage and time conditions including electrochemical reduction of the ITO at 850 °C in molten CaCl₂, following of a In-Sn alloy electrolysis in a solution of aqueous ammonium chloride at 2.80 V to synthesize their hydroxides and finally post heat treatment at 400 °C during 10.0 hours. In contrast, ionic liquids have the advantage of being highly pure and can be easily recycled, making them an attractive alternative solvent for electrodeposition processes.

Furthermore, ionic liquids are chemically and thermally stable, have good electrical conductivity, and melt at 100°C, which makes them easier to work with than molten salts. Unlike traditional organic solvents, which are volatile and can catch fire, ionic liquids are the perfect conjugate electrolytes because they don't evaporate. ILs are also called "designer solvents" because there are numerous cation and anion combinations that could alter the solvent's properties in a big way. This lets the solvent be fine-tuned for specific processes (Welton, 2018).

There has been a lot of interest in the use of ionic liquids in electrochemical applications because of their complex behavior on charged surfaces. This is very different from the behavior of traditional dilute electrolytes, which have structures full of large, dense ions (Fedorov and Kornyshev 2014). Among the nonaqueous electrolytes, ILs are a promising candidate for fine-tuning electrolytes for specific electrochemical processes due to their high potential in electrochemical applications as a result of their unique behavior on charged surfaces, which is distinct from that of classical conjugates.

Electrochemical processes using ILs and DESs on behalf of aqueous electrolytes have been receiving attention because of the convenient properties of ILs and DESs

for electrodeposition, low freezing point, non-volatility, and high thermal stability due to the poor ionic coordination and the delocalized charge of at least one ion in their structure (Inman et al., 2022). ILs are organic salts that typically contain an inorganic anion and an organic cation which demonstrate wide electrochemical window, where metals with very negative standard potentials such as indium can be electrodeposited without hydrogen evolution risk (Inman et al., 2022).

Wouters' group (2019) lately published researches on the indium electrodeposition in 1,2-dimethoxyethane (DME) and poly(ethylene glycol) (PEG400) ionic liquids. DME-based electrolyte was used to create indium deposits with roughly shaped particles at room temperature, while PEG400 electrolyte at 160 °C produced spherical particles (Monnens et al., 2019). ILs offer to stop hydrogen evolution by providing a larger electrochemical window that is simultaneously seen in aqueous solutions during electrodeposition, supporting the idea that indium reduction occurs in multiple steps.

Matsumiya et al. (2018) demonstrated the recovery of In via a combination extraction and electrodeposition technique. Indium was selectively removed from Ni(II) and Zn(II) using ionic liquid tri-butyl-phosphate in n-hexyl-trimethylammonium bis(trifluoromethylsulfonyl)amide and subsequently recovered by direct electrodeposition of the loaded organic phase at -1.0 V, -1.5 V, and -2.0 V.

The electrochemical behavior of indium in another form of hygroscopic ionic liquid, namely 1-butyl-1-ethyl-piperidinium bis(trifluoromethylsulfonyl)imide, including 0.1 M InCl_3 was described, as was the effect of chloride ions upon the In(III)/In(0) electrochemical system (Traore et al., 2011). The findings demonstrated that the presence of chloride ions significantly altered the electrochemical behavior of indium, resulting in a shift in the reduction potential and a decrease in current density. The research conducted by Liu and colleagues reveals important information about the electrochemical attitude for the In(III)/In(0) pair in the 1-butyl-1-methylpyrrolidinium dicyanamide IL electrolyte. (Liu et al., 2017).

Matsumiya and coworker's (2018) analysis sheds light on the cathodic peaks observed for In(III), Ni(II), and Zn(II) metals in an 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methane sulfonamide aqueous solution. These studies maintain important knowledge for the electrochemical behavior of metals in ILs for the fields of recovery technology. Additional research in this area could lead to the creation of more efficient and environmentally friendly technologies.

Alongside the favorable properties of ILs, DESs are usually cost effective and environmentally friendly due to their unique structures. The majority of the ionic liquids exhibit high sensitivity to water and instability against oxygen. DESs which was first suggested by Abbott et al. (Abbott et al., 2003) are strong alternative of ILs for electrodeposition of metals. DESs are nontoxic, biodegradable and low-cost products compared to room temperature ionic liquids which steer them for large-scale applications. When amides, acids, sugars, or alcohols of any kind are combined with quaternary ammonium salts, the resulting DESs are simple to synthesis, do not react with water, exhibit good ionic conductivity, have a high thermal stability, and are well soluble in metal salts (Alcanfor et al., 2017). In addition, due to the hydrogen bonding structure, DESs are chemically inert towards water, and their production is much simpler than that of ionic liquids.

Rahman and coworkers (2015) investigated electrodeposition of indium phosphide in a 1:2 molar ChCl:urea DES electrolyte at 80 °C. They came to the conclusion that the instantaneous mechanism was used for Mo surface nucleation and the progressive mechanism was used for Au surface deposition. The findings suggest that the substrate choice can significantly affect the electrodeposition route and the morphology of final deposited material. The potential applications of indium phosphide deposited using this method require additional research.

Similar to the preparation of Copper indium gallium selenide (CIGS) film for solar cell applications, indium is electrodeposited over previously deposited Cu layer in 1ChCl:2EG (molar ratio) DES including 0.05 M InCl_3 to investigate nucleation-growth mechanism and morphology of electrodeposited indium surface at various

bath temperatures (Alcanfor et al., 2017). At lower bath temperatures, an indium layer electrodeposited at 80 °C generated nanorods measuring between 75 and 250 nm in diameter. Using ethaline (1ChCl:2EG) for the electrodeposition of indium over a previously deposited Cu layer in CIGS film for solar cell applications has proven to be effective.

Co-electrodeposition of indium, copper, and gallium on a Mo electrode from reline (ChCl:U – 1:2) was examined to determine how the composition of the solution affected the electrodeposition behavior, crystallization and deposit morphology (Malaquias et al., 2015). The composition of the DES solution was found to influence the morphology and crystalline structure of the deposited alloys, with higher gallium concentrations resulting in smoother and denser films. Therefore, DESs preferred as the electrolyte in a number of electrochemical processes.

2.4 Electrodeposition: Principle and Mechanism

The conventional electrochemical deposition system involves three-electrodes namely working, reference, and counter electrode. In a typical system, the counter electrode serves as the anode and the working electrode as the cathode (Rai et al., 2021). Through generating an electrical potential at the cathode, metals are electrodeposited there. Metal ions (M^+), dissolved in electrolyte (aqueous or nonaqueous solution) and reduced to form electrodeposited metal (M^0) which is also called a cathodic deposition via the following equation:



Through the Nernst equation, the equilibrium potential (E^{eq}) controls this reversible electrochemical reduction-deposition (Rai et al., 2021):

$$E^{eq} = E^0 + \frac{RT}{nF} \ln \frac{a(M^{n+})_{ox}}{a(M^0)_{red}} \quad (17)$$

where R denotes the ideal gas constant, T stands for temperature, and F for the Faraday constant. Moreover, E° is the normal electrode potential measured at standard conditions of 1M concentration, 1 bar pressure at 298 K (Rai et al., 2021).

Because of the concentration difference of the reactant molecules in the bulk electrolyte and also the mass transfer to the electrode, the electroreduction/electrodeposition of the desired metal ions may take place at various potentials than that of the equilibrium Nernst potential (Rai et al., 2021). The discrepancy between the thermodynamically calculated reduction potential (equilibrium potential) and also the potential that exists when the redox event is empirically seen for a specific reaction is described as overpotential deposition (OPD) (Rai et al., 2021). When the metal's reduction process happens at smaller negative potentials than the equilibrium potential, underpotential deposition (UPD) is detected (Rai et al., 2021). UPD occurs when the electrodeposited metal interacts more strongly with the metal surface of the electrode than with itself, indicating that metal deposition may be created onto the other metal substrate more readily than it can be formed on itself (Nasirpour, 2017).

The primary reaction mechanism underlying the reduction of indium and tin from ITO film is depicted in the diagram Figure 2.4. The reduction reaction from indium(III) through indium (0) is a multistep process that is dependent on the type of electrolyte. The reduction mechanism of indium (III) to indium (0) can be accomplished through a two-step deposition reaction employing chloroindate (III) ionic liquids as reducing agents. Due to their ionic structure, these liquids also serve as metal sources, template agents, and stabilizing agents. (J. Estager et al., 2012); (Carpenter & Verbrugge, 1994).



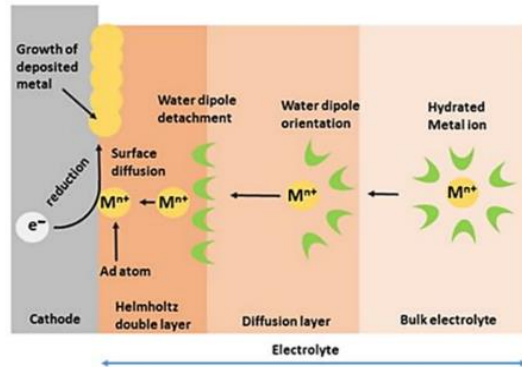
The potential and current distribution determine the rate of deposition, morphology, and properties of the deposited material. Understanding this mechanism is important

for controlling the effectiveness and quality of electrodeposited materials in various applications. Homogeneous deposition with a uniform thickness is the best case. This is determined through how metal ions continue moving towards the electrode, the polarization there at electrode, the configuration of the electrolytic system, the location and structure of electrodes in the electrochemical cell, the electrolyte's properties, such as resistance, and indeed the interface between of electrolyte and electrode (Rai et al., 2021). Furthermore, the study of electrodeposition can also aid in the optimization of the processes, which are generally used in industries like aerospace, automotive, and electronics.

Electrodeposition mechanism for recycling valuable metals such as indium covers four main steps as shown in Figure 2.4 A. First, with the applied potential, metal ions move from the electrolyte through the cathode (Rai et al., 2021). Along with this transportation, hydrated ion layer get out at the cathode electrode–electrolyte interface. Finally these metal ions adsorbed onto the cathode as growing metal clusters and transformed into the bulk aggregations (Rai et al., 2021).

The early electrical double layer (EDL) model dates back to Helmholtz (Wang et al., 2009). EDL is based on two parallel charging layers developed between the electrode/electrolyte interface, first of which involves ions adsorbed onto the electrode via surface charging that are firmly anchored due to chemical interactions (Figure 2.4 A). The second layer namely diffusion layer involves ions are drawn to the surface charge using the Coulomb force, and electrical screening of the primary layer. On contrary, diffusion layer consists of nonrigid, cozy moving ions in electrolyte that are being affected by electrical attractive forces and thermal motion.

(A)



(B)

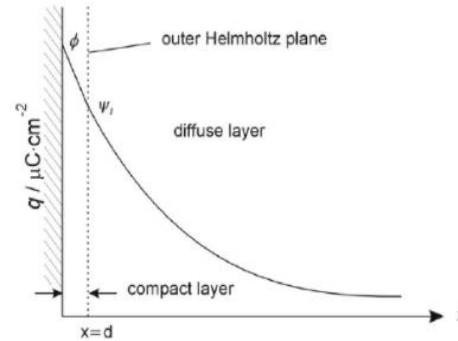


Figure 2.4 A) Diagram of the electrodeposition mechanism (Rai et al., 2021) B) GCS model of an electric double layer (Wang et al., 2009).

Gouy-Chapman-Stern (GCS) model is used for traditional aqueous electrolytes which considers effects of ion size, specific adsorption onto the surface, solvent polarization/dipole moment interactions and metal electronic effects as demonstrated in Figure 2.4 B (Li & Huang, 2020). GCS model is not adequate for describing the electrode/ionic liquid interfaces due to large and asymmetric structure of ions tend to distribute in multilayer form with lattice saturation at applied voltage. In conclusion, for complex electrolyte/ionic liquid character there is a significant progress need for theoretical modeling (Su et al., 2010).

CHAPTER 3

EXPERIMENTAL PROCEDURE

In the present study, we employed electrodeposition as a method to deposit zinc on ITO coated glass using DES. The electrodeposition process is a widely used technique that involves the deposition of metals onto a substrate by passing an electrical current through a solution containing metal ions. In our study, we used DES, which is a relatively new and promising alternative to traditional solvents due to its low cost, biodegradability, and non-toxic nature. Our research focused on optimizing electrodeposition parameters mainly electrolyte type and composition. Electrolyte type and composition significantly effect the electrochemical mechanism such that in aqueous electrolyte very dense zinc deposition was observed onto the ITO electrode surface while in DES indium reduction from ITO was investigated.

Teherefore, our project involves a comprehensive study of indium recovery and zinc deposition covering various electrodeposition parameters as well as characterization using a wide range of techniques. We aimed to provide a detailed account of our experimental techniques, including any challenges we encountered.

To ensure the rate of recovery of indium and zinc deposition on the ITO electrode surface and electrochemical process mechanism, we employed several techniques for characterization. These included X-ray diffraction (XRD) analysis to determine the crystal structure and phase purity of the deposited films, scanning electron microscopy (SEM) to study the morphology and surface topography of the films, X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) to determine the elemental composition of the samples and Cyclic Voltammetry (CV) experiments to suggest on oxidation/reduction mechanism during electrochemical process.

3.1 Materials

Commercially available ITO glass obtained from Sisecam, zinc chloride (Sigma-Aldrich, Germany), potassium chloride (Merck, Germany), choline chloride (Sigma-Aldrich, China), urea crystal (Isolab Chemicals, Germany), ethylene glycol (Sigma-Aldrich, Germany), acetone and ethanol were used without further purification. All solutions were prepared from p.a. grade chemicals and up grade distilled water.

3.2 Electrochemical Experiments

During the electrochemical experiments, a 2-electrode system was used, which is the simplest form of an electrochemical system consisting of a cathode and an anode. Distinctively from the 3-electrode system, this set-up does not contain a reference electrode, which has the role of measuring and controlling the working electrode potential without passing any current. A potential difference is created between the cathode (-), namely working electrode, and the anode (+) (counter electrode). The negative electrode is the cathode, while the positive electrode is the anode. The substrate is the cathode in cathodic deposition, while the counter electrode is the anode.

In this two-electrode system, the constant voltage applied with power supply between two electrodes: the counter electrode and the working electrode (Figure 3.1). The counter electrode, also known as an auxiliary electrode in literature, is an integral part of the electrochemical system. Using the two electrode setup, the counter electrode serves two purposes. It completes the circuit, enabling charge to pass throughout the cell, and it also keeps the interfacial potential constant independent of current. Under most circumstances, it is difficult to meet both of these requirements. Maintaining a steady counter electrode voltage while current flows is extremely challenging with a two electrode system. With a two electrode system in addition to a lack of correction of the voltage drop in the solution, results in inadequate management of the working electrode's potential. The working electrode,

on the other hand, is the sample on which the reaction and deposition occur during the electrochemical experiment. Its shape and size can be customized based on the final application area, enabling it to be adapted to a wide range of uses.

While the counter electrode has little or no contribution to the electrochemical reaction, its total surface area is a key factor that determines the source of electrons and the rate of the reaction. To ensure that the system works efficiently, the counter electrode should have a higher surface area than the working electrode. This not only increases the number of electrons available for the reaction but also ensures that the limiting factor is the surface area of the working electrode. Moreover, the current can be measured anywhere in the circuit by connecting a multimeter in series to the system as depicted in Figure 3.1. This allows for non-precise monitoring of the current change and gives insight that the system is operating as expected.

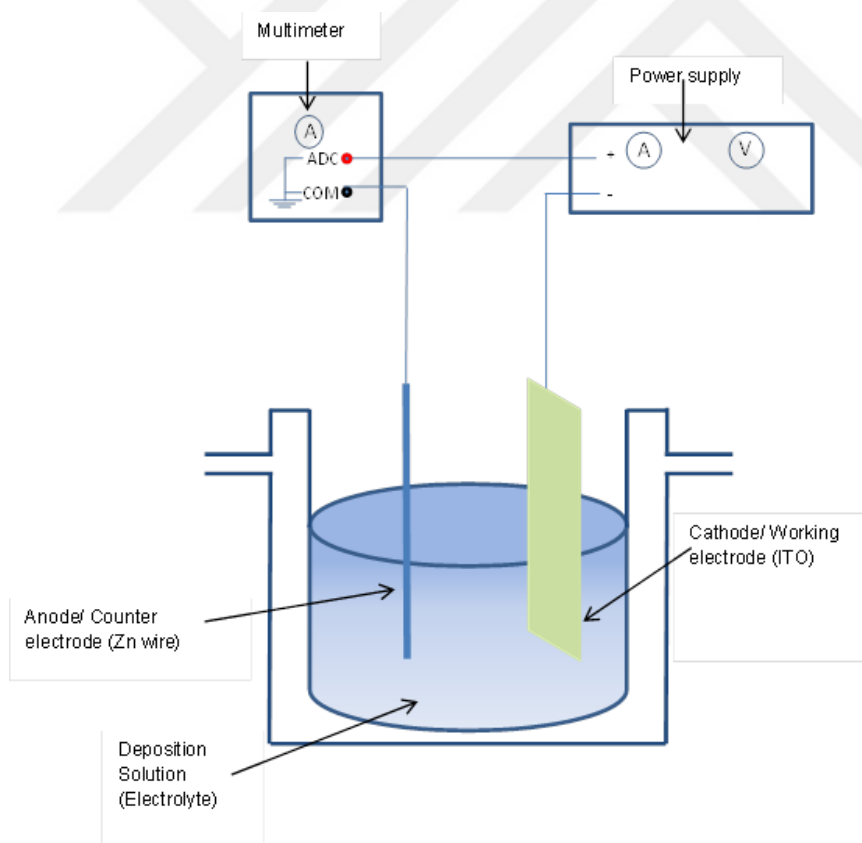


Figure 3.1. Schematic diagram of the 2 electrode electrodeposition experimental setup

3.3 Electrochemical System and Parameters

Electrochemical parameters affect the efficiency and stoichiometry of the electrodeposited metal. These parameters include voltage, time, composition of the electrolyte solution, pH, and temperature. In order to specify optimal experimental parameters, mainly the type of electrolyte solution, electrochemical process time, pH of the electrolyte, and concentration of the supporting electrolyte (ZnCl_2) were chosen. ZnCl_2 was used as a zinc precursor in ChCl-based deep eutectic solvents (DES) because anions in electrolytes also contribute to electrochemical systems. To minimize the anion effect during the electrochemical process, DES and precursors with the same anion structure are preferred. The values of these parameters were changed to study the individual effects of them as well as their interactions to cover all the combinations.

Aqueous solutions and ChCl based DESs, namely reline and ethaline, were examined with significantly different ionic structures and properties as electrolytes during electrochemical experiments. Following this, concentrations of water and zinc chloride precursors were studied in DES in order to observe their effect on the ionic network and mechanism of electrochemical processes. Besides, modifications on the working electrode surface were investigated at different pHs of the electrolyte and electrolysis times after electrochemical treatment.

The electrodeposition procedure was carried out in a two-electrode configuration, in which a Zn wire (7 cm) behaved as the counter electrode and the ITO coated glass ($6 \times 2 \times 0.2$ cm) with a sheet resistance of 20 ohm/sq was used as the working electrode. ITO thin film thickness was about 168 nm, which was acquired from film supplier Sisecam. During the experiments, we utilized Indium Tin Oxide (ITO) as a working electrode. ITO surfaces are known to contain several defects, such as oxygen vacancies, substitutional Sn^{4+} , interstitial In, nonstoichiometric InO_x , various grain boundary orientations, and different In:Sn ratios. These intrinsic and extrinsic defects can significantly impact the electrode's performance and, thus, are essential

to investigate. The working and counter electrodes were placed parallel to each other, separated by a distance of 7 mm, as shown in Figure 3.2.

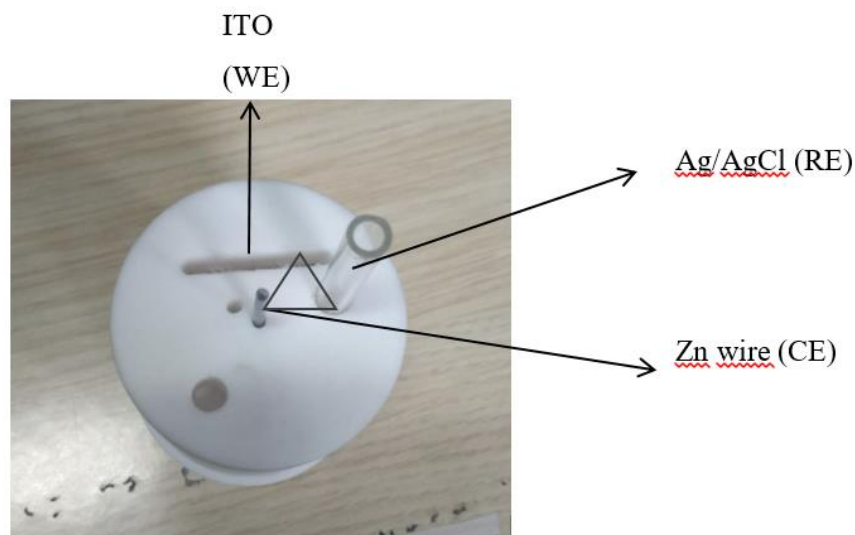


Figure 3.2. Top view of working, counter and reference electrode layout

In order to achieve analogous outcome for electrochemical processes in a controlled and predetermined area, the electrolyte solution in the jacketed pot was set to 70 ml. This was done for all trials regardless of the variations in the other parameters of the experimental setup. The controlled and predetermined area was 4 cm x 2 cm for all the trials. To ensure that molecular oxygen was supplied to the electrochemical system, air was blown with a flow rate of 40 ml/min by using aquarium air pump into the system for 10 minutes before the experiment was initiated. The electrodes were placed in Teflon holders from top to bottom, as shown in Figure 3.2. These steps were taken to ensure that the experimental results were reliable and consistent.

An electrochemical experimental setup can be seen in Figure 3.3, which covers a water circulating system, a jacketed pot including electrolyte and electrochemical chamber units, a power supply unit to provide electric current at -1.6 V, and a multimeter that was connected to follow the current change with time. The air blowing was conducted at the lowest limit during the experiment.

The electrochemical cell used in the experiments was equipped with a heating jacket that was connected to a thermostatic circulation water bath and electrolyte solution. To ensure that the electrolyte solution temperature was maintained at 80 °C, the heating jacket was used. Indium has a melting point of 156.6 °C, which poses a challenge when depositing adherent metallic indium at temperatures approaching its melting point. Thus, it is preferred to keep the temperature below 100 °C. Therefore, In our experiments, we maintained a constant temperature of 80 °C to ensure the metal deposition on ITO substrate was optimal.

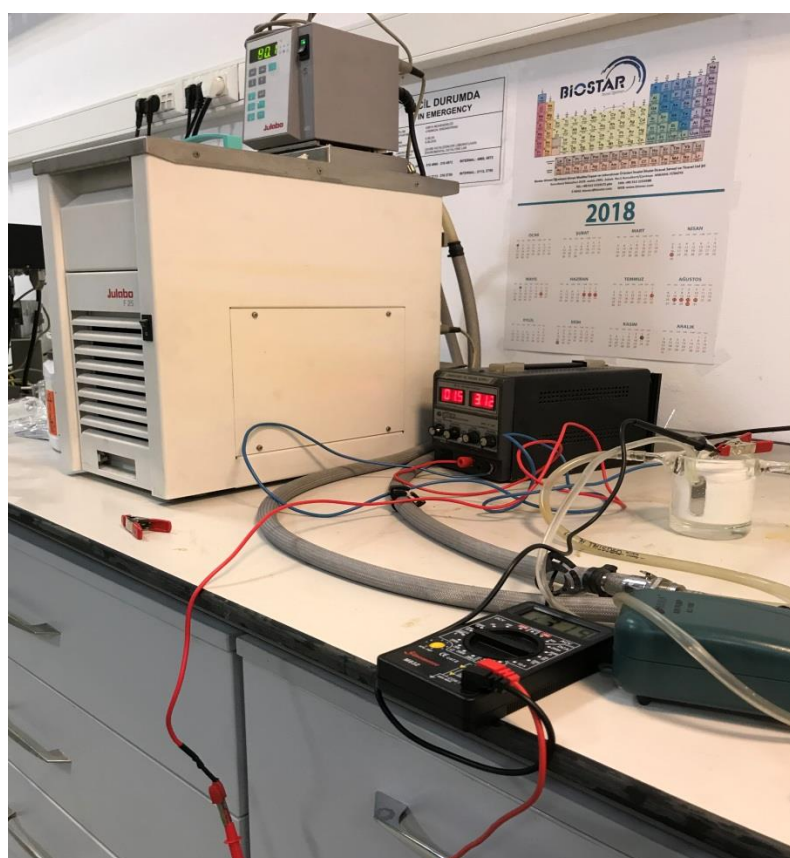


Figure 3.3. Two-electrode experimental set-up for following current up during the experiment

3.3.1 Electrolyte Solution

In order to investigate the impact of ionic structure, hydrogen bonding network, and physical properties of electrolyte solutions on the surface morphology of deposited zinc and ITO, a series of electrochemical deposition experiments were conducted. The experiments employed a variety of solutions, including water, ethaline, reline, and aqueous solutions of reline and ethaline. During the experiments, the deposition process and recorded any changes to the surface morphology of the deposited zinc and ITO were observed. These observations were then used to draw conclusions about the relationship between the properties of the electrolyte solutions and the surface change of the working electrolyte. Overall, the experiments provided valuable insights into the mechanisms underlying electrochemical deposition and the factors that influence its outcomes.

The first electrochemical experiments were applied to distilled water solutions, which are the most studied and oldest electrolytes for benchmarking. These early experiments helped establish a foundation for future studies of various electrolytes. The films were electrodeposited in a aqueous bath containing 5×10^{-3} M ZnCl_2 as a zinc precursor and 0.1 M KCl. All these chemical products were dissolved in the bath solution to prepare an electrolyte. The bath temperature was set to 80 °C and oxygen padding was implemented into the system by air blowing. Moreover, films were deposited under a potentiostatic condition of -1.6 V for 30 minutes.

After the electrochemical experiments, the deposits were rinsed with distilled water and dried at 70 °C in the incubator for a day. In order to improve the film quality, the deposits were annealed at 300 °C for 10 minutes before characterization.

To further expand the scope of the experimental investigations, different electrolyte solutions were tested. These included reline, ethaline, reline:ethaline binary mixtures, and aqueous reline/ethaline. Besides electrolyte type, among the electrochemical process parameters supporting electrolyte, zinc precursor,

deposition time, and calcination temperature, various values were investigated with a 2-electrode configuration.

3.3.2 Reline, Ethaline, Reline:Ethaline Binary Mixtures and Aqueous Reline/Ethaline Preparation as Electrolyte

Reline was created by combining choline chloride (ChCl) with urea in a 1:2 molar ratio (ChCl: urea). For 2 hours, the mixture was mixed at 400 rpm and 70-80 °C, or until a homogeneous, clear, colorless liquid was created. Ethaline was also made by combining ChCl and EG in a 1:2 molar ratio (ChCl:EG).

Aqueous mixtures were created by combining DES with water in such a sequence of DES/water molar ratios in order to achieve the appropriate amount of hydration. DES (Reline and Ethaline)/water mixtures at various molar ratios (x), called as ethaline/reline-xMR, were prepared. Reline/water mixtures were created in a series of 1 choline chloride: 2 urea: x water molar ratios (defined as x MR hydrated/aqueous reline). In addition, an ethaline/water mixture (1 chloride : 2 EG : x water) indexed as x MR hydrated/aqueous ethaline was prepared. A homogeneous, transparent, colorless solution was created by mixing at 400 rpm per minute at about 70 to 80 °C. All of these DES/water mixtures (hydrated/aqueous DESs) including the corresponding weight and molar percentages, are described in Table 3.1.

Solutions were prepared directly before or up to 1 day before the experiment. These prepared pure and hydrated/aqueous DESs were stored in desiccators until deposition to avoid water contamination prior to electrochemical studies.

Table 3.1 The list of DES sample compositions which were applied in this study

Mixture	ChCl:U:W ratio	Water, mol %	Water, wt %
Pure reline	1:2:0	0	0
1MR reline:water	1:2:1	25	6.48
3MR reline:water	1:2:3	50	17.22
4MR reline:water	1:2:4	57	21.71
5MR reline:water	1:2:5	62.5	25.74
9MR reline:water	1:2:9	75	38.43
Mixture	ChCl:EG:W ratio	Water, mol %	Water, wt %
Pure ethaline	1:2:0	0	0
1MR ethaline:water	1:2:1	25	6.39

Subsequent to the works that studies were conducted to determine how the properties of DES changed when there was water present throughout the electrochemical experiments, the influence of reline/ethaline binary mixtures on the deposits was also investigated. Therefore, variety molar ratios of reline and ethaline were added as 50% and 90% mol ethaline until a uniform, transparent, colorless liquid developed which were referred to as 1:1 and 1:9 (reline:ethaline) molar ratios (MR), respectively. Again, these binary solutions were prepared directly before measurement or at least 1 day before the experiment and stored in a desiccator until deposition to avoid water contamination.

3.3.3 Deposition Area

The electroactive area of the substrate electrodes is a crucial parameter for electrochemical experiments. It enables to control the extent of the nucleation mechanism, making it an essential component of the overall experimentation process. In order to standardize the working electrode area, a total of 70 ml of electrolyte solution was used in all electrochemical studies.

To conduct the electroreduction experiments, a two-electrode electrochemical cell was utilized, with ITO coated glass serving as the working electrode. The active surface area of the working electrode was 8 cm² (4 cm x 2 cm), allowing for precise and accurate measurements. Additionally, the utilization of a two-electrode system ensured that the results were reliable and consistent.

Overall, the careful consideration of the electroactive area of the substrate electrodes and the use of a standardized electrolyte solution, as well as the utilization of a two-electrode electrochemical cell with an ITO coated glass working electrode for a precise active area, were key factors in ensuring the accuracy and reliability of the electrochemical experiments conducted.

3.3.4 Supporting Electrolyte

Supporting electrolytes play a crucial role in determining the final results of surface deposits, such as their morphology, composition, and size. In the initial trials with DES, 0.1 M KCl was used as the supporting electrolyte, as it is a typical supporting electrolyte in aqueous systems. However, it was discovered that KCl did not dissolve in pure reline or ethaline. This led to the selection of ZnCl₂ instead of KCl, as it, too, has similar anion moieties with the ChCl-based DESs used in this study. This choice helped to avoid some possible anion exchanges, and ZnCl₂ is also capable of fully solvating in the reline and ethaline solutions.

Moreover, the Cl^- ions and other anions in the DES solution tend to adsorb on the working electrode. This was mainly studied to adjust or orient the deposits. In general, Cl^- ions do not or can only create complexes via metal ions to a very small extent. This was another significant motivation for specifying ZnCl_2 as a supporting electrolyte. Therefore 0.1 M ZnCl_2 was dissolved in DES mixing at 400 rpm for 20 minutes at 70–80 °C.

It's also important to note that the supporting electrolyte's role was taken into account because it influences the electrical double layer (EDL) structure and current intensity throughout the electrochemical experiment when its concentration is raised. In this context, electrochemical experiments were carried out in reline with different ZnCl_2 concentrations (0.1 M, 0.2 M, and 0.4 M) and without a supporting electrolyte, ZnCl_2 , under the same conditions, such as deposition time (30 min), current (-1.6 V), and temperature (80 °C) with a 2-electrode configuration. These experiments aimed to better understand the effect of various concentrations of supporting electrolyte on the final results of surface deposits and to ensure that the conclusions drawn from the study were robust and reliable.

3.3.5 Electrolyte pH

Along with the electrolyte content, its pH also has a significant effect on the electroreduction experiments since the electrolyte acts as a medium for the movement of electrons and forms the electric circuit between the electrodes. Solution pH changes the current densities for reduction of the indium metal, which influences the reduction rate.

The solution selected for electrochemical experiments was an aqueous reline solution possessing a 3 M ratio of water (3 MR hydrated reline). The solution pH was adjusted in the range of 8 to 5 by the addition of acetic acid. Table 3.2 shows the bath composition at different pHs.

Table 3.2 Electrolyte bath composition and pH values

Bath composition	pH
140 ml 3 MR Aqueous Reline	8.47
140 ml 3 MR Aqueous Reline + 0.1 Molar ZnCl_2	8
140 ml 3 MR Aqueous Reline + 0.1 Molar ZnCl_2 + 0.5 ml acetic acid	6
140 ml 3 MR Aqueous Reline + 0.1 Molar ZnCl_2 + 1.0 ml acetic acid	5

3.3.6 Preparation of Working and Counter Electrodes

As the working electrode, a glass substrate covered in indium-doped tin oxide (ITO) was utilized, with a width and length of 2 cm and 6 cm, respectively. ITO thin film thickness was about 168 nm, which was acquired from film supplier Sisecam. Zinc wire 7 cm in length and 1 mm in diameter was utilized as a counter electrode during experiments. Before each experiment, the working and counter electrodes were carefully cleaned to ensure optimal performance and accurate results. The cleaning process involved multiple steps to thoroughly remove any impurities or contaminants.

First, the ITO-coated glass electrodes and zinc wires were washed with a specially formulated detergent to remove any grease or residue that could interfere with the experiment. Next, they were submerged in an ultrasonic bath for 15 minutes in acetone solution, ethanol solution, and distilled water, respectively. This was done to dislodge any remaining particles or debris that could affect the outcome of the experiment.

After each ultrasonication step, substrates were washed with distilled water in order to remove any residual solution and ensure that the electrodes were completely clean. They were then ultrasonicated for an additional 5 minutes in distilled water to ensure

that all remaining impurities were removed. Finally, both working and counter electrodes were dried at 70 °C in an incubator for a day before use in electrochemical experiments, ensuring that they were completely dry and free from any moisture that could interfere with the results.

3.4 Post Treatment

After the electrochemical experiments, the samples went through a washing process using distilled water to ensure that any impurities were removed. After the washing process, the samples were dried in an incubator at a temperature of 70 °C for one day.

To investigate the annealing contribution to film quality, the samples were characterized whether they were annealed or not. This allowed us to determine if driving off impurities or volatile constituents could improve film quality. The post-heat treatment was carried out in a calcination furnace that had a quartz glass cylinder tube inside a heated furnace. The furnace allowed for indirect high-temperature processing within a controlled atmosphere.

The samples were then either left as reduced or subjected to 15-minute post-deposition heat treatments. The heat treatments were performed at various temperatures ranging from 150°C to 500°C using a calcination furnace in the presence of air blown into the furnace with a flow rate of 40 ml/min. This allowed us to test the effect of various heat treatments on the morphology and crystallinity of the surface.

3.5 Cyclic Voltammetry Studies

Cyclic voltammetry (CV) is a method used to investigate reaction pathways involving electron transport during electrochemical processes. The current was monitored according to the value of the linear potential sweep, which would be

repeated cyclically throughout the CV trials. Due to the fact that, ions and species on the surface of the electrolyte react at different potentials and with different intensities, the CV enables qualitative and quantitative detections in one cycle. CV provides processes for oxidation and reduction, including their mechanisms and rates during the forward and reverse scans for subsequent cycles. Overall, Cyclic voltammetry is a valuable tool for understanding the fundamental processes that take place during electrochemical reactions.

The electrochemical characterization and reduction behavior of indium were determined using various voltammetry devices. These devices include the VersaSTAT3 cyclic voltammetry at Atatürk University, the Bipotentiostat Model AFCBP1 from Pine Instrument, and the Gamry Reference 600 Potentiostat/Galvanostat, both located at Gazi University.

All of the CV setups used for this work were computer-controlled and consisted of a potentiostat with three electrodes. The CV tests were repeated several times until the reduction and oxidation peak intensities decreased or disappeared. Electrochemical characterization was occurred at a temperature of 80°C by circulating water at the same temperature through the jacketed pot in a three-electrode configuration. ITO served as the working electrode, Ag/AgCl used for the reference electrode, and zinc wire served as the counter electrode. Figure 3.4 depicts the cyclic voltammetry set-up with a 3-electrode system.



Figure 3.4. A potentiostat is connected to three electrodes in a cyclic voltammetry setup: the working electrode (WE), the counter electrode (CE), and the reference electrode (RE). In a jacketed pot, the electrode tips were immersed in electrolyte solution.

CV studies focused on pure reline, pure ethaline and aqueous reline solutions, which were used as electrolyte solutions with varying molar ratios (MR) of water content. Pure DESs and 1 MR, 3 MR, and 9 MR hydrated reline including 0.1 M ZnCl_2 as a supporting electrolyte were analysed. Moreover, 3 MR hydrated reline solution was tested both with and without 0.1 M ZnCl_2 as a supporting electrolyte. Additionally, we conducted cyclic voltammetry on aqueous reline solutions with 3 MR water content including 0.1 M ZnCl_2 at different pH (5-8) levels to observe any variations in behavior under different acidic or basic conditions. To standardize the

experimental area, a 70 ml electrochemical bath solution was used for all CV studies as in the case of electrochemical treatments.

3.6 Characterization and Analysis of the Samples

X-ray diffraction is a strong, non-destructive method for determining material crystal structure. The Department of Chemistry provided a Rigaku Miniflex X-Ray Diffractometer with a CuK (30 kV, 15 mA, $\lambda = 1.54051$) source. The misaligned pattern was observed from the XRD analysis. Therefore, several samples were re-characterized with the Bruker S8 Tiger Diffractometer device, which was supplied by the Department of Metallurgical and Materials Engineering. Rigaku Miniflex XRD is a powder instrument, and measurements were performed directly from the glass surface, which can cause a -1.69 shift at the 2θ peak positions as a consequence of sample height.

Peak position (2 theta value) corrections were made afterwards by adding 1.69 to all patterns obtained by using the Rigaku Miniflex Diffractometer. The range of 2 theta degrees was set between 20° and 70° with a scanning speed of 2° per minute.

TEM images were taken in the METU Central Laboratory. TEM imaging was performed to get crystallographic information on reduced metals on a Jeol 2100F High Resolution TEM operating at a beam voltage of 200 kV. Recovered metals were detached from the glass surface with a blade in order to prepare TEM samples.

SEM images were taken in METU Central Laboratory. SEM images were recorded by a Quanta 400F field emission SEM electron microscope with 1.2 nm resolution for the purpose of morphological analysis of the recovered metals on the surface.

Elemental characterization and composition were accomplished using EDX in both TEM and SEM due to the fact that the development and detection of X-rays are same in both. The samples were also subjected to elemental mapping at the microstructural scale using scanning electron microscopy (SEM) and energy dispersive X-ray

spectroscopy (EDS). All characterizations were applied to the WE before and after electrochemical treatment.

X-ray photoelectron spectroscopy (XPS) was performed on the non-reduced and reduced ITO coated glass samples, which is an effective method for surface analysis that can be used to determine chemical composition and state. XPS measurements were performed in the METU Central Laboratory.

The surface resistivity of ITO coating was performed by using the four-point probe technique, which relies on providing contact between the test material's surface and probes arranged linearly onto a square pattern. ITO film resistivity measurements were implemented in Türkiye Şişe ve Cam Fabrikaları A.Ş., Science and Technology Center.

The PerkinElmer Lambda 1050 UV/Vis/IR Spectrometer has been used to measure the transmittance and both coated and uncoated reflectance spectra of the ITO coated glass slides and of the ITO glass after electrochemically treated in pure/aqueous reline. The transmittance and reflectance of indium oxide and reduced indium metal were measured in the 280-2500 nm spectral range at room temperature in Türkiye Şişe ve Cam Fabrikaları A.Ş., Science and Technology Center.

CHAPTER 4

RESULTS AND DISCUSSION

Considerable research has been mainly focused on the impact of the electrochemical parameters throughout the electrolysis experiments applied in DES, such as the composition of the electrolytic bath, the cation/anion concentration and type of dispersion in the bath, the presence of precursors or supporting electrolytes, the pH value of the solution, the electrolysis time, and the surface properties of the electrodes. These parameters have a significant impact on the efficiency and selectivity of the electrochemical reactions occurring in DES. Understanding the effects of these parameters can lead to the development of more efficient and sustainable electrochemical processes. In this chapter, the changes on ITO films under different experimental conditions are reported. Each of the above parameters occupies a section.

In addition, alterations in microstructure and their effects on physical or chemical property changes of the substrate surface will be systematically exposed in this chapter. This comprehensive approach will provide a thorough understanding of the electrolyte properties, which is essential for developing and optimizing surface modification techniques. Ultimately, this knowledge can be applied to improve the performance and functionality of DESs in a variety of applications, including electrochemistry.

The measurements of the ITO coating used as the working electrode in the electrolysis experiments are presented prior to the detailed results and discussions. These measurements are crucial for understanding the performance and modifications of the working electrode during electrochemical treatment. Indium doped tin oxide (ITO) has the same crystal structure and physical/chemical properties as indium oxide (In_2O_3), as detailed in the literature review part of this scientific

report. As stated in the published literature, indium oxide data were utilized for all measurements, including XRD data.

Figure 4.1 shows the X-ray diffraction patterns of the ITO thin film that was employed as working electrode during electrolysis experiments in this study. Polycrystalline structure with the plane of In_2O_3 (222) of the cubic phase was observed at 30.58° with highest intensity in accordance with the standard data (JCPDS Card No. 06-0416) as depicted in Figure 4.1. Other three notable peaks due to the diffraction of the (400), (440) and (622) planes of the cubic phase of the standard data were observed at 34.46° , 51.08° , and 60.77° , respectively.

The total miscibility of In and Sn atoms in the In_2O_3 lattice is demonstrated by the absence of any spectral peaks indicative of In, Sn, SnO , and/or SnO_2 (Figure 4.1). It is also indicated in the literature that each Sn (IV) atom in ITO material substitutes for an In (III) atom, increasing the material's conductivity by providing a free electron. As a result, ITO keeps its cubic In_2O_3 structure all the way to the point when SnO_2 can no longer dissolve in In_2O_3 .

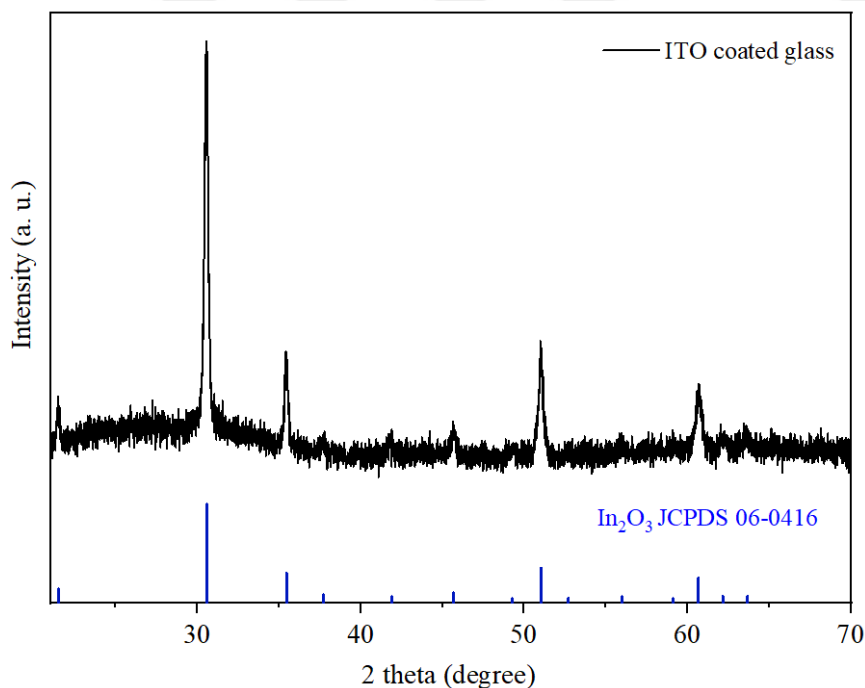


Figure 4.1. XRD pattern for untreated ITO thin films

Scanning electron microscopy (SEM) measurements of ITO working electrode were also performed for better comparison of surface morphology after electrochemical treatments such as electroreduction, zinc electrodeposition etc. To eliminate the potential effects of electrolytes on the ITO surface, samples were soaked in electrolyte solution (reline) for 30 minutes and then rinsed and dried at 70 °C. This is referred to as untreated ITO. Before analysis, electrochemically treated samples were subjected to the same procedures to confirm the nature of electrodeposition and the effect of electrodeposition-related parameters.

The SEM images revealed that the electrochemically untreated ITO has a smooth surface morphology, making it suitable for further electrochemical studies. As depicted in Figure 4.2, unlike electroreduced surfaces, on which sphere-like particles are typically uniformly distributed, the morphology of bare ITO reveals a smooth surface devoid of particle growth. Future experiments will investigate the surface roughness of the ITO electrode after electroreduction and/or zinc electrodeposition.

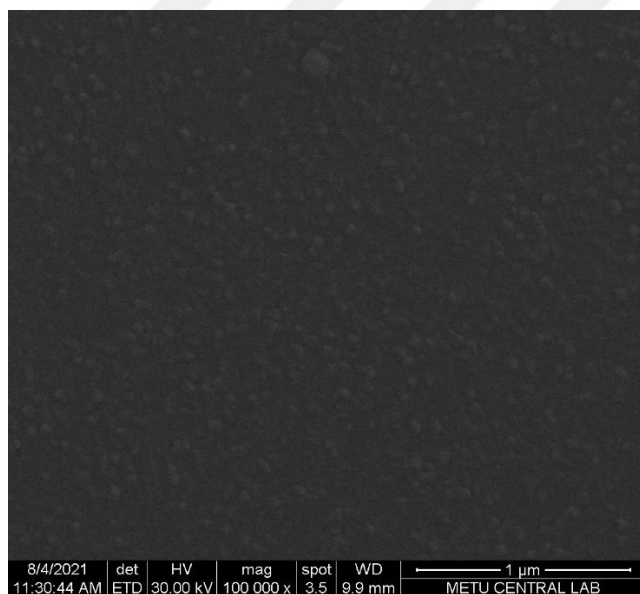


Figure 4.2. SEM image of the nondeposited bare ITO sample

During SEM imaging, the distribution of indium and tin over the untreated ITO sample was analyzed using elemental mapping analysis. As depicted in Figure 4.3, energy-dispersive X-ray (EDX) elemental mapping verifies the uniform distribution

of indium (In L_a, 3.286 keV) and tin (Sn L_a, 3.443 keV) atoms over the entire analyzed surface. This indicates that the ITO sample has a uniform composition and is appropriate for use as a working electrode.

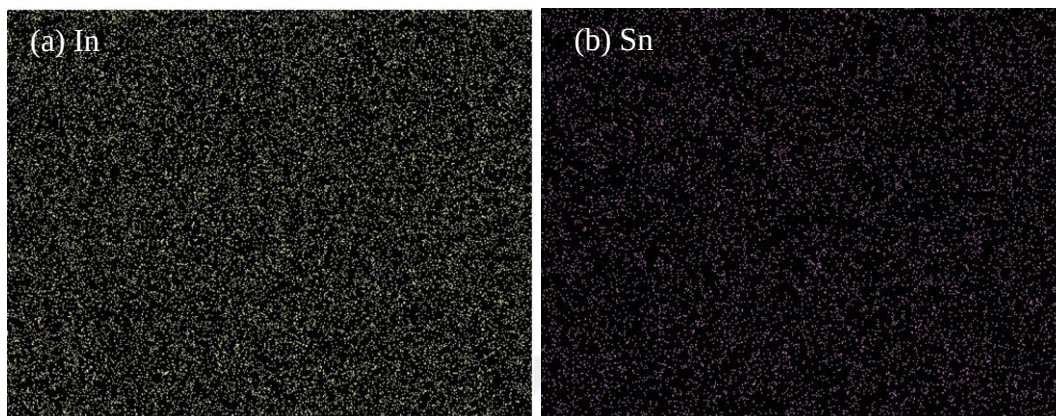


Figure 4.3. Elemental mapping analysis for In and Sn metals of untreated ITO sample

Before discussing the influence of deep eutectic solvent type electrolytes influence on microstructure and properties, the chapter begins by discussing the ZnO electrodeposition process that was studied in aqueous solution.

4.1 Electrodeposition of ZnO in Aqueous Solution

4.1.1 Structural Property and Surface Morphology of Electrodeposited ITO Samples after Zinc Deposition Films in Aqueous Solution

Zinc deposition experiments were performed using an aqueous solution that contains ZnCl₂ as a zinc precursor and KCl as a supporting electrolyte with concentrations of 5 mM and 0.1 M, respectively, at an electrodeposition potential of -1.6 V at a constant temperature of 80 °C. The morphology and structure of the deposits were characterized using SEM and XRD analyses. XRD analysis of the working electrode indicates the presence of Zn and ZnO over the surface (Zn JCPDS no. 04-0831 and ZnO JCPDS no. 36-1451) (Figure 4.4). The presence of Zn and ZnO on the surface indicates that the electrodeposition process involved both reduction and oxidation

reactions. Additionally, no ITO-related substrate peak is observed. The absence of an ITO peak indicates that the deposits were sufficiently thick to completely cover the substrate. Zn and ZnO are likely the primary components responsible for the electrochemical activity observed at the working electrode, given their presence. The presence of Zn and ZnO suggests that they are the main components responsible for the electrochemical activity observed in the working electrode.

Deposition of zinc metal was confirmed with Zn (002), Zn (100), Zn (101), and Zn (102) observed at 36.31, 38.98, 43.22, and 54.36 degrees , respectively. In addition, XRD patterns of zinc oxide exhibit prominent peaks at scattering angles (2θ) of 31.77, 34.40, 36.26, 47.51, 56.61, 62.80, 67.92, and 69.06, which are assigned to scattering from the 100, 002, 101, 102, 110, 103, 112, and 201 crystal planes. The most intense peak corresponds to the (002) plane in the XRD at 34.41, which indicates orientation along the (c-axis) perpendicular to the substrate. This suggests that the crystal structure of the sample is highly oriented along the c-axis, which is an acceptable characteristic for certain applications such as in electronic devices. Further analysis of other XRD peaks can provide additional information about the crystal structure and quality of the sample. Even though the preferential crystal orientation is through the (002) plane, in general, peak intensities for all zinc planes are close to each other, which demonstrates a good crystallization state with a larger grain size as it was also demonstrated from SEM images below.

The electrodeposited working electrodes were calcined for 10 minutes at 500 °C, and XRD analysis was also performed on the calcined sample. Calcination is a thermal treatment process that produces a chemical reaction by heating the material at high temperatures. This method can be used to convert zinc metal deposited on an ITO surface into ZnO under atmospheric conditions. In addition, the calcination process can affect the intensity and location of these peaks, which can be used to determine the sample's degree of crystallinity and purity. Zinc oxide is a versatile substance with numerous applications in fields such as electronics, cosmetics, and medicine, as detailed in the literature review section of this investigation. It is possible to convert zinc metal into ZnO through thermal treatment, as demonstrated in Figure 4.4.

As shown in Figure 4.4, the intensity of peaks assigned to zinc metal at scattering angles of 36.31, 38.98, and 43.22 (2θ) has decreased. Alternatively, although the intensities of all zinc oxide peaks increased after calcination, those of ZnO crystal planes at 2θ values of 31.77, 36.21, and 56.61 increased significantly. These peaks correspond to the (100), (101), and (110) planes, respectively, of the hexagonal wurtzite structure of ZnO. These results suggest that zinc metal is oxidized to form zinc oxide during the deposition process. Observed crystal planes in zinc oxide's XRD patterns indicate a polycrystalline structure with a preferred orientation along the (101) direction. In addition, the SEM images revealed that the morphology of the zinc oxide particles was predominantly hexagonal with some irregular shapes, which may have been the result of the growth conditions during deposition.

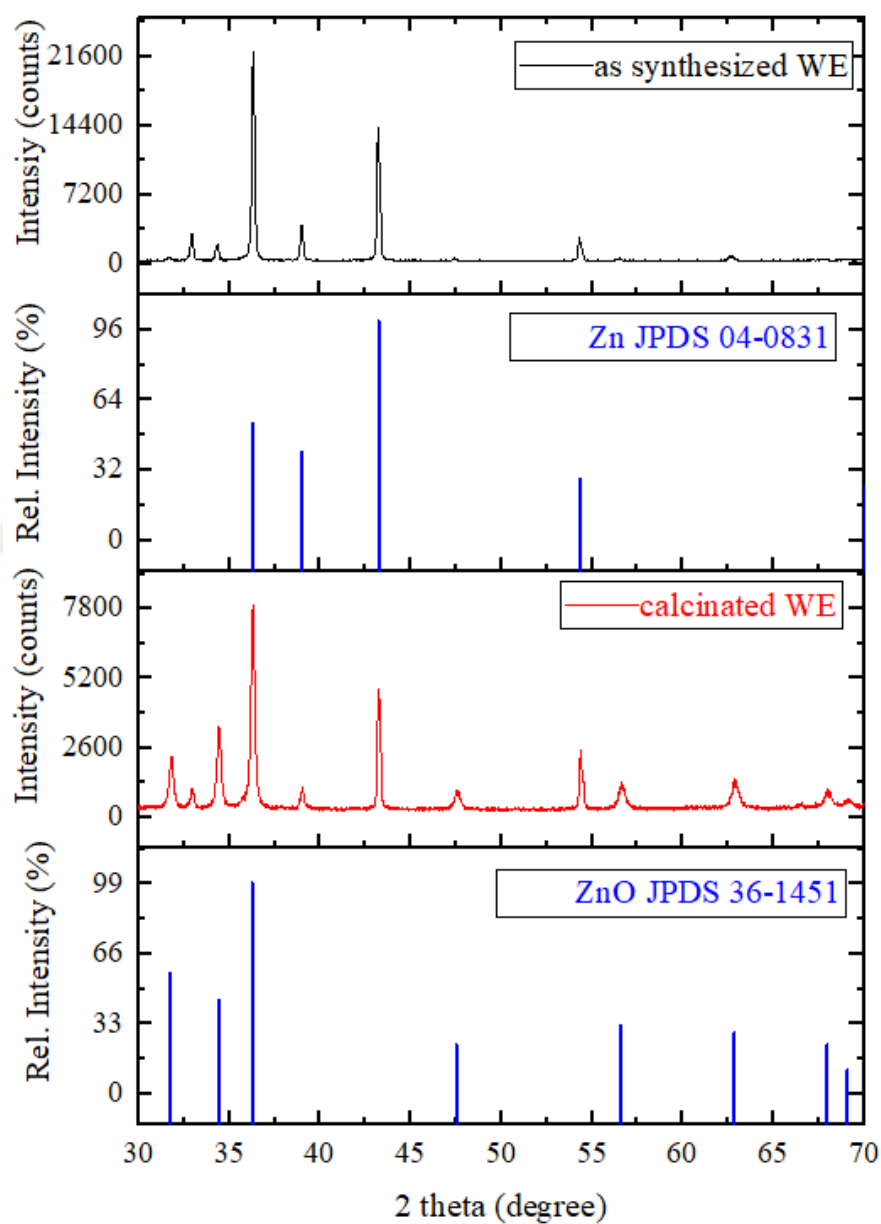


Figure 4.4. XRD patterns of the working electrodes after zinc electrodeposition in an aqueous solution containing ZnCl_2 and KCl . Working electrode after electrodeposition (colored in black); working electrode after calcination in air at 500°C for 10 minutes (colored in red)

Figure 4.5 compares the surface morphology of zinc electrodeposits over working electrodes before and after calcination. The calcination process resulted in a significant change in the surface morphology of the zinc electrodeposits, with the

calcined deposits exhibiting a more uniform and smoother surface compared to the non-calcined ones. This change in morphology is attributed to the removal of organic impurities and improved crystal growth during calcination. The solid deposit on the surface was adhered very well to the ITO substrate, and samples exhibit a uniform distribution of particles having 20–25 μm diameter. The particle size of the deposit became slightly larger after calcination at 500 $^{\circ}\text{C}$ for 10 minutes. This indicates that the calcination process led to the sintering of particles, resulting in a denser and more stable deposit on the substrate.

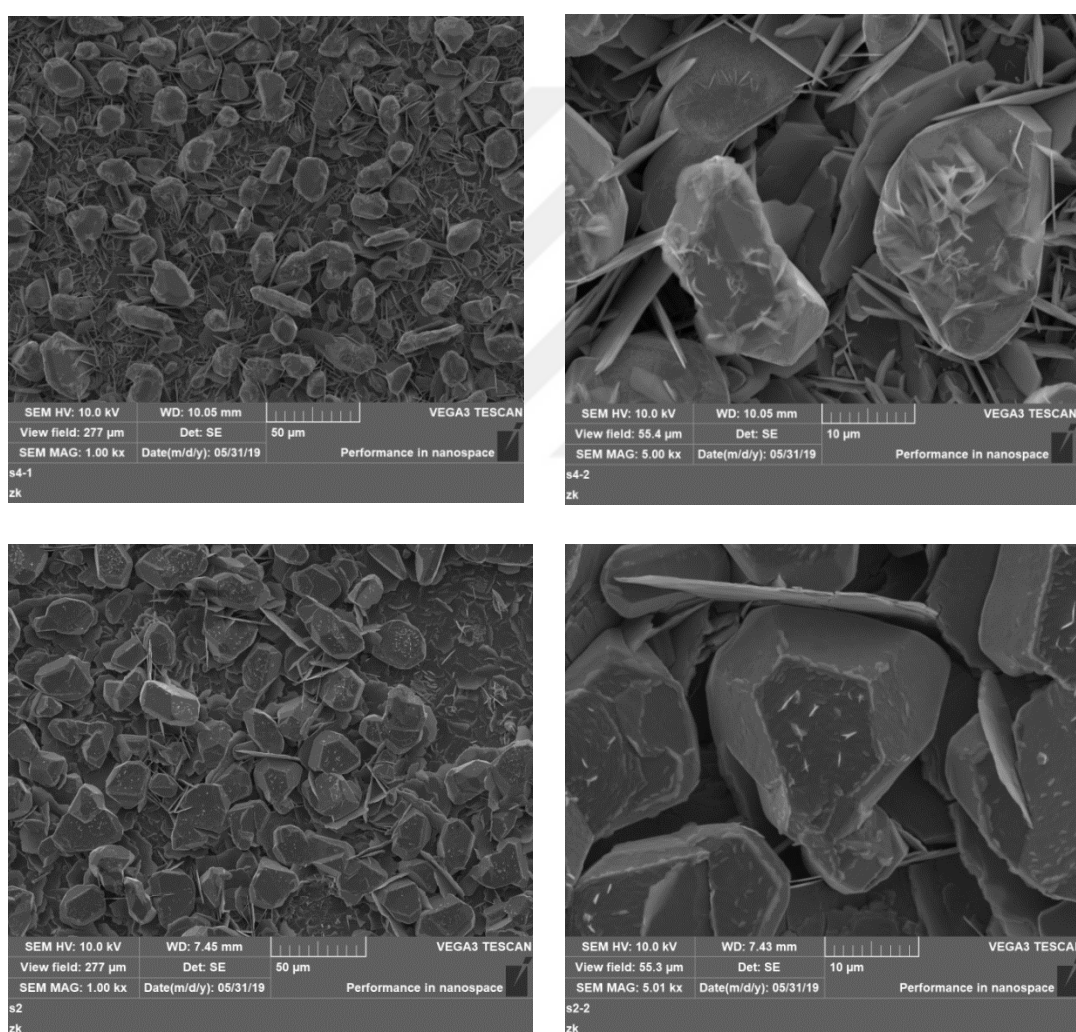
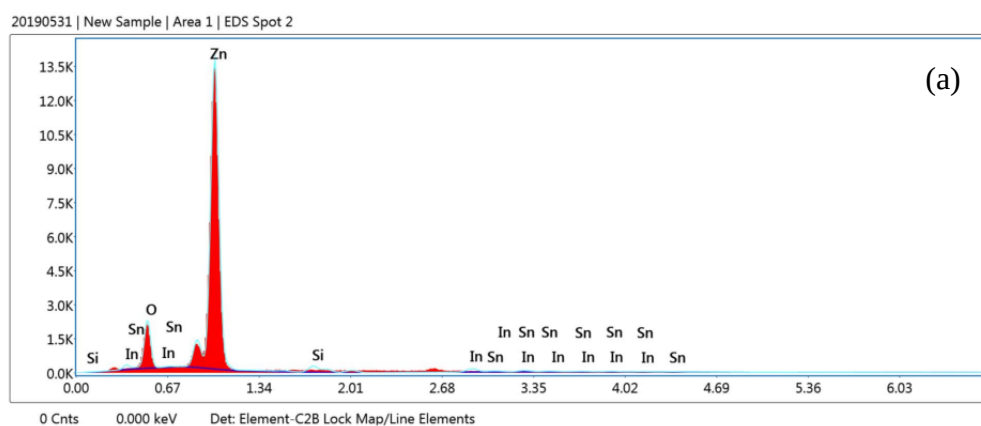


Figure 4.5. Scanning electron microscopy (SEM) images of working electrodes after zinc deposition. As-synthesized (top) and after calcination at 500 $^{\circ}\text{C}$ for 10 minutes (bottom).

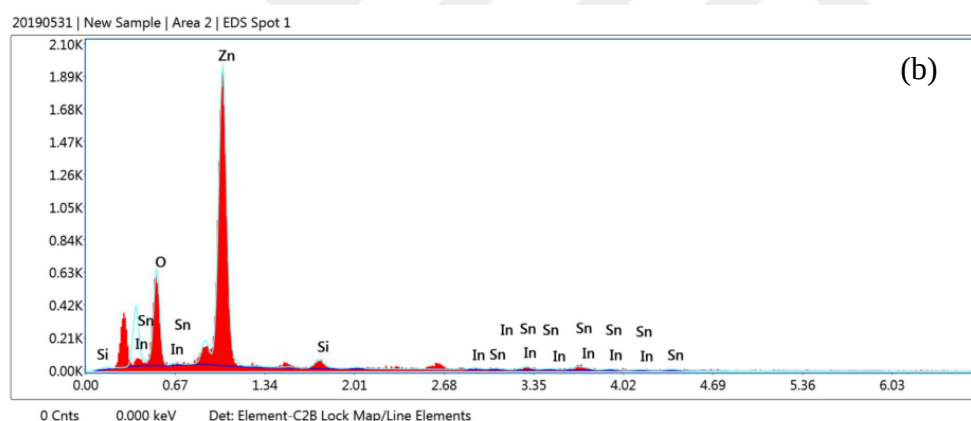
EDX spectra for an electrodeposit obtained from the 5 mM Zn^{2+} system confirm the presence of the zinc particles in the electrodeposited sample (Figure 4.6). The absence of any other impurities or foreign elements in the sample was also revealed by the EDX analysis, indicating the high purity of the electrodeposited zinc particles. In addition, soft indium and tin signals originating from the substrate surface were detected. The dense deposit formation may have caused a shadowing effect on the substrate surface, which may have resulted in the detection of faint indium and tin signals.





Smart Quant Results

Element	Weight %	Atomic %	Error %
O K	8.15	26.39	7.94
ZnL	87.46	69.28	2.68
SiK	1.69	3.12	8.80
InL	2.07	0.93	20.25
SnL	0.62	0.27	46.13



Smart Quant Results

Element	Weight %	Atomic %	Error %
O K	14.61	40.96	8.73
ZnL	78.05	53.55	3.70
SiK	2.19	3.50	18.41
InL	3.67	1.43	38.87
SnL	1.48	0.56	41.85

Figure 4.6. EDX spectra of zinc electrodeposited working electrodes prepared in ZnCl_2 -deionized water containing KCl as a precursor at a deposition potential of - 1.6 V and 80 °C (a) as deposited (b) after calcination at 500 °C for 10 minutes

Energy-dispersive spectroscopy analysis performed for electrodeposited film indicated the dominant presence of zinc over the ITO surface. In addition, an increase in the oxygen content was observed after calcination. This can be attributed to the calcination process occurring under air conditions that cause the oxidation of zinc metal. These results are in line with XRD analysis. The XRD analysis showed the formation of zinc oxide as the main product, which confirms the oxidation of zinc during the calcination process. Moreover, the increase in oxygen content is expected to enhance the catalytic activity of the material. This is because oxygen vacancies can act as active sites for various catalytic reactions.

4.2 Electrochemical Experiments in Deep Eutectic Solvents (DESs)

In this investigation, the effect of DESs containing choline chloride (ChCl) as a hydrogen bond acceptor (HBA) and urea and ethylene glycol (EG) as hydrogen bond donors (HBD) on the electrochemical behavior of an ITO-coated glass electrode is investigated using a variety of parameters. In the experimental procedure section of the thesis, the detailed synthesis method, water content characterization, and purity of DESs are provided. This section of the study aims to investigate a particular HBD effect on the electrochemical behavior of an ITO electrode and provides insight into the electrochemical behavior induced by DESs. Due to the fact that both reline and ethaline have the same type of HBA but different HBD and also different alkyl chain lengths, they were investigated for this purpose. Using DESs as electrolytes, this investigation can contribute to the development of more efficient and sustainable electrochemical processes.

This section of the research aimed to compare the electrochemical behavior of DESs derived from conventional aqueous solutions. In addition, the electrochemical application potential of reline and ethaline, as well as their binary mixtures and aqueous solutions, was assessed. The results identify reline and its aqueous solutions as a potential candidate for the efficient and selective recovery of indium from

electronic waste, which is in marked contrast to the diffusion pattern and reactions that lead to zinc deposition in the aqueous medium.

4.2.1 Electrochemically Processed ITO Films in Pure Deep Eutectic Solvents: Supporting Electrolyte

The zinc electrodeposition experiments conducted in aqueous electrolytes were repeated in deep eutectic solvent electrolytes for comparison. The experiments were performed using relin and ethaline containing 5 mM ZnCl_2 and 0.1 M KCl at 80 °C. by applying a -1.6 V DC potential difference for 30 minutes. However, it was observed that at even 80 °C, supporting electrolyte KCl does not dissolve in relin and undissolved KCl particles precipitate at the bottom of the electrolyte solution during experiments. This could potentially affect the accuracy of the experimental results, as the undissolved KCl particles may interfere with the electrochemical reactions taking place. In order to examine this possibility, the effect of the presence of KCl in relin and ethaline during zinc electrodeposition was investigated with control experiments. The control experiments were conducted without the addition of KCl to the electrolytes. The XRD analysis of working electrodes obtained after electrodeposition in relin and ethaline containing 5 mM ZnCl_2 in the presence of 0.1 M KCl was compared with the XRD analysis of working electrodes obtained without supporting electrolyte KCl.

As it is shown in Figure 4.7, almost the same diffraction patterns were observed for both relin and ethaline electrolytes with or without the supporting electrolyte KCl. However, higher intensities were observed in the working electrode electrodeposited in supporting electrolyte KCl in both deep eutectic solvents, revealing that KCl is sparingly soluble in the electrolytes studied and that it enhances the ionic conductivity of the electrolytes. This notable improvement was attributed to the role of K^+ ions in promoting a more uniform deposition process by increasing the ionic structure of the electrolyte. However, since its limited solvation in the electrolyte, the results showed that the presence of KCl in relin and ethaline did not lead to a

significant improvement in the crystallographic orientation of the zinc deposits. Therefore, it was recommended to remove any undissolved particles from the electrolyte solution before conducting electrochemical experiments.

In addition, since the supporting electrolyte contributes significantly to the electrochemical process, it may be necessary to propose alternative supporting electrolytes that are completely soluble in reline or ethaline and do not precipitate under experimental conditions. In accordance with this circumstance, the amount of ZnCl_2 added to provide zinc ion was increased, taking into account the high solubility of zinc chloride in these solutions and avoiding the introduction of a new ion. This method optimized the electrochemical process and ensured that the supporting electrolyte did not interfere with the desired reaction. In addition, the increased concentration of ZnCl_2 supplied sufficient zinc for the reaction without introducing unwanted ions. In the subsequent experiments, the concentration of ZnCl_2 in the electrolyte was increased from 5 mM to 0.1 M. Zinc chloride acted as a supporting electrolyte rather than the zinc precursor in reline or ethaline, as zinc electrodeposition was inhibited in these solutions, which will be discussed in full depth later.

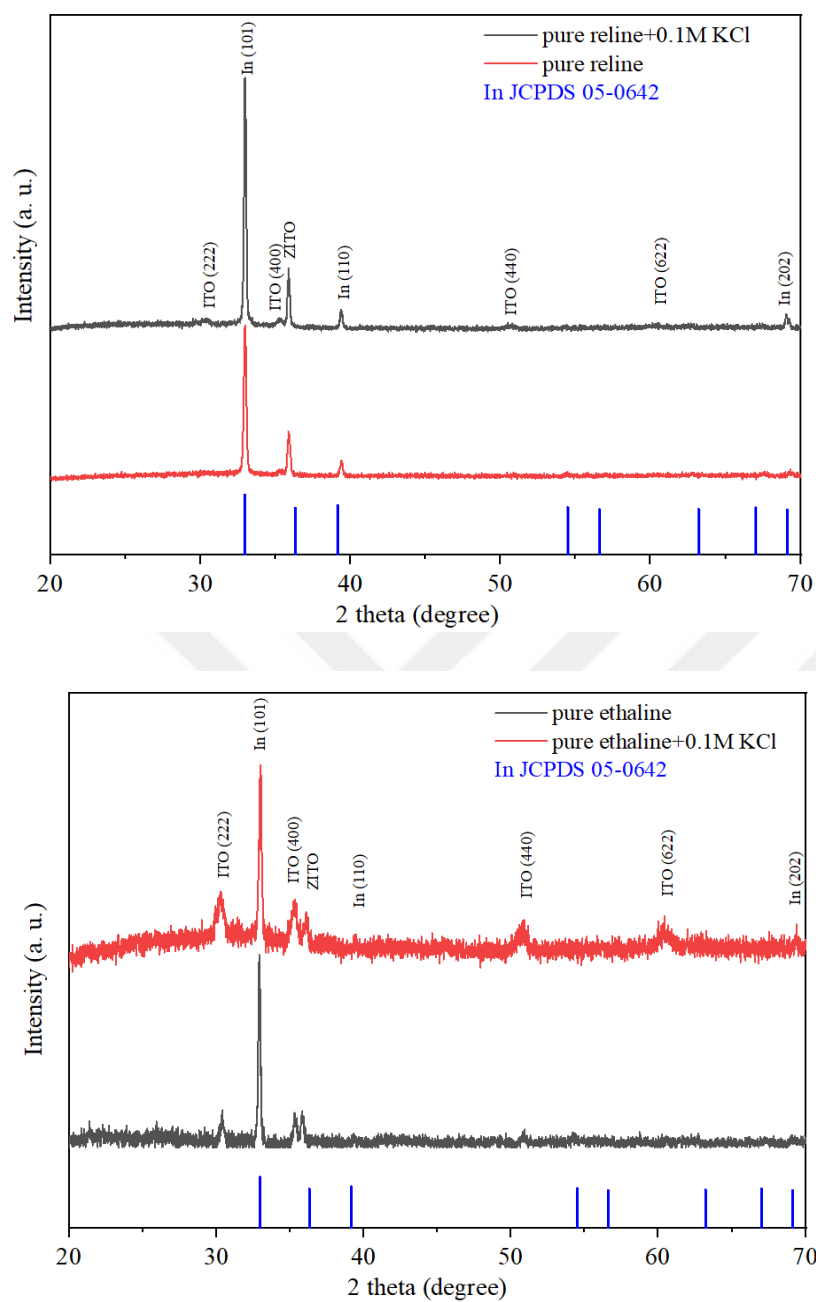


Figure 4.7. XRD patterns for comparing the effect of supporting electrolyte (KCl) on the structure of working electrode surfaces electrochemically treated in 0.1 M ZnCl_2 solutions of reline (top) and ethaline (bottom)

4.2.2 Electrochemically Processed ITO Films in Pure Deep Eutectic Solvents: Hydrogen Bond Donor

HBDs in the reline and ethaline structures adsorb on the ITO surface, preventing the adhesion of zinc ions to the substrate surface, as shown by the X-ray diffractogram. As a result, ions in the reline act as a barrier adjacent to the electrode surface, causing indium reduction rather than zinc electrodeposition, which is the focus of this study: the effect of electrolyte chemical and physical properties on the electrical and optical properties of ITO films. This result is entirely distinct from the results of experiments conducted in aqueous solution.

In experiments conducted under identical conditions (temperature, voltage, supporting electrolyte, electrodes, etc.) in an aqueous medium, an intense zinc deposition was observed on the surface as shown in the earlier sections (Figure 4.4), whereas the XRD analyses of the reline and ethaline electrolytes did not reveal a peak corresponding to the zinc crystal structure. At 32.96° , 29.23° , and 69.21° (2θ) values, the peaks belonging to the planes of indium (101), (110), and (202), respectively, indicating the reduction of indium in the ITO structure, were detected in the electrochemical experiments conducted in both DES. In the experiments, only electrolyte changes were made in order to observe significant variations in the results. This indicates that the electrolyte plays a crucial role in determining the experiment's outcome.

In addition, these results may have implications for other electrochemical processes in which ion selectivity plays a role, given that DESs are predominantly composed of complex and large cations and anions. It is essential to conduct additional research into the effects of different electrolytes on electrochemical processes in order to gain a deeper understanding of their mechanisms. Consequently, the crystal structure of samples electrochemically processed in reline and ethaline, which have distinct HBDs and consequently distinct properties, were also compared. The comparison of various DESs can shed light on the effect of their properties on the recovery

efficiency of indium. This information can be used to optimize the design of DES-based reduction processes for indium recovery in a sustainable manner.

As discussed in the literature review section of this study, the electrochemical mechanism differs between aqueous solutions and DESs because DESs have asymmetric and large anions and cations that tend to form multilayers when a voltage is applied. EDL is valid for aqueous electrolytes, allowing zinc ions to move from the ZnCl_2 precursor in the solution to the ITO-coated glass surface of the working electrode. Since zinc ions can therefore reach the surface, these ions are reduced and deposited on the ITO electrode surface. Due to the compact and multiple layers formed by the structure of the ions in the electrolyte, zinc ions were unable to reach the surface of the working electrode during the experiments conducted in DES.

In contrast to the aqueous solution, no zinc crystal structure was discovered during XRD experiments with DES. Due to the nature of the interface between the working electrode and the electrolyte, the indium metal in the structure of the ITO film was reduced during experiments conducted in DES solution. These suggest that the use of DES as an electrolyte could potentially limit the deposition of zinc on the working electrode surface, which, on the other hand, has implications for the development of more efficient and effective electrochemical systems in this study.

ITO film crystallization patterns, which were before and after being electrochemically treated and analyzed in reline and ethaline, were investigated through XRD patterns (Figure 4.8). As seen in Figure 4.8, the XRD patterns of all ITO films revealed a well-defined crystalline structure with diffraction peaks corresponding to (211), (222), (400), (431), (440), and (622) crystalline planes, which correspond to In_2O_3 reference peaks in body-centered cubic (BCC) form. The presence of these diffraction peaks validates the high-quality ITO film used as the working electrode, which was also highlighted in Figure 4.1 at the beginning of this section.

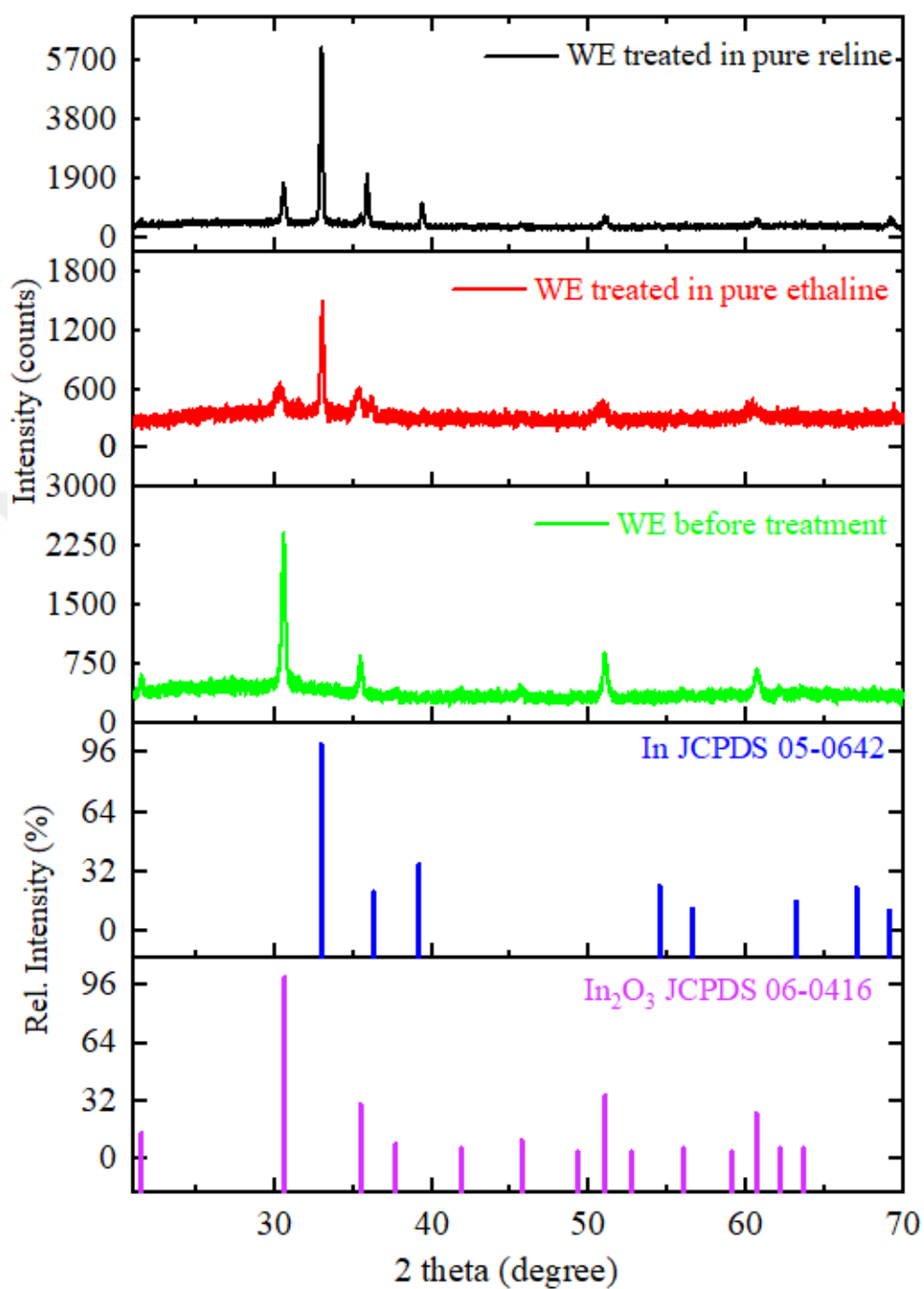


Figure 4.8. XRD patterns of the working electrode (WE) before electrochemical treatment and treated in both pure reline and pure ethaline. The bar graphs represent the XRD patterns of In_2O_3 and indium metal references.

On the other hand, the evolution of indium oxide to indium after electrochemical treatment in DESs is illustrated in Figure 4.8. After 30 minutes of treatment in DES, the In_2O_3 peaks for the working electrode show a significant decrease in intensity. At the same time, the peaks for indium with a tetragonal crystal structure in the database (JCPDS # 05-0642) were also seen. The major peak was identified as the indium (101) crystalline plane, which was indicated by the peak that appeared at 32.96 degrees (Figure 4.8). The decrease in indium oxide peaks and the sight of indium peaks suggest that the electrochemical treatment in DESs can effectively reduce indium oxide to indium. Moreover, this conversion indicated that ITO film can not withstand the electrochemical treatment in DESs and maintain its structural integrity, making the DES a promising candidate for use in metal recovery applications as an electrolyte.

Both ethaline and reline exhibited identical XRD patterns related to indium at two theta positions corresponding to the (101), (110), and (202) planes (Figure 4.8). This indicates that both eutectic solvents behave similarly due to the similar cationic compounds they contain. In contrast, the results demonstrated that the XRD peaks in the samples obtained with reline are significantly more intense and smooth, indicating a higher crystallinity, as can be observed in either Figures 4.7 or 4.8.

This finding suggests that reline could be a more suitable electrolyte for indium reduction where high crystallinity is desired. Further discussions are needed to explore the potential advantages and limitations of using either of the eutectic solvents that caused this crystallographic difference. Therefore, it is necessary to briefly mention the main differences of both DESs, which are detailed in the literature review section.

Reline and ethaline, both of which are ChCl based DESs, have different physical properties that are directly related to intermolecular forces. At 80 °C the pHs of reline and ethaline, which are important factors for shape controlling deposition, are about 8.5 and 4.1, respectively (Mjalli et al., 2016). The pH measurements demonstrate that reline has a relatively high concentration of OH^- ions, whereas ethaline has a

high concentration of free H^+ ions. These differences in pH can significantly affect the deposition of materials, making it crucial to choose the appropriate DES for a specific application. Additionally, the intermolecular forces of DESs can be tuned by adjusting their composition, making them versatile solvents for various electrochemical applications. The viscosities of reline and ethaline are measured as 552.0 cP and 32.1 cP at 30 °C (Mjalli et al., 2016) and decrease at higher temperatures. Ethaline is nearly 20 times less viscous than reline. In addition, for pure reline and ethaline at 0.1 MPa pressure and 20 °C their densities are 1118.84 kg.m⁻³ (Lapena et al., 2019) and 1200.1 kg.m⁻³ (Yadav et al., 2014), respectively.

The pure reline has a smaller molar volume than the pure ethaline, which points to a more compact structure. This difference in molar volume may be attributed to the difference in molecular structure and intermolecular interactions between the two compounds. This difference also reinforces the higher hydrogen bond network formation in reline compared to ethaline. The higher hydrogen bond network formation in reline can be attributed to the presence of additional amine groups in its molecular structure, which allows for more hydrogen bonding sites. The increased crystallinity of the samples obtained with reline, as can be observed from Figures 4.7 & 4.8, can be attributed to the difference in intermolecular interactions and hydrogen bond network formation, which has implications for electrochemical stability.

Furthermore, different peak intensities indicate distinct reduction rates, consistent with the measured current's time course (Figure 4.8). As it affects the conversion rate during electrochemical processes in DESs, the current transition is also an important topic to shed light on. Therefore, the currents of ethaline, reline, and water electrolytes change with time. All of these were also discussed in a separate section that follows, but it is essential to note the difference between these measurements for reline and ethaline in order to examine the crystallographic change in greater detail. During the electrochemical treatment of ethaline, a current of approximately 40 milliamperes was observed, followed by a rapid decrease to microamperes within an average of two minutes. In addition to this rapid decrease, the current was highly variable during the remaining 6–12 minutes of the experiment, fluctuating between

800 μA and 200 μA within seconds. In experiments involving a pure reline solution bath, the initial 30 mA current level was measured, followed by a drop to microampere rates within 5-6 minutes.

These findings suggest that the presence of large, complex ions in a solution can significantly affect the conductivity and stability of an electric current. Moreover, when these two ChCl-based DESs were compared, it was discovered that the current values were relatively higher throughout the electrochemical process and that the decline in current was slower for reline. This sudden decrease in current for either DES may be attributed to the formation of a passive multilayer on the electrode surface, which inhibits the further electron transfer that was also discussed in various parts of this study. The results suggest that the choice of DES can significantly affect electrochemical performance and that reline may be a more suitable option for indium reduction rather than ethaline according to current measurements and XRD analysis.

In addition to the contribution of different physical properties and current changes to the electrochemical treatment in reline and ethaline, the effect of zinc chloride on these solutions has been investigated in the literature. As intimately debated in the preceding section, 0.1 M ZnCl_2 was dissolved in reline and ethaline, which were used as supporting electrolytes, since KCl was not dissolved in these solvents and ZnCl_2 did not behave as a zinc source as both are used in traditional aqueous electrolytes. The inclusion of zinc chloride in the solutions may have altered the behavior of the reline and ethaline, affecting the electrochemical reactions that occurred. Therefore, it is important to consider the potential impact of zinc chloride on the results obtained from the experiments, which should also be discussed.

Andrew P. Abbott and coworkers (2011) investigated the viscosity, conductivity, and density changes in reline and ethaline via the addition of ZnCl_2 . They claimed that the addition of 0.1 M ZnCl_2 to reline leads to an essential reduction in viscosity, exhibiting a fall of about 50 %. In addition, similarly, as a function of ZnCl_2 concentration, the conductivity of the reline gradually increases, which increases

twice by the addition of 0.1 M ZnCl_2 , as does the viscosity. In contrast to reline, ethaline is relatively less sensitive to changes in ZnCl_2 amount. Ethaline including 0.1 M ZnCl_2 demonstrates a negligible decrease in either viscosity or conductivity in the solution structure in comparison with its pure form.

Urea is a much stronger hydrogen bond donor compared to ethylene glycol, which leads to higher viscosity and surface tension. Stronger hydrogen bonding reduced the average void size for reline in addition to these features. The addition of ZnCl_2 to the reline disturbs the hydrogen bonding network between of compounds by stimulating an increase in average void size, hence boosting the reline's mass transport capabilities. This suggests that the addition of ZnCl_2 could potentially enhance the performance of reline in applications that require efficient mass transport, such as in electrochemical treatment obtained in this investigation. However, the relatively weak hydrogen bonding network in ethaline leads to a higher proportion of larger voids that would be less susceptible to disruption upon the addition of a zinc chloride solute. Further studies with different ZnCl_2 concentrations were explored and discussed in later parts of this study in order to discuss the optimal concentration of ZnCl_2 to achieve the desired mass transport properties while maintaining the structural integrity of reline.

To sum up, completely different from the electrochemical reactions that take place in the aqueous electrolyte under the same conditions, all these dissimilar properties for both ethaline and reline may facilitate the electroreduction of indium; nevertheless, even reline has much lower conductivity due to its higher viscosity compared to ethaline. With pure reline, a more crystalline and compact film was obtained than with ethaline when comparing both XRD results (Figure 4.8). This result can be attributed to the hydrogen bonding effect, which is stronger in reline, rather than the conductivity characteristics of the solutions. The stronger hydrogen bonding effect in reline leads to a more ordered arrangement of the ionic chains between the working electrode and electrolyte interphase, resulting in a denser and more crystalline metal reduction. Despite the presence of complicated free chlorides in both solutions, urea is a better hydrogen bond donor than ethylene glycol, which

would be blocking chloride adsorption at the electrode surface as part of the electrochemical multi ion stacking mechanism. This may support the more apparent characteristic indium crystal peaks in XRD for reline and the much clearer waves observed in voltammetric experiments, which were discussed later in this chapter at the CV analysis part.

These findings highlight the importance of considering the chemical properties of solvents in electrochemical studies, as they can have a significant impact on the behavior of ions at electrode surfaces. The effects of binary mixtures of these DESs and hydrated DES on electrochemical reactions were investigated further in order to develop more efficient and precise electrochemical processes.

4.2.3 Electrochemically Processed ITO Films in Binary Mixtures of Deep Eutectic Solvents

When reline and ethaline are mixed with each other, different bonding and arrangement of compounds are possible, resulting in different properties important for electrodeposition such as pH and conductivity. For instance, a 90 mole % reline/10 mole % ethaline mixture has the highest conductivity value at any temperature between 20 and 80 °C. This finding suggests that the conductivity of the electrolyte can be optimized by adjusting the ratio of reline and ethaline. The specific combination of reline and ethaline can also affect the efficiency and effectiveness of the electrochemical process, which is used for metal reduction in this study. For this reason, reline and ethaline mixtures with 1:1 and 1:9 (reline:ethaline) molar ratios are prepared in order to have the opportunity to study different deposition parameters.

As can be seen from Figure 4.9, XRD patterns for both binary mixtures of reline and ethaline show that reduction of indium occurred in analogous 2 θ positions with different intensities. The similarity in the XRD patterns suggests that the reduction of indium is not significantly affected by the molar ratio of reline and ethaline in the mixture. This could be mainly due to the stronger hydrogen bonding character of

urea compared to ethylene glycol, as the presence of reline regulates the intermolecular structures and dominates the electrochemical properties of the solution. Furthermore, it can be highlighted that the use of urea as a hydrogen bonding agent can be a promising strategy for controlling the electrochemical behavior of indium even in reline-ethaline mixtures at different ratios.

The data obtained from pure reline and ethaline solutions are supported by current measurements (Appendix B) from experiments with mixtures. Throughout the experiment, the current values in the ethaline-weighted mixture decreased more rapidly than in the DES-weighted mixture, and lower values were recorded. However, it was observed that the data were more stable when the measurements made with the mixture containing high ethaline (90% mole ethaline) were compared with pure ethaline. This can be explained by the effect of strong hydrogen bonds of reline, albeit small in quantity, as discussed in the XRD patterns. These measurements indicate that the presence of a single DES has no appreciable impact on the electrochemical process of the mixture. Therefore, the concentration and characteristics of each component play a major role in determining the conductivity of mixtures.

Due to the fact that current measurements are performed manually with a multimeter, which is not very sensitive in a 2-electrode setup, and that the changes are very rapid and pronounced, these values can only serve as a guide for comparing the results. With these data, it does not appear possible to reach a definitive conclusion. Use a more sensitive instrument for current measurements and conduct additional tests to confirm the observed trend in the values. In order to obtain more precise and dependable measurements of the electrolyte behavior at the working electrode surface, which promotes mechanisms and reactions, CV measurements were performed and discussed in this section.

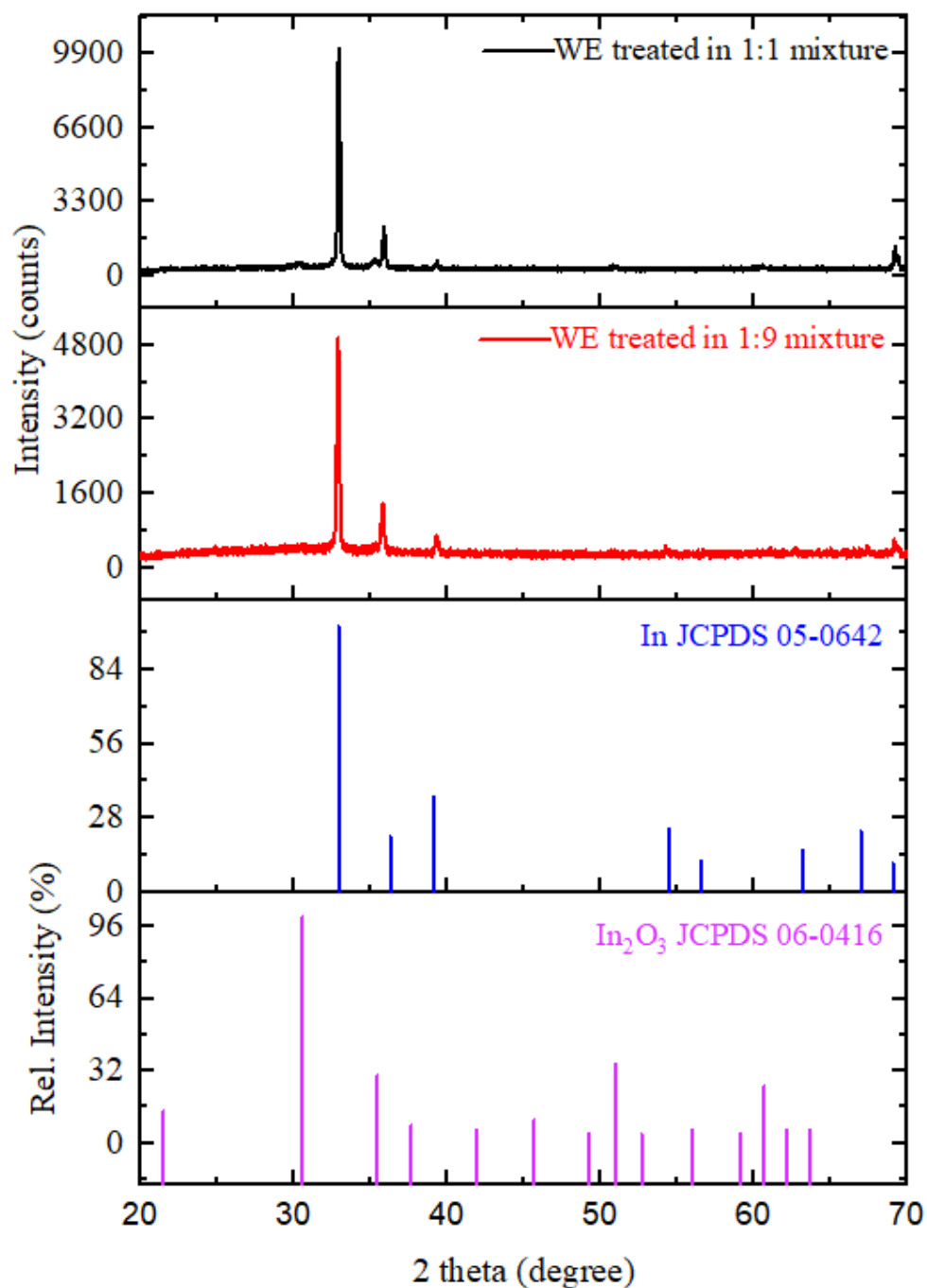


Figure 4.9. XRD patterns of the working electrode prepared in 1:1 and 1:9 mole fraction of reline:ethaline binary mixtures

As can be seen from Figure 4.9, XRD patterns for both binary mixtures of reline and ethaline at different ratios exhibit reduction of indium, which indicates the binary

mixtures of reline and ethaline can be effective in recovering indium from ITO. From the X-ray diffraction analysis strong (101) XRD peak (2θ of 32.96°) was observed in both solutions corresponding to the formation of tetragonal body centered indium. It should be also noted that intense indium peaks observed even for 90 % ethaline containing binary mixture, when compared to the XRD analysis of the samples prepared in pure ethaline. This could be attributed to the higher hydrogen-bonding capacity of urea compared to ethylene glycol, as the presence of reline regulates the intermolecular structures and dominates the electrolysis experiment. The results suggest that the presence of urea in the reduction process could lead to the formation of a more ordered structure, which could have a significant impact on the electrochemical properties of the material.

Using Origin 2018 Labview software, the full width at half maximum (FWHM) was computed from the XRD patterns to estimate the crystal size of the samples. Due to their finite dimensions, crystals are not ideal. A perfect crystal would extend indefinitely in all directions. The FWHM should not depend on the material, but the deviation from perfect crystallinity causes a broadening of these peaks that corresponds to a greater FWHM. This broadening can be caused by defects, impurities, or strain in the crystal lattice. The study of peak broadening in X-ray diffraction can provide valuable information about the quality and structure of materials. The FWHM is connected to instrumental broadening, crystallite size, and nonuniform strain. The lattice strain is caused by the particle boundaries, lack of long-range order, and point defects that define the amorphous portion of a sample. In conclusion, the FWHM of a diffraction peak has been used as an empirical parameter in the scientific literature to determine the crystal size of a material.

FWHM for the mixtures of reline and ethaline were compared with their pure counterparts (Figure 4.10). The clear full width at half maximum intensity (FWHM) was detected on the strongest (101) diffraction plane from XRD. It can be found that the main peaks are consistent with the standard most intense diffraction peak of indium metal that was detected at (2θ) value of 32.96° degree (JCPDS 05-0642) as also mentioned several times above.

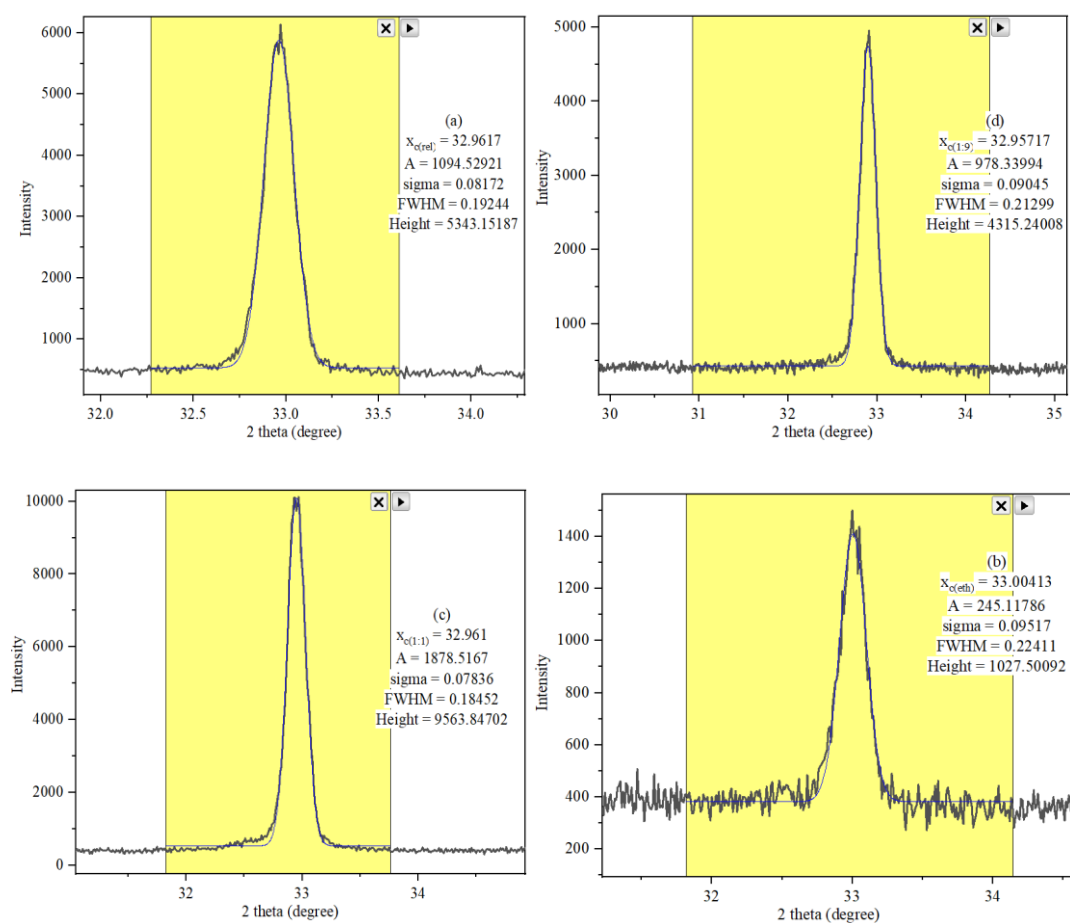


Figure 4.10 FWHM values calculated on the most intense (101) diffraction plane observed from the WE surface electrochemically treated in a) pure reline, b) pure ethaline, c) 1:1 reline:ethaline mole mixture and d) 1:9 reline:ethaline mole mixture

Comparing the FWHM values depicted in Figure 4.10, it may be concluded that the reduced indium on the surfaces treated with a 1:1 ethaline:reline mixture is significantly more crystalline than the reduced indium on the surfaces of samples treated with pure ethaline. This suggests that the addition of reline to ethaline enhances the reduction of indium, possibly due to the increased H-bonding capabilities of the mixture. In fact, the calculated FWHM values are narrow and close for both the mixture of 1:1 ratio and pure reline. This can be explained by the predominance of urea in the structure of reline, as mentioned above, and by the strengthening of hydrogen bonds caused by the combination of the two DES discussed in Mjallin's study. Since there is limited information in the literature about

DES mixtures, additional research is necessary to fully comprehend this phenomenon. Therefore, rather than focusing on mixtures, hydrated DES, which attracts more interest from researchers and has potential applications in a variety of disciplines, has been investigated.

The FWHM values above 0.20° for samples electrochemically processed in pure ethaline or in mixtures containing a high percentage of ethaline (90% molar ratio) indicated that the samples possessed relatively low crystallinity, which could be attributed to the crystals' finite dimensions and the presence of defects in their structures. Nonetheless, these samples displayed some degree of ordered atomic arrangement. However comparably to other samples treated in reline and binary mixture containing equal amount of both the level of order was still lower than have FWHM values below 0.20° .

The FWHM value can be used to estimate the degree of disorder or crystallinity in a material, with a larger FWHM indicating a more disordered or amorphous structure as discussed. However, caution this parameter is not always a reliable indicator of crystallinity. Therefore, it should be noted that other methods, such as electron microscopy and spectroscopy techniques, can provide more detailed information about the structure of a material which were also examined and discussed in this section.

Finally, it is important to mention that the detection of metallic tin by X-ray diffraction (XRD) is not a guarantee in all the reduced indium tin oxide (ITO) samples. This may be attributed to the low concentration of tin in the ITO film. It should be taken into consideration that the detection of metallic tin is not always a requirement for the desired properties of indium recovery which was the main point of recovery studies. In fact, in some cases, the absence of metallic tin may even be desirable as it can prevent the additional separation processes and increase in costs. Overall, while metallic tin may not always be required for indium recovery, careful consideration of all factors is necessary to ensure a successful and cost-effective process.

4.2.4 Electrochemically Processed ITO Films in Hydrated Deep Eutectic Solvents

Likewise, with binary mixtures of reline and ethaline eutectic solvents having different physical and chemical properties, the effect of the presence of water in deep eutectic solvents at various mole fractions on the electrochemical reduction of ITO over a working electrode was investigated. According to the literature, as discussed in the related part, the presence of water in the DES significantly affected the electrolyte characteristics such as viscosity, diffusion coefficient, and conductivity, all of which mainly act on electrochemical reduction of ITO. Reline has a higher viscosity than ethaline due to the extensive hydrogen-bond network. Besides, a larger viscosity will also result in a lower diffusion coefficient. The diffusion coefficient of pure reline is on the order of $10^{-13} \text{ m}^2/\text{s}$. This means that the diffusion of ions in pure reline is very slow, which was also associated with the absence of deposits of zinc ions in the reline on the electrode surface. Low diffusion coefficient and high viscosity of reline that are hindering mass transport is also supported by its low ionic conductivity, other important property of electrolyte, that provide ion transportation to the electrode upon applied voltage. Therefore, the addition of water to reline can significantly increase its diffusion coefficient, increase conductivity and improve its ion transport properties which could potentially lead to the deposition of zinc ions on the electrode surface.

Furthermore, in deep eutectic solutions containing a low amount of water, the number of hydrogen bonds increases due to HBD-water molecular interactions. However, excessive amounts of water cause the diffusion coefficient to increase, which weakens the urea-anion interactions. Thus, the ions are relatively free to diffuse, and compared to other physical properties such as pH and density, the change in viscosity and conductivity was higher (Shah et al., 2014). This suggests that the concentration of water in deep eutectic solutions plays a crucial role in determining their physical properties. Therefore, controlling the amount of water can help optimize the properties of these solutions for electrochemical applications.

Aqueous/hydrated DES and their physical and chemical properties have been discussed in detail in the literature part of this study. The main impressive point of this investigation is that the addition of water to DES can modulate the physicochemical properties of the electrolyte and hence provide shape-specific, shape-controlled, or even selective synthesis during electrochemical experiments. This finding opens up new possibilities for the design and optimization of electrochemical processes particularly in the field of indium reduction from ITO, where DES, especially reline, have already shown great potential as sustainable electrolyte for reduction as working through heretofore. Further research is needed to fully understand the potential of hydrated reline in electrodeposition of zinc or electroreduction of indium as achieved with water and DES, respectively.

In order to obtain the hydrated DES solutions, reline and ethaline compounds are mixed with water in the proper ratios to prepare the desired compositions. For instance, 1 MR indexed hydrated DES solutions were prepared to have molar ratios of 1:2:1 M $\text{ChCl}:\text{Urea}:\text{Water}$ and $\text{ChCl}:\text{EG}:\text{Water}$ for reline and ethaline, respectively. This preparation procedure has been extensively explained in the experimental procedure section and how hydrated DES referred within the scope of the study according to the water concentration is summarized in Table 3.1 in the relevant section. The study aimed to investigate the physicochemical properties of the hydrated DES solutions, including their hydrogen bond strength, viscosity, and pH to the electrochemical process.

In accordance with this purpose, hydrated DES studies were initiated by adding water at a concentration of 1 molar, referred as 1 MR reline and ethaline. This treatment is significant due to the fact that the addition of 1 molar ratio water to reline affects the physicochemical properties and behavior in a different manner than higher amounts by strengthening the hydrogen bonding structure, as demonstrated by experimental and theoretical literature studies cited in the literature review section. Therefore, its effect on the electrochemical process of the working electrode should be investigated using various techniques of characterization. The crystalline structure determined by

XRD indicated that at a 1 M water-reline and water-ethaline systems can be observed from the Figure 4.11.

The differences between the patterns collected in reline and ethaline are visible, as can be seen from Figure 4.10. The peaks in the ethaline pattern are broader and less intense compared to those in the ethaline pattern, indicating a difference in chemical composition. Indeed, in the latter pattern for the ethaline-1M water system, mainly the substrate signals are detected, and negligible indium reduction occurs on the surface, unlike pure ethaline. This suggests that the presence of water in the ethaline system has a significant negative effect on the reduction of indium on the surface. Besides, the surface of the sample prepared in aqueous ethaline demonstrated high signal-to-noise XRD data that was more of an amorphous structure than crystalline, similar to the sample patterns obtained in pure ethaline electrolyte shown in Figure 4.8 and 4.10 above.

Furthermore, the crystallinity of the samples was estimated empirically by calculating the full width at half maximum (FWHM) from the XRD patterns with Origin 2018 Labview software. Crystals are not ideal due to their finite dimensions. An ideal crystal would broaden in all directions indefinitely. In some cases, the film signal cannot be isolated because such a powerful reflection cannot be inhibited by tilting the sample. To minimize the signal contribution from the substrate, it is recommended to use X-ray diffraction at grazing incidence, which does not enable the X-ray to penetrate deep into the sample. But regarding this study the substrate diffraction phenomenon is also important since the intensity of these signals give us a suggestion on the recovery rate of indium reduction. Before resorting to much more laborous characterization methods, this approach can provide valuable insights into the reduction process of indium and optimize the electrolysis parameters. In our case for all samples studied in reline or aqueous reline even ITO XRD signals were detected that was in agreement with the signal coming from the substrate, sufficient signals detectable by XRD technique from the reduced indium metal. Furthermore, chemical analysis were also executed that these changes enlarged at least several nm deep of the ITO coating.

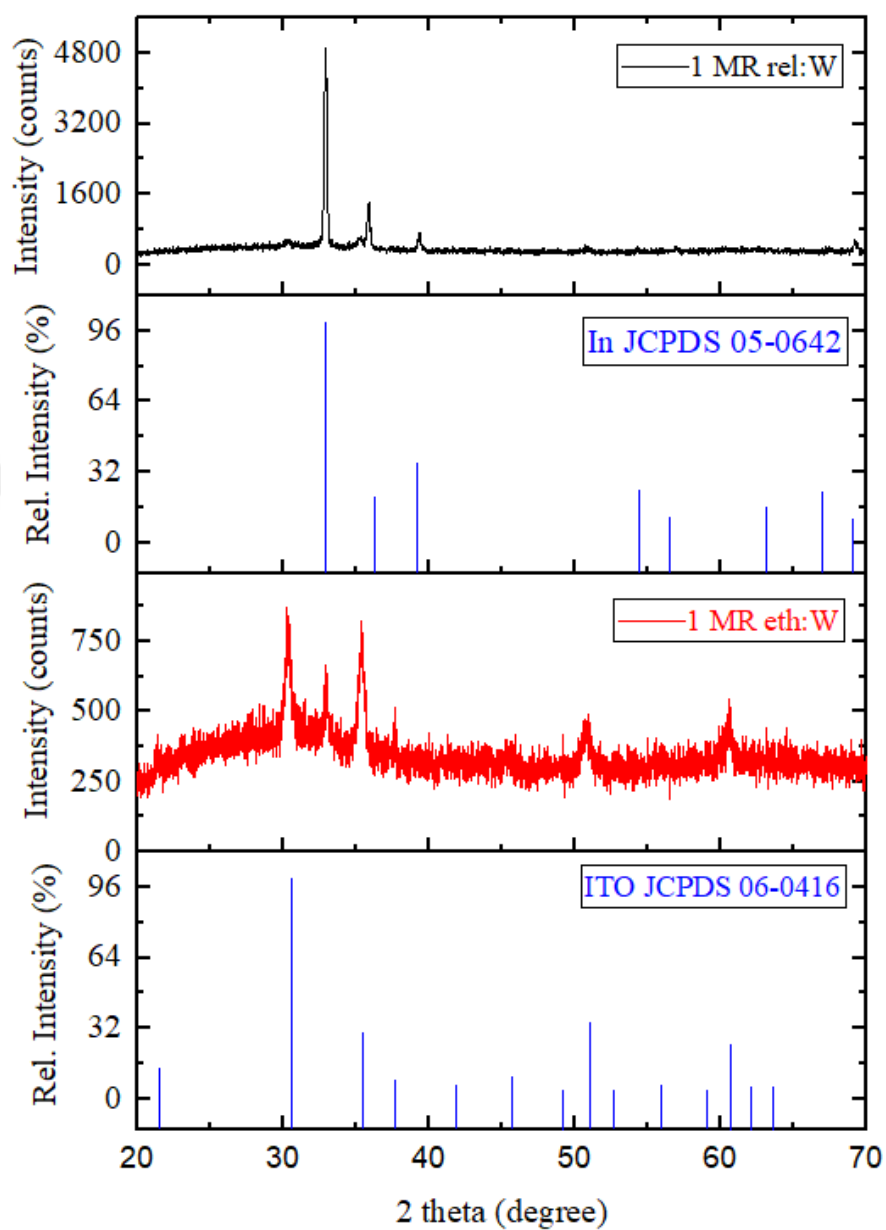


Figure 4.11. XRD patterns of the sample prepared in 1 MR water including reline and ethaline aqueous solutions

In this study, for all samples studied in reline or hydrated reline, even ITO XRD signals were detected that were in agreement with the signal coming from the substrate, indicating sufficient signals detectable by the XRD technique from the

reduced indium metal. Furthermore, chemical analysis were also executed that these changes go at least a few nm deep of the ITO coating. However the signals coming from the substrate is relatively mild compared with pure and hydrated ethaline as can be observed from the Figures 4.8 and 4.11, respectively.

Indeed, the hydrogen bonding structure of the ions and molecules in the DES structure mainly makes them highly water miscible. This property impacts their physicochemical properties, and hence even a small amount of water affects the electrochemical reactions that occur during the experiment, as in the ethaline case. However, for the same amount of water, the mechanism operated in the reverse direction, which could be attributed to the intermolecular coordination numbers of DESs and molecular interactions in the solutions as mentioned above. It was elaborated at the literature part of this research that there are some studies conducted the relationship between the water content of DES and intermolecular coordination numbers which is correlated with the hydrogen bonding ability of the components in DES.

The presence of water did not affect the urea but was associated with ethylene glycol molecules, which provokes the same amount of water to change thermophysical properties and intermolecular interactions in different ways for different DESs, even if they include the same type of anions in their structure. This suggests that the behavior of DESs in the presence of water is complex and dependent on their specific chemical composition. Moreover, ethaline is very acidic at all temperatures while reline basic due to the fact that pH indicates the ratio of H^+/OH^- ions in the solution, which is also defined in the literature part of this report. Therefore, the different behavior of ethaline and reline in the presence of water could be attributed to their different pH values, which affect their interactions with water molecules and ultimately their overall behavior. These findings indicate the different electrochemical behavior of hydrated reline explained according to XRD analysis (Figure 4.11).

The results of experiments done in different DES based electrolytes, reline and ethaline, suggest that electrochemical treatment of ITO coatings in reline and hydrated reline causes crystalline indium to be recovered from ITO because of the strong hydrogen bonding network structure. This indicates that the electrochemical treatment of ITO coating in reline could potentially enhance its properties for waste electronic equipment recovery applications. Since the results of this study could pave the way for more efficient and cost-effective methods for recovering valuable materials from electronic waste, to fully understand the extent of these structural changes and their impact on performance, hydrated reline electrolytes at different water concentrations were also investigated.

Figure 4.12 illustrates the surface crystal structures of the working electrode as the result of electrochemical experiments with reline solvents containing pure reline, 1MR, and 3MR water. In order to understand the effect of the solution species on the electrode structure, XRD experiments were compared in either pure or 1 MR aqueous reline electrolyte solutions (Figure 4.12). XRD peaks related to indium were more significant with higher intensities for 1 MR aqueous reline compared to pure reline (Figure 4.12), which can be attributed to the hydrogen bonding strength affected by the concentration of water. In other words, the crystalline structure determined by XRD indicated that at a reline-1M water system, water molecules do not affect the diffusion of ions and hydrogen bonding network in reline; indeed, intensities of indium peaks increase rather than treated in pure reline (Figure 4.12). This suggests that the addition of 1MR water enhance the electrochemical performance of reline, possibly due to improved hydrogen bonding strength.

This improvement can be attributed to consolidation of choline-urea interaction by adding low amount water to reline (Hammond et al., 2017). Since reline has a great deal of hydrogen bonds among urea and the anion, it may be stated that this interaction defines the hydrogen bonding infrastructure. Moreover, in the existence of a low amount of water, urea molecules interact more powerfully with one another and water, indicating that hydrogen bonding interactions among these components ($\text{NH}_2\text{-NH}_2$ and OH-NH_2) become stronger (Shah and Mjalli, 2014). These

researches, as their findings were discussed in the literature survey section of the thesis, suggest that the hydrogen bonding network plays a crucial role in the indium reduction rate. Because of the fact that at a low water fraction, i.e., 1 MR water content, due to the strengthening of urea-urea and urea-choline interactions hydrogen bonding increased, X-ray diffraction patterns suggested that this increase improved the indium metal reduction during electrochemical treatment of ITO. The results of this research deliver insights into the mechanism of indium reduction and could potentially lead to the development of more efficient reduction processes.

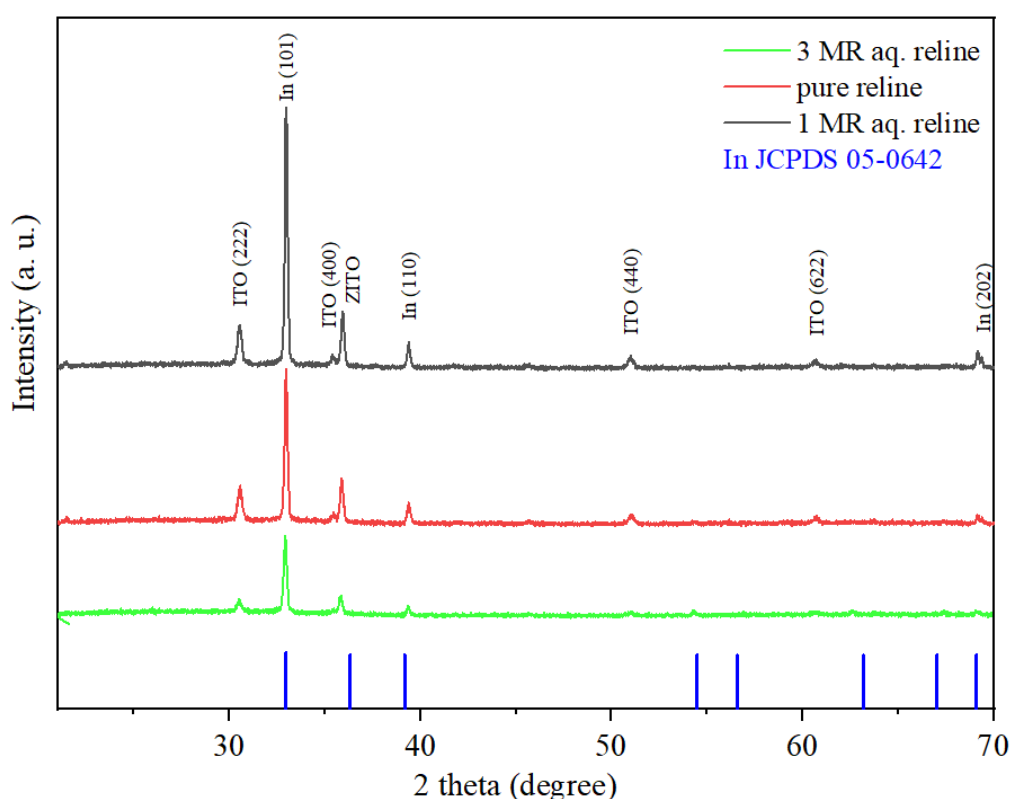


Figure 4.12. XRD patterns of the sample prepared in pure reline and 1 MR aqueous reline

In contrast, water hydrolyzes both urea and chloride ions at increased water concentrations, which causes a gradual decrease in the hydrogen bonds between choline and urea as well as urea and urea. The result of this situation can also be seen at the bottom pattern of Figure 4.12. Samples electroreduced in 3 MR aqueous

reline exhibited relatively low intensity compared with their pure and 1 MR water containing forms. This indicates that the strength of hydrogen bonds between choline and urea or between urea molecules is weakened as the water concentration increases, leading to a decrease in the indium reduction rate which can be observed from the indium crystal intensities shown in Figure 4.12. From these results, it was suggested that the indium reduction mechanism mainly depends on the molecular interactions and hydrogen bond strength of the DES.

To sum up, the XRD patterns presented in Figure 4.12 show that indium oxide was reduced at different levels in the samples obtained by using pure reline, 1MR reline:water, and 3MR reline:water electrolyte samples. Again, for all the samples similar to the surfaces obtained in pure DES type electrolytes, zinc deposition was not observed in hydrated reline. As can be seen again in Figure 4.12, the main indium metal peak (101) at 2θ of 32.96° on the surface of the electroreduced samples increased to the highest level when 1MR reline:water is used as electrolyte and decreased when electrochemical experiment applied in 3MR reline. These results enrich our understanding of the effect of hydrogen bonding strength of electrolyte on the electroreduction of indium metal and suggest that 1MR reline:water with highest hydrogen bonding is the optimal electrolyte for this process.

Further investigations with hydrated reline were performed to observe the involvement of hydrogen bonding strength on the electroreduction of indium metal. With the increase in water content to 5 MR, indium peak intensities decreased due to weakened hydrogen bonding interactions, as expected, while surprisingly, peaks attributed to zinc metal have arisen when compared with their lower water content counterparts.

At higher water ratios, the enhanced urea–urea interactions begin to disrupt, as revealed by the weakening in hydrogen bond strength. Since both urea and chloride ions are hydrolyzed with water to a certain extent, the blocking effect of large and complex ions that prevent Zn from accumulating on the surface is weakened, which results in Zn crystals, as can be observed from Figure 4.13. This suggests that the

presence of water plays a crucial role in the behavior of molecular interaction in reline by decreasing hydrogen bonding strength and increasing ionic diffusivity that assist accumulation of zinc ions on the working electrode surface.

From the same plot (Figure 4.13), it can be observed that diffraction patterns concerning indium crystalline peaks did not disappear but got less intense with the increasing water fractions. This outcome again proved the indium reduction rate dependency to the interaction between molecules and hydrogen bonding of the electrolyte. In other words, at the 5 MR and 9 MR water fractions, both urea and anions show higher diffusivity, which also exhibits the change of the electrochemical mechanism. The reduction rate of indium is directly related to the concentration of water in the electrolyte, which affects the hydrogen bonding and molecular interactions in the system. The electrical double layer (EDL) model for aqueous solutions or ion layering (multilayers) valid for DES was applicable at the hydrated reline-electrode interfaces during electrochemical experiments that facilitated both zinc deposition and indium reduction for hydrated reline containing greater than 5 MR.

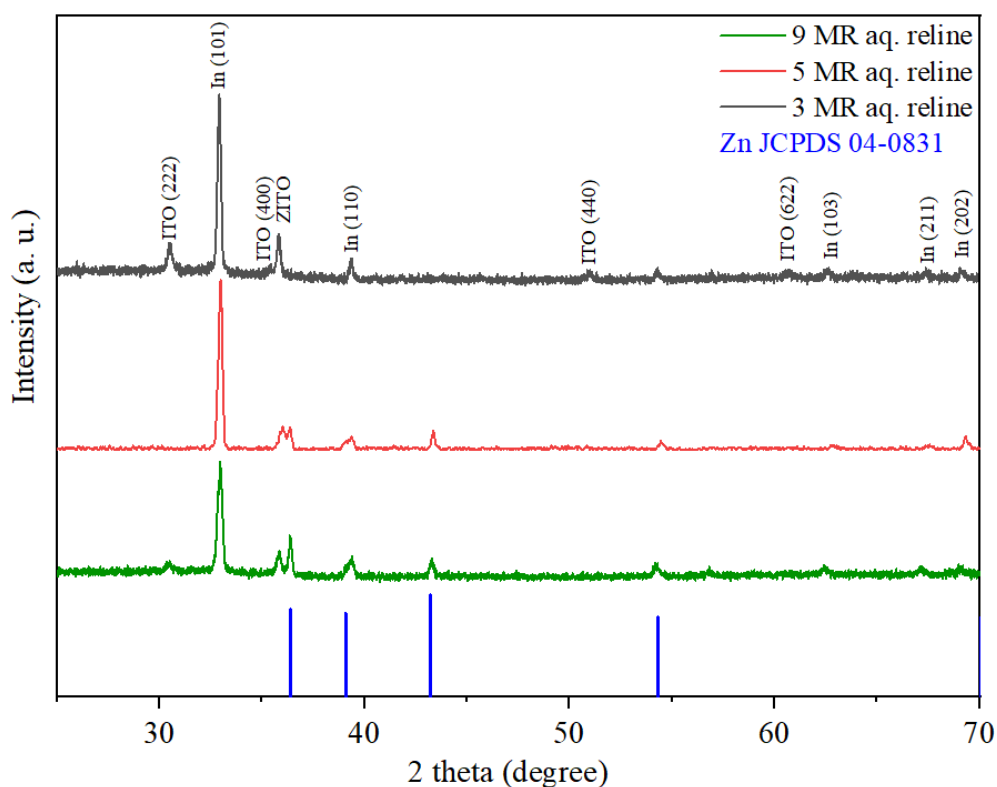


Figure 4.13. XRD patterns of the samples prepared in pure reline and aqueous reline with different water content (3 MR, 5 MR and 9 MR water:reline solutions)

When the molar ratio of water/reline was increased to 9 MR, similar XRD diffraction data was observed with 5 MR, but the ability of reline was altered due to an increase in the amount of water (Figure 4.13). Hydrogen bond networks slightly change below the reline/water ratio of 5 MR, but beyond this amount, the ability to reline is altered. This alteration in the ability of reline is attributed to the disruption of hydrogen bonding networks between the reline molecules caused by an excess amount of water, which affects the overall process. In addition to the indium peaks, the characteristic zinc peaks reflected at X-ray incidence angles of 36.33° , 39.06° , 43.31° , and 54.34° presented in the X-ray diffractograms that are indexed to (002), (100), (101), and (102) orientations, respectively (Figure 4.13). The choline-urea interaction and hence hydrogen bonding effect does not completely disappear above 5 MR water content, so the XRD pattern also includes peaks attributed to scattering from the indium (101), (110), (103), (211), and (202) crystal planes.

For further investigation of this significant change in the electrochemical mechanism, a number of experiments centered on the 9 MR water-reline solution have been designed. In order to gain more insight concerning both reduction and electrodeposition mechanisms, the 9 MR ratio water content experiment was repeated again with all parameters remaining the same except electrodeposition time, which was kept at 15 minutes (Figure 4.14). The results showed that the electrodeposition of the metal ions was more efficient at a longer deposition time, which suggests that the reaction kinetics are dependent on the deposition time. Further experiments with varying deposition times could provide a better understanding of the electrochemical mechanism, which was extensively performed and discussed in follow-up sections.

From Figure 4.14, it can be clearly seen that during the electrochemical period, in about the first 15 minutes, indium is exposed to the surface due to the hydrogen bond network effect and also the interaction energies between the complex and large molecules of reline. Moreover, from Figure 4.14, it was evidently visible that ion-layering was created between the ITO electrode and electrolyte, which was not totally blocking as in the case of pure and low water amounts but extending zinc deposition time onto the electrode. This suggests that the presence of higher water content in the reline electrolyte enhance the electrochemical deposition of zinc onto the electrode by weakening the molecular interactions.

The ion-layering phenomenon is attributed to the presence of water molecules that create diffusion paths between the ITO electrode surface and electrolyte substitute of EDL phenomenon for aqueous solution, allowing zinc ions to diffuse more easily towards the electrode. Therefore, optimizing the water content in the electrolyte can lead to improved electrochemical deposition performance. Zinc ions reach the surface of the electrode and accumulate due to the weakening of the hydrogen bond structure caused by intermolecular interactions, despite the decrease in conductivity caused by the reduction of ITO to indium metal on the surface. Furthermore, when XRD patterns recorded from electrochemical treatments at different times were compared, zinc crystal peaks became visible at 30 minutes while ITO peaks coming

from the substrate disappeared, which also indicated the primarily rapid formation of indium followed by the mild accumulation of zinc onto the surface.

As the electrodeposition continued after 30 minutes, zinc was also deposited onto the surface, indicating that as the water amount increased in the system, hydrogen bonds between the components of reline were broken, and instead of these antecedent ones, new bonds with water molecules began to form, which gave rise to the zinc formation onto the substrate (Figure 4.14). This observation highlights that the deposition process is complex and involves multiple stages, with indium forming rapidly and zinc accumulating more slowly. The findings from this study provide valuable insights into the potential use of reline as a electrolyte for metal deposition.

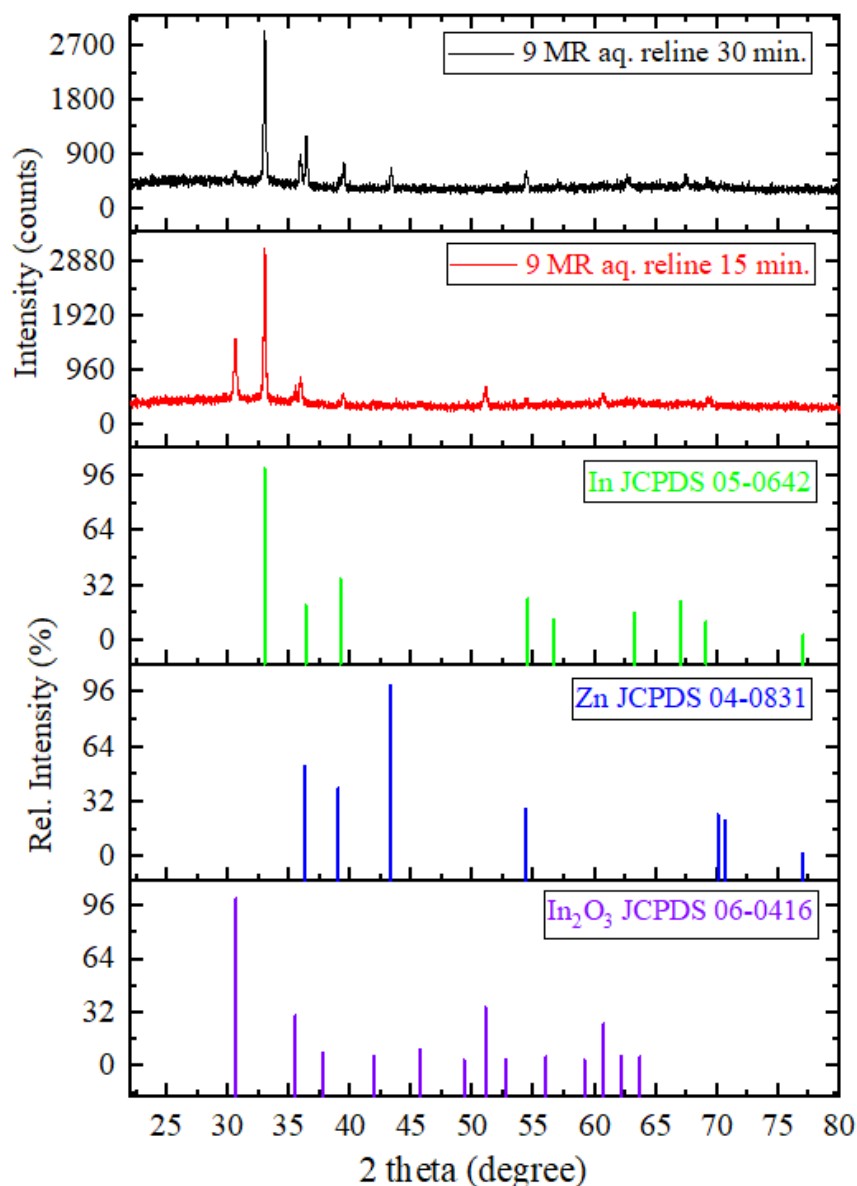


Figure 4.14. XRD patterns of the sample prepared in 9 M ratio of water/ reline solution at different electrodeposition time

The crystal framework of the ITO film, which had been electrochemically processed in 9 MR aqueous reline, shifted slightly to a higher angle corresponding to In_2O_3 ; this was another significant finding. This indicates that the In_2O_3 crystal lattice has shrunk as a result of the substitution of a Zn-doped In or interstitial site. Despite the fact that a ZITO peak was also observed for the electrochemical treatments in DESs,

which were marked in all the above-mentioned X-ray diffractograms, samples treated in a 9 MR reline:water solution suggested a significant structural change in ITO, as shown in Figure 4.13 or 4.14. As evidenced by both graphs, zinc metal deposition onto the substrate enhanced ZITO formation, which was to be expected as the Zn surface concentration increased. The formation of ZITO peaks and the density variation of these peaks in response to test conditions may be interpreted as a signature of the formation of new structures between zinc and ITO films.

In conclusion, the XRD results suggested that the phase separation was caused by the decomposition of indium, tin, and oxygen from each other on the ITO glass substrate during the electrochemical treatment in reline due to the high number of hydrogen bonds and interaction energies between the components, particularly the choline-urea interaction. After treatment in reline, the working electrode exhibits extremely intense and narrow peaks that may correspond to zinc-doped ITO structures since this peak was observed at 35.90° , which was between and very close to the strongest standard pattern of ZnO at $2\theta = 36.25^\circ$ (corresponding to the reflection from the 101 crystalline plane) and $2\theta = 35.46^\circ$ of the reference In_2O_3 (400).

In addition, the relative intensities of this peak have been altered by the addition of water additives to reline, which can be attributed to the fact that crystal morphology on films varies according to reaction conditions such as additives, pH, and reaction time, which all affect the intensity of each XRD peak. This discovery is important for the development of new materials with enhanced properties and applications in a variety of fields, including optoelectronics and energy conversion. Since the scope of this study focuses on the reduction of indium metal in DES to optimize the deposition process and explore the potential of ZITO in various applications, additional research is recommended for future work.

4.2.5 Surface Morphology and Composition of Electrochemically Processed ITO Films in Pure and Aqueous Deep Eutectic Solvents

The surface morphology of the working electrode before and after electrochemical experiments was investigated by SEM, and EDX was used additionally for the elemental research of the samples. Figure 4.15 shows the SEM micrograph and EDX spectrum of the ITO thin film surfaces before the treatment. As can be seen from the figure, the film reveals homogeneous, crack free growth. The nanosized particles are well covered over the glass substrate. Moreover, the EDX spectrum confirms the presence of In, Sn, and O elements in prepared films. Within the experimental error, the weight fraction is approximately equal to their nominal stoichiometry, which is consistent with results for ITO films (Socol et al., 2019).

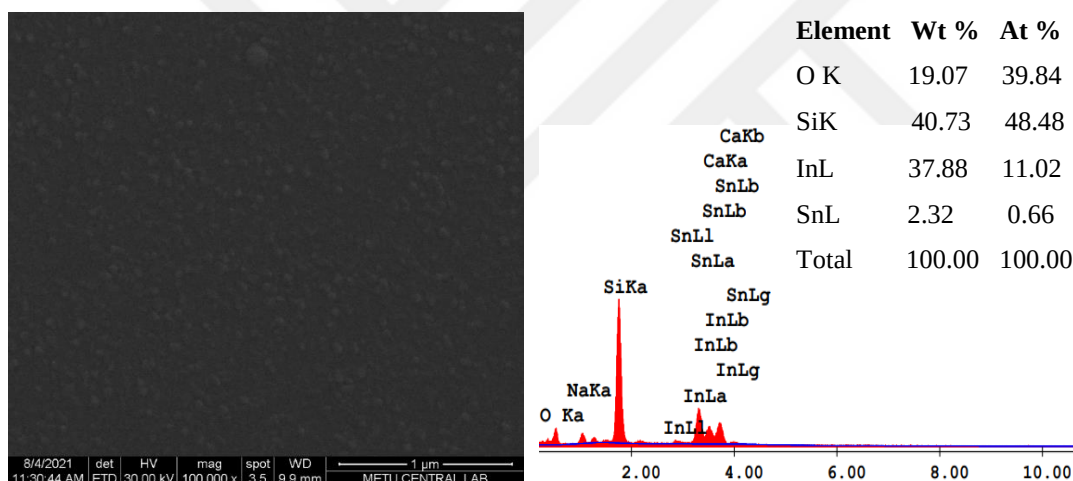


Figure 4.15. SEM image for the ITO coated glass film before electrochemical treatment

Scanning electron microscopy images in Figure 4.16 for either the electrochemically treated surfaces with pure reline or aqueous reline solutions showed the formation of spherical particles. The image suggests that the electrochemical treatment of surfaces with reline solutions can lead to the formation of nanosized spherical indium particles. In addition, images indicated the extracted indium particles on the top of the substrate after electrochemical experiments in pure reline and also in 1 MR

water:reline solutions were more crystalline and significantly larger with a higher diameter, which is in accordance with the XRD analysis, which displayed more intense and sharper indium peaks when compared with the 3 MR water:reline correlate. In addition, the 1 MR water:reline SEM image revealed a homogeneous, closer size distribution of nanometric indium nanoparticles that are more homogeneously dispersed throughout the surface of the substrate relative to the sample surface obtained in the 3 MR water:reline electrolyte. In line with the crystal structure of these samples, the morphological examinations also suggest that the concentration of water in the electrolyte has a significant impact on the size, distribution, and crystallinity of the extracted indium particles.

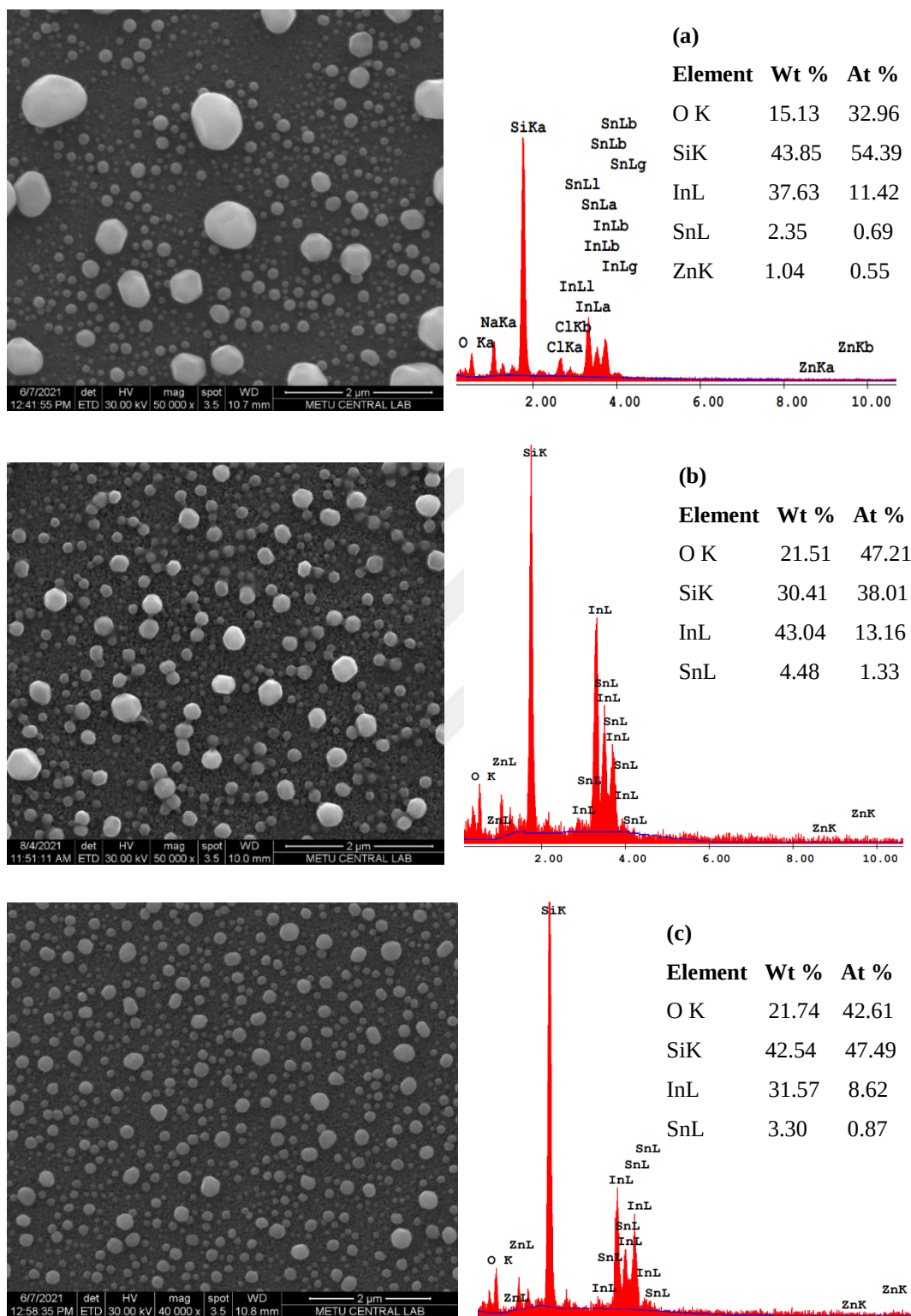


Figure 4.16. SEM image for the ITO film electroreduced in (a) pure reline solution (b) 1 MR water:reline solution (c) 3MR water:reline solution.

In Figure 4.16 (a–c), SEM images of the electrochemically treated ITO substrates in aqueous and pure relene solutions are presented. When these images were compared with the surface image of untreated ITO film, rather than a smooth surface, almost spherical particles were easily identified. These particles were found to be uniformly distributed on the surface of the working electrode, and their size and density have changed with the concentration of the relene solution. These particles were associated with indium metal since XRD spectra showed that no detected diffraction peaks of Sn or additional treated surfaces were found in the prepared samples; only indium crystal planes were observed after electrochemical treatment in relene. It is also clear that when the samples were obtained in relene with various water concentrations, larger particles were observed in 1 MR water:relene, which promoted the indium reduction, and for higher water contents, crystalline sizes reduced, which is consistent with XPS data. Water behaved as a cosolvent by modifying the physicochemical properties of relene for the 1 MR amount.

EDX analyses were used to determine the samples' elemental composition, and the results are reported in Figure 4.16 (a–c). The percentage atomic content and weight of the elements detected on the surfaces determined by EDX are also shown in the figure. The EDX spectrum confirmed the presence of indium (In $L\alpha$, 3.286 keV), oxygen (O $K\alpha$, 0.525 keV), and tin (Sn $L\alpha$, 3.443 keV) over the surface. On the other hand, the zinc (Zn $L\alpha$, 1.012 keV) peak was not observed as expected in the samples that were treated in pure and hydrated relene up to a 3 MR water:relene solution, which is in good agreement with the XRD results. The absence of the zinc peaks is attributed to the ion layering phenomenon on the electrode surface, which inhibits the deposition of zinc ions.

The surface morphology of the sample electrochemically treated in 9 MR water:relene was also analyzed by SEM (Figure 4.17). The SEM analysis revealed a significant change in the surface morphology of the sample after electrochemical treatment in a higher water content relene solution, with the formation of unhomogenous particles

and a rough surface. In addition, filamentous structures were sighted on indium particles of different sizes. This image suggests that the electrochemical treatment in a higher water content reline solution caused complex reactions on the surface of the working electrode, leading to the formation of these structures. EDX analysis of the sample indicated the presence of 6.58 wt% Zn (Zn L α , 1.012 keV) , which is in line with XRD results. The filamentous structures observed on the indium particles may be attributed to the presence of Zn; however, further investigations, such as elemental mapping, were performed to determine the exact composition of these structures.

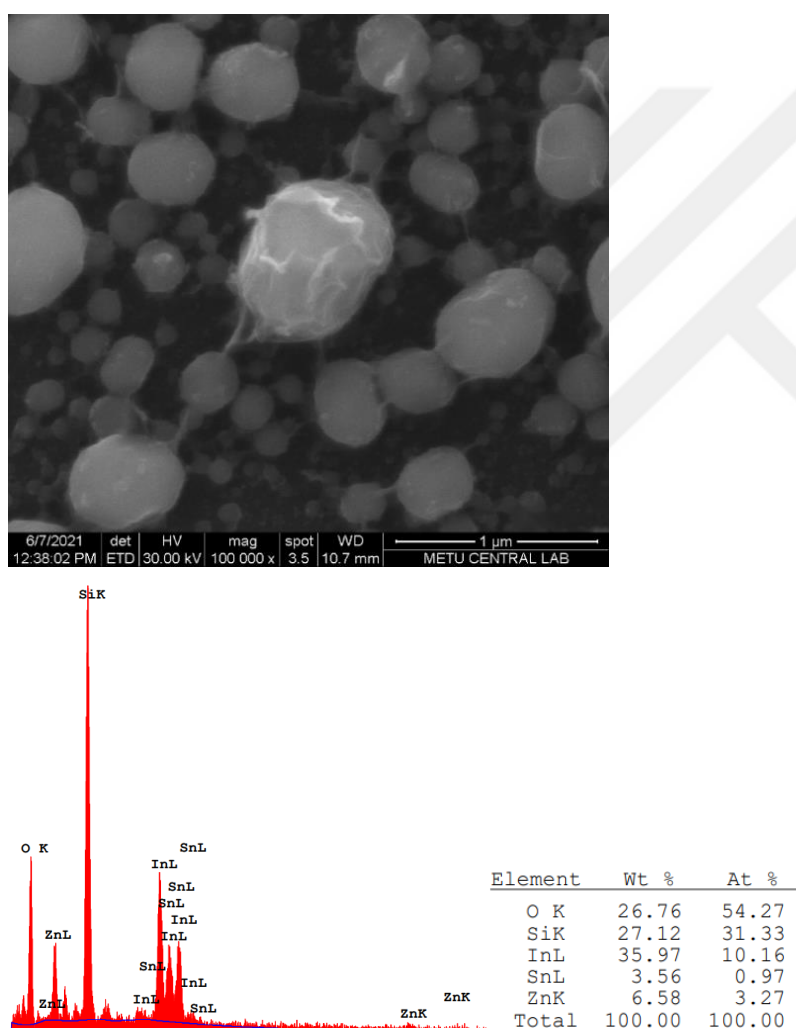


Figure 4.17. SEM image (top) and EDX pattern (bottom) of the working electrode which was electrochemically in 9 MR water:reline solution

The distribution of indium, tin, and zinc over electrochemically treated ITO samples was analyzed by EDX mapping. As shown in Figure 4.3 previously, an untreated ITO surface has a uniform distribution of In and Sn elements. On the contrary, EDX mappings for the samples electrochemically processed for 30 minutes in reline solutions demonstrated that the indium signals are evenly distributed within the spheres, confirming the reduction and separation of indium metal during electrochemical treatment in reline. The results obtained from the EDX mapping indicated that the electrochemical treatment in reline solutions caused a non-uniform distribution of In, Sn, and Zn elements on the working electrode, indicating a modification of the ITO surface.

The EDX mapping analysis for treated samples in pure and 3 MR water:reline solutions is shown in Figures 4.18 and 4.19, respectively. When the mapping images from these figures are compared, it can be suggested that the relative concentration of indium atoms is significantly higher at the same level as particles. In addition, the distribution of tin and silica is more uniform than that of indium, which also suggests that the spherical particles observed in SEM images are composed of indium-rich material. Moreover, for the coatings electrochemically processed in hydrated reline (3 MR), smaller indium particles are formed compared with pure reline, which is also in line with the SEM images above. This indicates that the presence of water in the DES based electrolyte affects the reduced particle size distribution and morphology, as well as the crystallinity discussed in the previous section. Therefore, the use of reline as an electrolyte can be a promising approach to controlling the properties of indium reduction by a simple electrochemical method.

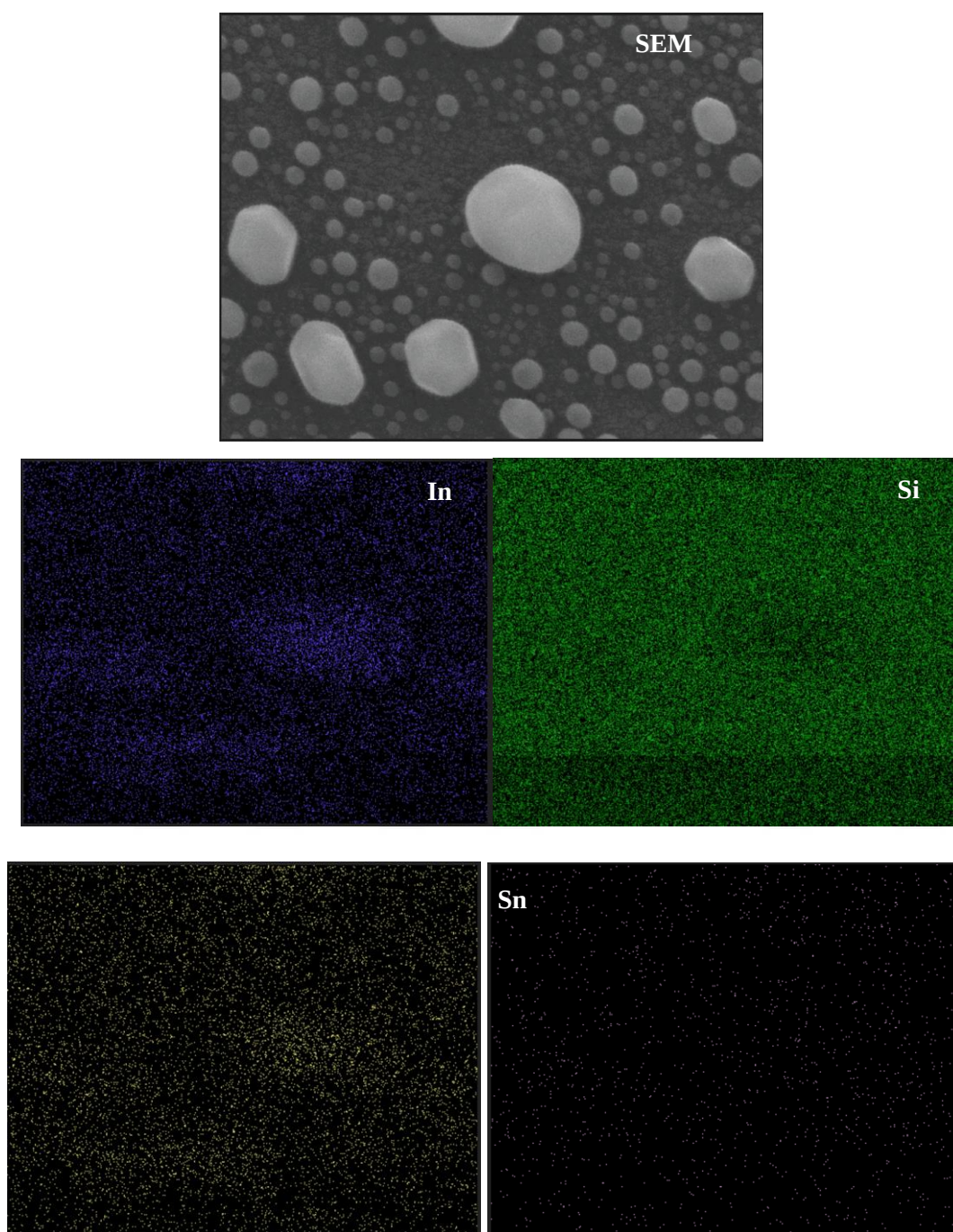


Figure 4.18. SEM image and elemental mapping analysis of electrochemically treated substrate in pure reline for indium, silica, tin and zinc elements

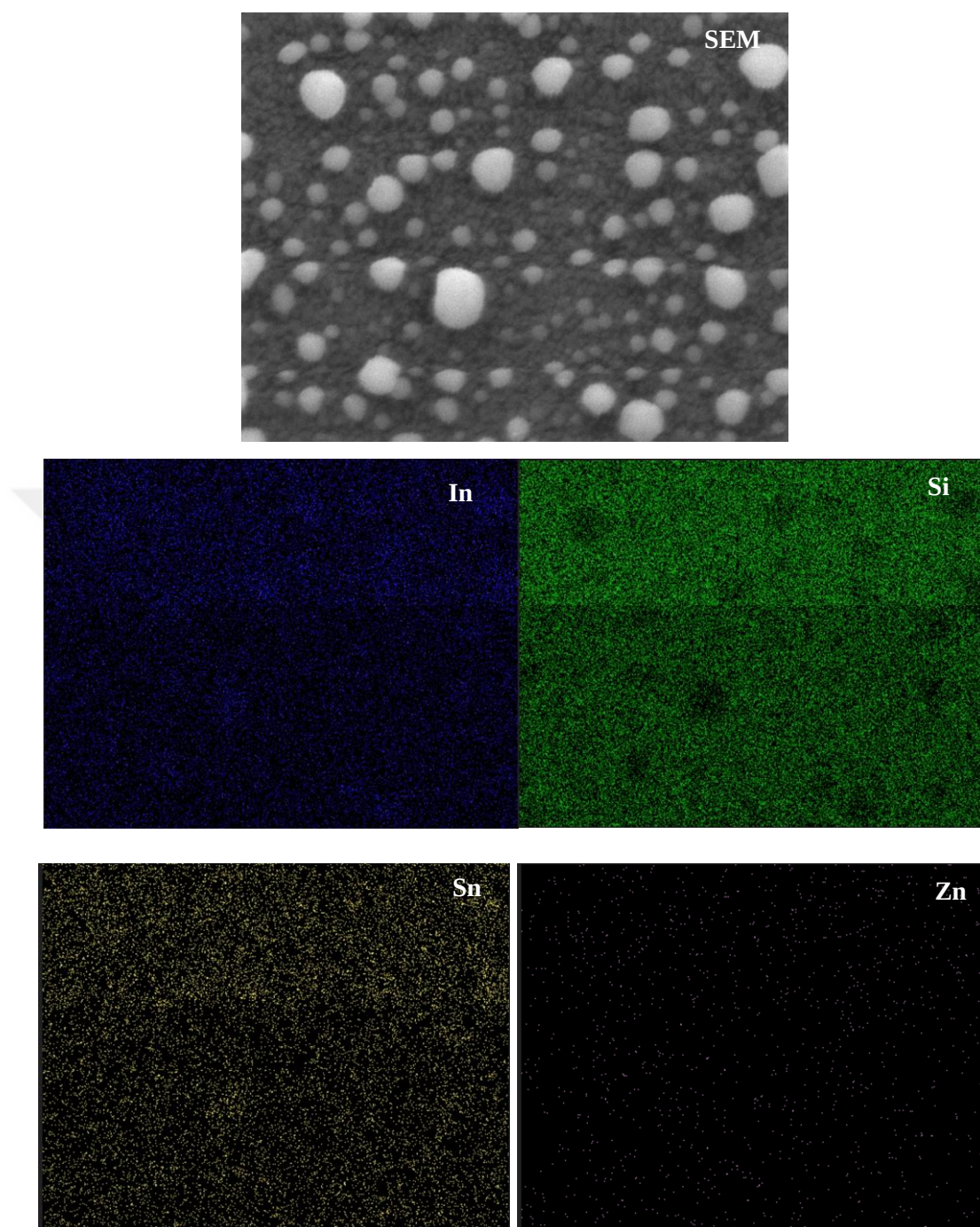


Figure 4.19. SEM image and elemental mapping analysis of electrochemically treated substrate in hydrated reline (3 MR) for indium, silica, tin and zinc elements

When the water content of the reline solution increased to 9 MR, as can be observed from the Figure 4.20, the EDX elemental analysis also validated the zinc metal

formation onto the working electrode surface, likewise the XRD analysis. The elemental maps illustrated that zinc formed over and around the indium particles, which were observed as fibrous structures around indium particles in the SEM image. In addition, the observation of zinc around the indium particles strengthens the claim that the indium metal is first separated from the ITO, and then zinc accumulation occurs. In other words, for the 9MR reline:water electrolyte, while the presence of reline promoted the reduction of indium at applied voltage mainly due to the interaction of the complex structures and hydrogen bonding network, the presence of water in the electrolyte caused the zinc to nucleate on the surface by weakening the interactions and diffusing into the reline during the electrochemical process.

This finding suggests that the zinc deposition may be a result of a secondary reaction rather than direct deposition from the precursor solution as in the experiments performed with an aqueous electrolyte. The primary reaction that was occurred on the electrode surface was indium reduction as discussed for all DES electrolytes. Moreover, the amount of water used in the synthesis the method plays a significant function in the formation and distribution of indium and zinc particles. The interactions between the ChCl or urea components, on the other hand, can be significantly weakened by too much water. Therefore, as the experiment continued, due to the higher water concentration, water molecules that were getting concentrated around the ChCl and urea groups weakened hydrogen bonding between them, allowing zinc deposition on the surface.

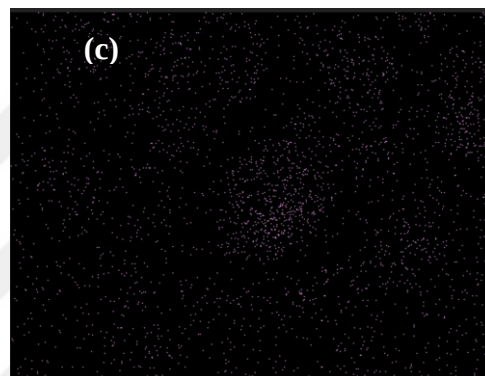
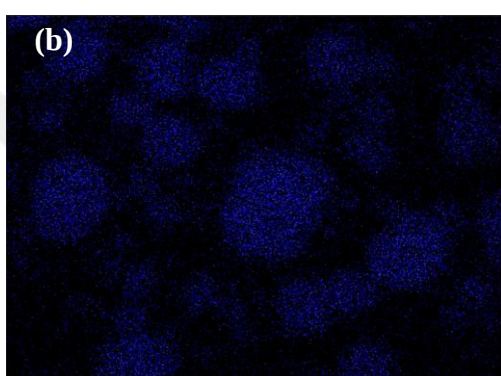
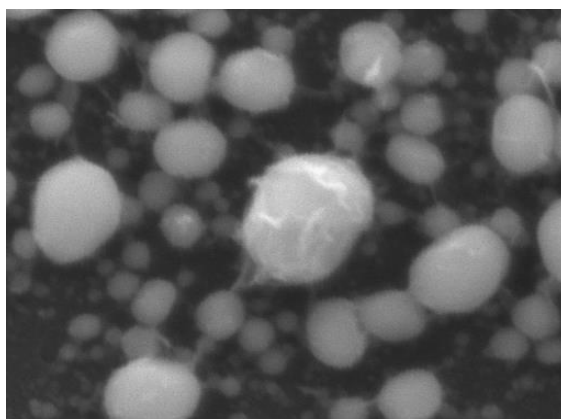


Figure 4.20. Working electrode treated in 9 MR reline:water solution (a) SEM image, elemental mapping analysis for (b) In, (c) Zn

Electrochemical experiments performed in deionized water displayed dense and edifice zinc deposits on the ITO surface, while electrochemical practices with DES indium and tin reduction at various rates based on water amount were observed in addition to zinc doping or deposition, even if just a bit with the same parameters. In accordance with the crystal structures of the same surfaces, the morphological and elemental findings suggest that the use of reline as an electrolyte causes a significant change in the electrochemical behavior of the ITO surface compared to deionized water, leading to different electrochemical patterns and elemental compositions. This difference is so significant that electrochemical treatment in water results in zinc deposition on ITO coatings, while in reline, ITO is reduced to indium. This highlights the importance of considering the electrolyte composition when designing electrochemical experiments for material synthesis and surface modification.

Moreover, the effect of water on electrochemical processes in hydrated reline was investigated and associated with the hydrogen bonding variation in various simulations and experiments in the literature. According to the literature data explained in detail at the various parts of the thesis, the amount of hydrogen bonds within these groups indicates a highest level at low water percentages, which showed uniform distribution with higher crystalline indium particles treated in 1MR reline:water solution. At the intermediate water fractions that are above 5 MR in this study, since the components of reline are hydrated with water, zinc deposition onto the reduced indium particles was observed as a secondary electrochemical mechanism. This finding also highlights the importance of water content in controlling hydrogen bonding and subsequent electrochemical mechanisms in reline-water solutions. At higher water fractions (above 10 MR), hydrated reline behaves like aqueous electrolyte since both urea and anions exhibit high diffusivity, which is also reflected in changes to transport properties like conductivity and viscosity. Therefore, above these fractions, experiments were not designed since the purpose of studying hydrated reline was to understand the relationship between water content and indium reduction during the electrochemical process.

Finally, all types of electrolytes included the same amount of ZnCl_2 , which behaved as a zinc precursor in deionized water solutions and, on the other hand, acted as a supporting electrolyte in DES based solutions. Moreover, comparisons between the electrochemically treated samples obtained from the EDX/SEM and XRD measurements are in good agreement with each other for all experimentation sets. To clarify mechanisms, more cyclic voltammetry was performed in a certain systematic way. The cyclic voltammetry results revealed that the electrochemical treatment led to changes in the surface chemistry of the samples, which could explain the observed improvements in their properties in line with other characterization studies.

4.3 Cyclic Voltammetry Analysis

The electroreduction of indium in DES electrolytes has been reported in this study, showing promising results. The choice of electrolyte significantly affects the reduction process and the morphology of the resulting indium deposits since the nature of the electrolyte, its concentration, and pH influence the reduction performance. SEM, EDX, and XRD analysis of the electrochemical treatment of the ITO working electrode in different DES and their aqueous mixtures showed that the indium reduction rate and recovered indium structure are strongly affected by the properties of an electrolyte. Therefore, the findings of this study indicated that the optimization of the electrolyte composition and conditions can lead to a more efficient and controlled reduction process for the synthesis of indium deposits. Further research, as CV suggests, could explore the electrochemical mechanism of electrolytes or modify their properties to enhance their electrochemical performance.

Along with reline solutions, deionized water solution was also examined in cyclic voltammetry since the XRD results discussed above showed that the electrochemical experiment outcomes were significantly different than in DES. Therefore, investigating the differences between DES and deionized water solutions in cyclic voltammetry could provide valuable insights into the behavior of different types of electrolytes. Furthermore, the results in reline, ethaline, and their aqueous solutions showed that the reaction occurred at the electrode-electrolyte interface, and so the behavior of the indium-indium oxide and zinc in the electrochemical systems was significantly affected by DES and the water concentration in DES.

Regarding all these findings, cyclic voltammetry experiments were designed in water, DES, and hydrated DES at various water concentrations to understand the effect of electrolyte concentration on the electrochemical behavior. The scan rate was set at 50 mV/s, which is intended for better observations of all electrochemical processes. Eventually, according to the literature (Liu et al., 2015), the indium reduction is enhanced in an acidic media and inhibited in alkaline environment. Therefore, the effect of electrolyte pH was also investigated by CV measurements.

ITO coated glass samples were used as working electrodes, with an active electrode surface area of 6 cm². In addition, the reference electrode was a standard Ag/AgCl electrode, and zinc wire was used as the counter electrode. Pure reline (ChCl and urea at a molar ratio of 1:2) and its mixtures with water were tested as electrolytes containing 0.1 M ZnCl₂ as a zinc source. The working electrode was scanned for 5 cycles between -1.8 V and 0 at a scan rate of 50 mV/s. Moreover, the experimental procedure section provides a comprehensive description of the methodology used in the CV study, including the equipment and materials utilized. By observing five cycles in cyclic voltammograms, it becomes easier to analyze any potential shifts or variations in the electrochemical behavior. This allows for a more comprehensive discussion and interpretation of the data.

Once and for all, it is important to note that cyclic voltammetry studies were performed via different potentiostats for each parameter set of the electrochemical experiments, making direct comparison difficult for the different parameter analyses. This could have introduced some variability in the results obtained from each potentiostat, so careful consideration should be given when comparing the results obtained from different parameter sets of the electrochemical experiments. Therefore, comparative discussions were implemented for set data stacks performed through the same potentiostat. This approach allowed for a more accurate comparison between the different parameter sets as it minimized the potential influence of equipment variations on the results. Overall, this study provides valuable insights into the electrochemical behavior of the tested materials under different conditions.

4.3.1 Cyclic Voltammetry Analysis for Aqueous Solution

The deionized water solution was tested, as mentioned at the introduction of this section. Figure 4.21 shows voltammograms on ITO coated glass as WE in an electrolyte containing 0.1 M ZnCl₂ aqueous solution. At 80°C, voltammetric experiments were carried out on an ITO electrode in the potential range of -1.8 to 0

V/Ag/AgCl. The reduction process was reported to be completed in a single phase linked well with reduction of Zn(II) to Zn (0). This peak was displaced by more negative potentials when the CV cycling continued. The displacement of the peak I_c to more negative potentials suggests that the reduction process becomes more difficult as the CV cycling continues, possibly due to the accumulation of zinc chloride ions at the electrode. In addition, the anodic scan demonstrates one oxidation peak, which has a more stable displacement through cycles.

In terms of the standard hydrogen electrode, standard potential of zinc is 0.76 V. However, when the standard potential is matched to Ag/AgCl (+0.197 V vs. SHE), zinc has an expected potential of 0.957 V (Beheshti et al., 2020). According to the figure below, the main cathodic process for zinc reduction starts at around -0.8 V vs. Ag/AgCl and reached a maximum at about -0.9 V for the 2nd cycle. As the cycling progressed, a shift towards higher values was observed. The possible reaction for zinc metal formation is:



In addition, reduction potential is more positive than the theoretical value which is proposed as under potential deposition (UPD) in literature. According to the literature, this phenomenon occurs when the work function of a metal being electrodeposited is lower than the metal on the surface of the substrate, which is zinc and ITO in our case with the work function of 3.6 eV and 4.7 eV, respectively (Ruiz-Ocampo et al., 2017).

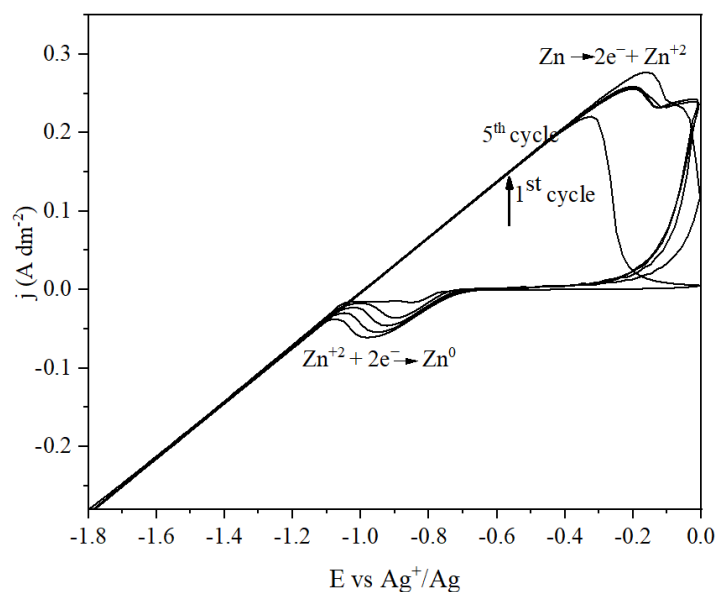


Figure 4.21. Cyclic voltammograms recorded from a solution containing 0.1 M ZnCl_2 in water on an ITO working electrode (WE) at 80 °C (5 cycle). The applied potential at the electrode was initially scanned from -1.80 V to positive direction. Scans were recorded with a rate of 50 mV s^{-1} .

4.3.2 Cyclic Voltammetry Analysis for Pure Reline

Figure 4.22 shows the results of a voltammetric study, which was recorded with respect to Ag/AgCl , of 0.1 M ZnCl_2 in pure reline using an ITO glass working electrode. The anodic and cathodic peak currents gradually increase during potential cycling, which indicates the reduction. The reduction peak broadens and shifts to a more anodic positions through higher cycles. On the other hand, the anodic scan shows two oxidation peaks, which, in the same manner as with reduction, become wider as the cycles continue and are displaced to more positive potentials. These observations suggest that the electrode surface is being modified during the cycling process, possibly due to the formation of a passivating layer regarding the ionic structure of reline and also the changes in the surface morphology as indium was reduced from ITO.

In the anodic direction, two oxidation currents at about -0.85 V and -0.3 V are ascribed to the electrochemical dissolution of In^0 to In^+ and the oxidation of In^+ to In^{3+} , respectively (Figure 4.22). On the other hand, a cathodic peak can be assigned to the reduction of In^{3+} examined at around -1.2 V. This suggests that the oxidation of indium is a multi-step process that occurs in two stages, while reduction occurs in one step directly from In^{3+} to In^0 . Here, the onset of the In reduction potential is $E = -0.81$ V, while the maximum potential observed above -1.2 V which was very broad. However, the very broad character of this cathodic wave puzzles that it includes a couple of In(III) reduction steps since the standard reduction potentials (E_0) of the redox couples are very close to each other apart from the In^+/In redox couple as summarized below equations (Deferm et al., 2019).



This observation suggests that the reduction of In(III) may involve a complex mechanism, possibly involving the formation of intermediate species or the direct reduction in one step of indium through In^{3+} to In^0 . Furthermore, when compared with the aqueous counterpart discussed above, zinc oxidation/reduction CV peaks were not observed at the surface, which is in accordance with XRD, XPS, and EDX observations. These findings highlight the importance of understanding the specific mechanisms involved in different electrochemical reactions performed in different electrolytes.

Similarly numerous systematic CV researches carried out by Abbott and coworkers (2009), (2010), (2011); two step oxidation behavior has been observed with associated IL systems. These surveys discussed the main motivation of this two

phase oxidation and one phase reduction was the deposition of two distinct morphologies; microcrystals at higher overpotentials and nanostructures at lower overpotentials (Abbott et al., 2011). As explained above, the fact that oxidation occurs in two phases, In to In⁺ and In⁺ to In³⁺, is apparent with peaks at $E = -0.29$ V and $E = -0.84$ V, respectively (Figure 4.22). The current density decreases to about 0 when all the indium is oxidized into the solution. In fact, the standard reduction potentials of In to In⁺ is $E_0 = -0.14$ V and In⁺ to In³⁺ is $E_0 = -0.443$ V as can be seen from equations 17 and 14 respectively. Therefore, according to similar studies in the literature, the difference between the overpotentials of these two oxidation peaks directly affected the final morphology with recovered indium metals at various sizes, as observed from the SEM images in the preceding section. The results showed that the morphology of the deposited indium was strongly dependent on the potential difference during the electrochemical process.

Indium in the ITO structure is reduced to indium electrochemically via the following process. In addition, no visible bubble was observed during the electroreduction of In from the ITO electrode.



However, equation 18, which assumes a perfect In₂O₃ surface reacts, is unfeasible because electrochemistry is not selective; numerous reactions can take place at the same time and most likely progress unevenly through a number of intermediates. Therefore, the actual reaction mechanism may involve other species present in the electrolyte or on the surface of the electrode, leading to a more complex reaction pathway than what is represented by equation 18. Understanding these complexities is crucial for optimizing the performance of electrochemical devices that rely on In₂O₃ as an electrode material. Therefore, it is not possible to propose multiple potential routes or processes for the reduction or oxidation reactions given by stepwise partial reduction or oxidation of the In³⁺ and/or In mainly taking place at or near defects such as oxygen vacancies.

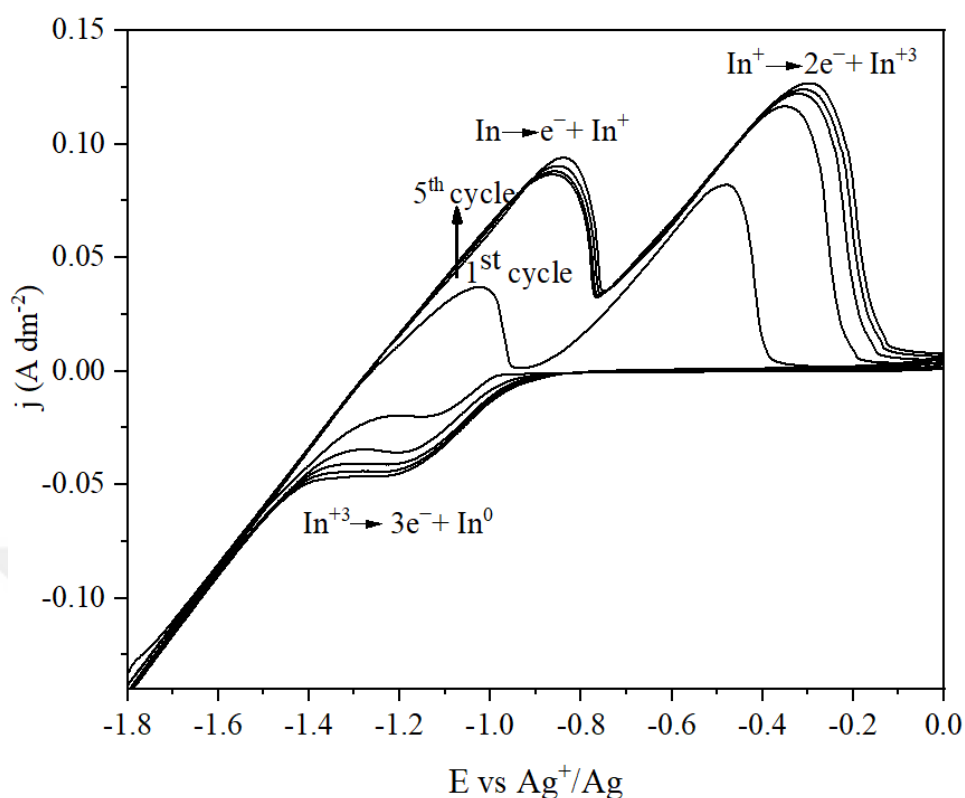
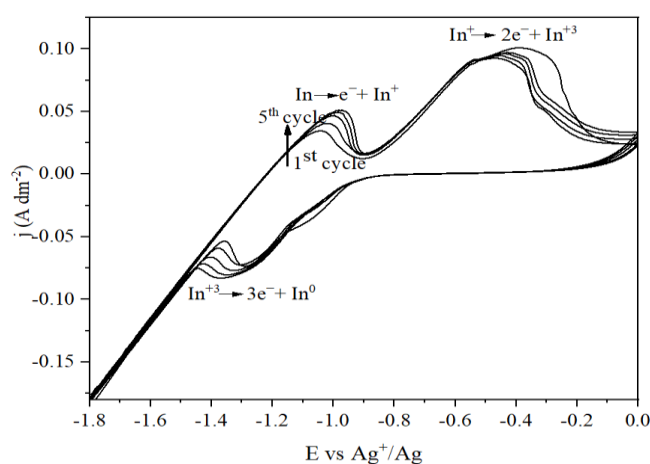


Figure 4.22. Cyclic voltammograms recorded from a solution containing 0.1 M ZnCl_2 dissolved in pure Reline on a ITO working electrode (WE) at 80 °C (5 cycle). The applied potential at the electrode was initially scanned from -1.80 V to positive direction at a sweep rate of $v_{\text{scan}} = 50 \text{ mV s}^{-1}$.

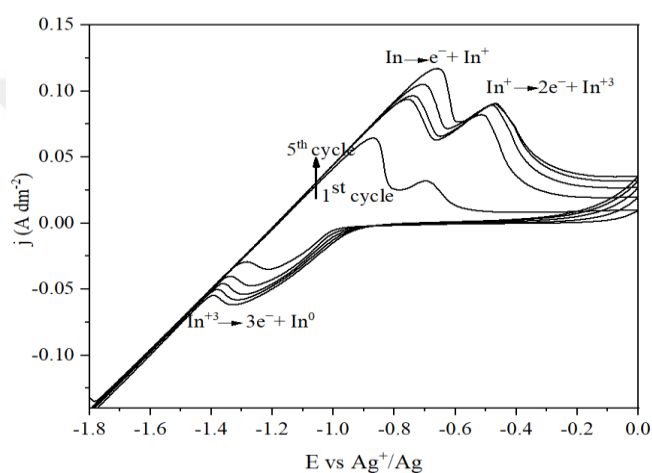
4.3.3 Cyclic Voltammetry Analysis for Aqueous Reline

The concentration of water in the reline is a critical factor that affects both the electrochemical process and the structure of the metal that is reduced on the surface since the hydrogen bonding capacity is directly related to the concentration of water present in the reline, as discussed in the XRD and SEM analyses in section 4.2. The electrochemical behavior of the ITO electrode was studied in hydrated reline electrolyte containing 0.1 M zinc chloride and various amounts of water. Similar to pure reline experiments, the potential was set at 0 to -1.8 V at a test temperature of 80 °C. The cyclic voltammetry test results are shown in Figure 4.23. The cyclic

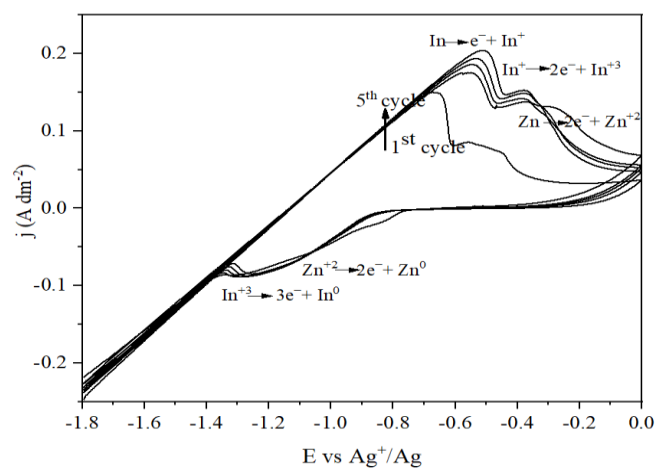
voltammetry test results are shown in Figure 4.23. The CV curve for the samples electrochemically treated in pure relin is slightly different from that of the samples treated in hydrated relin. The difference in the CV curve in Figures 4.22 and 4.23 could be attributed to the presence of water molecules in the hydrated relin, which might have affected the electrochemical behavior of the samples. Moreover, the difference between the experimental conditions of hydrated relins lies in the water content of the electrolyte, which leads to a change in molecular interactions and hydrogen bonding structure, as discussed in other analyses such as SEM, EDX, and XRD. These findings suggest that the presence of water molecules in the electrolyte should be taken into consideration when studying the electrochemical behavior of hydrated relines.



(a)



(b)



(c)

Figure 4.23. Cyclic voltammograms recorded from a solution containing 0.1 M ZnCl_2 dissolved in aqueous reline at a molar ratio of (a) 1MR, (b) 3MR and (c) 9MR on ITO at 80 °C (5 cycle). The applied potential at the electrode was initially scanned from -1.80 V to positive direction. Scans were performed with a rate of 50 mV s^{-1} .

In aqueous reline solutions containing different amounts of water, one broad peak was observed in the cathodic direction, which is attributed to the reduction of metallic indium at higher potentials than theoretical values, besides two significant oxidation peaks (Figure 4.23). These CV observations agree well with the results obtained in pure reline, except for the shift in oxidation potentials. Moreover, when the samples were treated in hydrated reline voltammograms were compared, the relative charge passed through each of the oxidative processes, which is related to the height of the curves, was increasing with increasing water concentration, which results in different morphologies as demonstrated in the SEM images in Figure 4.16. This change can be explained by the increase in solution conductivity with water. In order to make an approximate comparison with the experimental conductivity measurements in the literature (Shah and Mjalli, 2014) for reline with various water fractions, for 1 MR water content, the conductivity is below 6.85 mS/cm; for 3 MR hydrated reline, the conductivity increases to 9.36 mS/cm; and when the water fraction increases to 9 MR, this value increases more than 21.6 mS/cm. That is to say, the water concentration has an impact on the morphology of the samples due to the change in solution conductivity, which affects the relative charge passed through each oxidative process. These voltammograms have important implications for understanding the reduction mechanism of indium using hydrated reline.

Apparently, the amount of water present in the electrolyte significantly affects the redox behavior of the system. On the other hand, with increasing water content in the eutectic solvent, the anodic current increases. Characteristic redox peaks for the oxidation of indium ions are shifted to more positive potentials with increasing amounts of water in the reline solution. However, the anodic currents detected at potentials around -1.3 V vs. Ag⁺/Ag for all electrolytes do not change significantly with water concentration. This suggests that the presence of water in the reline solution affects the kinetics of the indium ion oxidation but not the overall electrochemical behavior of the system. Therefore, it can be speculated that while we observed that indium was reduced with the reduction peak in all reline solutions,

the shifts in the oxidation peaks indicate that the reduced metal particles are of different sizes.

As seen from Figure 4.23 (a) and (b), no oxidation or reduction peak of zinc metal appears at the 1MR and 3MR water concentrations, as in the case of pure reline. Only two oxidation peaks and a reduction peak appear, corresponding to the oxidation and reduction of indium. In particular, ion movement across an electrolyte to the electrode surface, discharge, and crystal growth processes are all parts of electrocrystallization. The lack of zinc oxidation or reduction peaks observed in the voltammograms can be attributed to the mainly complex molecules in reline, which exhibit a blocking effect by forming a barrier on the surface of the electrode. These molecules cover the electrode surface, which inhibits zinc ions in the electrolyte from being transported to the electrode and nucleating on the surface of the electrode. This blocking effect can be attributed to the highly asymmetric and large structure of the molecules in reline, which makes it difficult for zinc ions to diffuse through them and undergo oxidation or reduction reactions on the electrode surface. Moreover, Zn is a very active metal that interacts with these complex ions in the electrolyte, and reduction of Zn is unfavorable at higher pH, such as in reline solutions.

Table 4.1 Oxidation and reduction potentials of the samples treated in various electrolytes

Electrolyte	Oxidation Potential		Reduction Potential		
	max In(I)	max In(III)	max	initial	final
pure reline	-0.84	-0.29	-1.23	-0.93	-1.4
1MR water:reline	-0.97	-0.44	-1.37	-0.96	-1.44
3MR water:reline	-0.66	-0.47	-1.32	-0.93	-1.4

Comparing CV results obtained with a 3 MR water:reline solution to those obtained with 1 MR, sharper and narrower peak separations can be observed. The equilibrium potential for the cathode peak related to oxidation to the In(I) ion shifted to more positive values with increasing water concentration, except for 1 MR water content, as expected by the Nernst Equation. This shift was consistent with the increase in ionic conductivity, as shown in Table 4.1.

Moreover, when comparing the oxidation peak potential difference between two steps, oxidation to In(I) and oxidation to In(III), for hydrated electrolytes at different water contents, the 1 MR water:reline electrolyte with stronger hydrogen bonding and higher ion concentrations showed a higher oxidation potential difference. This difference can be attributed to the morphological difference discussed in the CV discussions for the electrochemical treatment in the pure reline part. As displayed in Table 4.1, the difference between the two oxidation peaks is 0.53 and 0.19 for the samples treated with 1 MR and 3 MR hydrated reline, respectively. The difference in oxidation mechanisms affects the recovery rate and morphology according to EDX, XPS, XRD, and SEM results. The final morphology of recovered indium metals in 1 MR hydrated reline showed larger particles than those obtained in 3 MR hydrated reline solution, as observed from the SEM images in the preceding section (Figure 4.16).

In addition to the previous findings, it is worth noting that the positive shift in the oxidation peaks of the samples treated in 3 MR hydrated reline continued throughout the cycling, indicating the possible formation of unreducible metal oxides over the surface of the working electrode. This occurrence was particularly significant during the first cycle, as the formation of unreducible metal oxides could hinder the electrochemical redox reactions of indium metals, leading to overpotential. However, as the experiment progressed, the occurrence was gradually observed for the continuous cycles. On the other hand, it is interesting to observe that the oxidation potentials were more stable for the sample electrochemically treated in a 1 MR reline:water solution. This finding suggests that there is a difference in the electrochemical behavior of indium metals in a 1 MR hydrated reline solution

compared to a 3 MR solution. Specifically, it is discussed in XRD and XPS analysis that a higher indium reduction rate occurs in a 1 MR hydrated reline solution than in a 3 MR solution, which could explain the observed differences in the oxidation potentials.

Furthermore, a slight shift in the reduction peak for all samples indicated that a higher overpotential was needed for nucleation processes during electroreduction of indium at a fresh ITO electrode. As the experiment continues, shifts significantly decrease, and peak intensities and positions become stable. Once the indium metal had been formed on the electrode surface, a much lower potential was needed for subsequent indium electroreduction. On the other hand, the shift of the redox peaks was not surveyed for the samples experimented in a 1 MR water:reline solution that was attributed to metal oxidation and indium recovery balance as long as the voltammetric cycling.

To sum up the peak shifts through anodic and cathodic directions, the reverse scans demonstrated slightly stripping waves, indicating that electroreduced indium particles can be reoxidized, which is attributed to the recovery rate. Moreover, the lower stripping of anodic peak was found to be because of the reduction of nanometal, while the higher anodic peak was due to the formation of bulk metal associated with morphology, which was in line with SEM images. On the other hand, both the cathodic and anodic peak currents for indium metals and ions increased continuously with cycling. This phenomenon implies that electroreduced indium is partially re-oxidized and that the active surface area of the working electrode or indium particles increases during potential scan cycles. Thus, it can be concluded that raising the cycle number of the potential scan increased the density of oxidized indium on the working electrode surface.

When the amount of water in reline is applied as 9 MR, it is expected to weaken the hydrogen bonds due to the interaction of water molecules with urea and ChCl, and zinc ions can reach the electrode surface. As can be seen from Figure 4.23 (c), the oxidation of indium to In (I) occurred at -0.51 V, and the oxidation of In (I) to In (III)

was observed at -0.38 V, which were closer than other samples treated in hydrated reline with lower water content. Besides, in the cyclic voltammetry experiments implemented by using 9 MR aqueous reline (Figure 4.23 c), a shoulder at -0.28 V was observed following the second oxidation peak of indium (In^+ to In^{+3}). This shoulder was observed towards the positive in the anodic direction and can be assigned to the oxidation of zinc.

Within the water content of aqueous reline which was experimented in this study, the properties of density and pH show modest variation from its pure form as mentioned in the literature survey part of this thesis (Table 2.4). On the other hand, this is not the case for the effect of water on the molecular interactions, viscosity and conductivity since increasing water content results in free movement of molecules in reline and increase in electrical conduction. From this point of view, the mechanism change mainly attributed to the change in molecular interaction dynamics and increase in current intensity with water content mainly associated with conductivity increase of the solution. The relationship between electrical conductivity, diffusion rate, and electron transport is crucial to understanding the current increase phenomenon. Conductivity affects the flow of ions and electrons, which in turn influences the rate of electron transport, which causes changes in oxidation currents.

Separately, the reverse scan of 9 MR was examined in cyclic voltammograms, the reduction initiated more positively than the sample processed in 3 MR aqueous reline with a wider reduction peak. Reduction started at -0.76 V and continued up to -1.36 V, which includes zinc and indium reduction, respectively. In other words, both indium and zinc are reduced over the working electrode surface when a 9 MR aqueous solution is employed, which is also consistent with the XRD results presented in the previous section.

In addition to an increase in current values with the number of cycles, it was observed that current values also increase due to an increase in water ratio, which can be associated with a change in conductivity. Another noteworthy point regarding current intensities is that peak intensity linked to the oxidation step of In (III) valence

was higher in experiments performed with 1 MR hydrated reline than in experiments performed with 3 MR hydrated reline. In other words, while the current value of the In (I) valence oxidation step was higher than the In (III) valence reduction step in trials performed with 3 MR water:reline solution, whereas the opposite was observed in applications made with 1 MR. Considering that +3 valence indium ions contribute to the mechanism in the reduction step, it can be explained that this step is a bottleneck for the oxidation. Therefore, In (III) oxidation step is more efficient than the other cathodic peak for the 1MR electrolyte associated with the highest recovery rate according to XRD and XPS analyses on the working electrode surfaces obtained in this electrolyte.

The increase in current and shift into positive potential can be explained by the higher mobility of ions, which also favors the mass transfer rate of ions from solution to the working electrode surface. These possibilities are directly related to the amount of water in the electrolyte solution, which has a strong influence on hydrogen bonding, especially between urea-urea due to the oxygen in urea, which is a strong HB acceptor, as also mentioned in various parts of this section while discussing other analyses (Hammond et al., 2017; Shah & Mjalli, 2014). Moreover, the addition of water can also influence the hydrogen bonding between urea and Cl^- rather than Ch^+ since urea makes stronger HBs with the anion than the cation (Celebi et al., 2019).

The interface region between the electrode and electrolyte plays a crucial role in determining the efficiency and mechanism of electrochemical processes, as discussed in several parts of this thesis. It was studied that for electrochemical applications in ionic liquids, the EDL has a multilayered structure rather than the monolayer that occurs in aqueous counterparts at the electrode-electrolyte interface, with multiple alternating layers of complex and large ions in the ionic liquid (Kirchner et al., 2013). However, in the matter of layering structure in ionic liquids during electrochemical processes, very few publications exist that suggest both anions and cations are present as multilayers between the electrode and electrolyte interface regions. The role of the chloride ion in modifying this layer has also been unclear. While there is no conclusive proof available, according to the observations,

a strong hydrogen bonding structure leads to more crystalline deposits and a higher indium recovery rate.

The concentration of water in the reline plays a significant role in the electrochemical process and the structure of the metal reduced on the surface. This is due to the hydrogen bonding capacity being directly affected by the concentration of water present. The adsorption of chloride on the electrode also contributes to the structure of the metal on the surface. However, the bulky asymmetric nature of cations in DES with a larger structure, which is three times higher than the ions in aqueous solution, leads to concentrated ionic media that is dissimilar to the GCS model of an electric double layer used for traditional aqueous electrolytes. This dense ionic multilayer inhibits the approach of $(\text{ZnCl}_4)^{2-}$ to the electrolyte, which possesses strong hydrogen bonding interactions. As a result, zinc deposition onto the surface is blocked, and a negligible anodic peak shift is observed for samples electrochemically treated in 1 MR water:reline with the highest hydrogen bonding strength, as reported in literature. In conclusion, the concentration of water in the reline should be carefully monitored and considered in any electrochemical process, as it plays a crucial role in the structure of the metal on the surface, and can impact the overall outcome of the process.

On the other hand, adding a higher amount of water changes the speciation and leads to a shift in oxidation potential. This shift may be related to the degree of chloride adsorption and its activity in the electrolyte bath. An increased amount of water content in reline tends to weaken the hydrogen bond structure. Likewise, water preferentially solvates the Cl^- anion, which provokes higher chloride activity, leading to large amounts of chloride adsorption on the working electrode.

Chloride adsorption is proposed to have a considerable effect on the oxidation mechanism by complicating it, as observed with significantly lower current density and a high overpotential shift. Additionally, as can be seen from the Table 4.1 above, the onset of reduction shifts cathodically by almost 30 mV from $E = -0.96 \text{ V}$ to $E = -0.93 \text{ V}$ for electrolytes containing 1 MR and 3 MR water, respectively. This shift

suggests that the presence of 3 MR water inhibits the indium reduction compared to its 1 MR water containing counterpart by decreasing the back (reverse) reaction.

4.3.4 Cyclic Voltammetry Analysis for Pure Reline and Pure Ethaline

Because of the intermolecular interaction across components, the physical characteristics of DESs influence their possible uses. Cyclic voltammetry (CV) was explored in either reline or ethaline to gain a deeper awareness of the influence of these features. Electrochemically treated ITO samples showed discrete crystal and morphological structures, depending on how strongly the salt and HBD form hydrogen bonds with each other. The electrochemical behavior of the ITO electrode was studied in both pure reline and pure ethaline electrolyte containing 0.1 M zinc chloride. The potential was set at 0 to -1.8 V at a test temperature of 80 °C.

Figure 4.24 displays the cyclic voltammetry measurements of the ITO working electrode in both reline and ethaline, containing 0.1M ZnCl_2 as the supporting electrolyte. This part of the cyclic voltammetry studies was performed by a computer controlled Gamry Reference 600 Potentiostat/Galvanostat at Gazi University with two-time repeatability. CV measurements in reline were also performed via different potentiostats, as discussed above in Figures 4.22 and 4.23. While it is possible to indium reduce an ITO electrode from both deep eutectic solutions, reduction from ethaline occurs at much smaller current densities.

Although reline is more viscous, a higher current was observed compared to ethaline. This can be explained by the kinematically controlled electroreduction of the zinc reaction, rather than the mass transfer of Zn^+ ions into the working electrode. Similar results were reported by Abbott et al. (2011). It is interesting to note that, even with the addition of ZnCl_2 which decreases the viscosity of the solution, the rate of deposition is initially faster in reline, which is considerably more viscous than ethaline.

In addition to current intensity, another indicator of the change in electrochemical behavior is the oxidation/reduction mechanism's steps. As shown in Figure 4.24, both oxidation and reduction occur in two steps in reline, whereas multiple stages are observed for the oxidation and reduction of indium in ethaline.

Hydrogen bonds in reline can be considered as $\text{Ch}^+ - \text{Cl}^-$, $\text{Ch}^+ - \text{urea}$, $\text{urea} - \text{Cl}^-$, and urea-urea bonds, with urea-urea being the most prevalent due to the presence of strong hydrogen bond acceptor oxygen in urea (Ashworth, 2016). In contrast, hydrogen bonds in ethaline include $\text{EG} - \text{Cl}^-$, $\text{EG} - \text{EG}$, $\text{Ch}^+ - \text{EG}$, and $\text{Ch}^+ - \text{Cl}^-$ interactions. Both ethaline and reline exhibit low ionic mobilities and conductivities. However, the electrochemical reaction mechanisms depend on the hydrogen bonding network within the deep eutectic solvent. Urea is assumed to form a stronger hydrogen bond interaction with ChCl than EG, as reported by Mjalli & Ahmed (2016). In ethaline, the reduction and oxidizing onset voltages and steps are significantly different from reline because the two liquids' ligand activity levels vary. In reline, there is a high interaction among urea and chloride ions, which effectively boosts chloride activity as compared to EG.

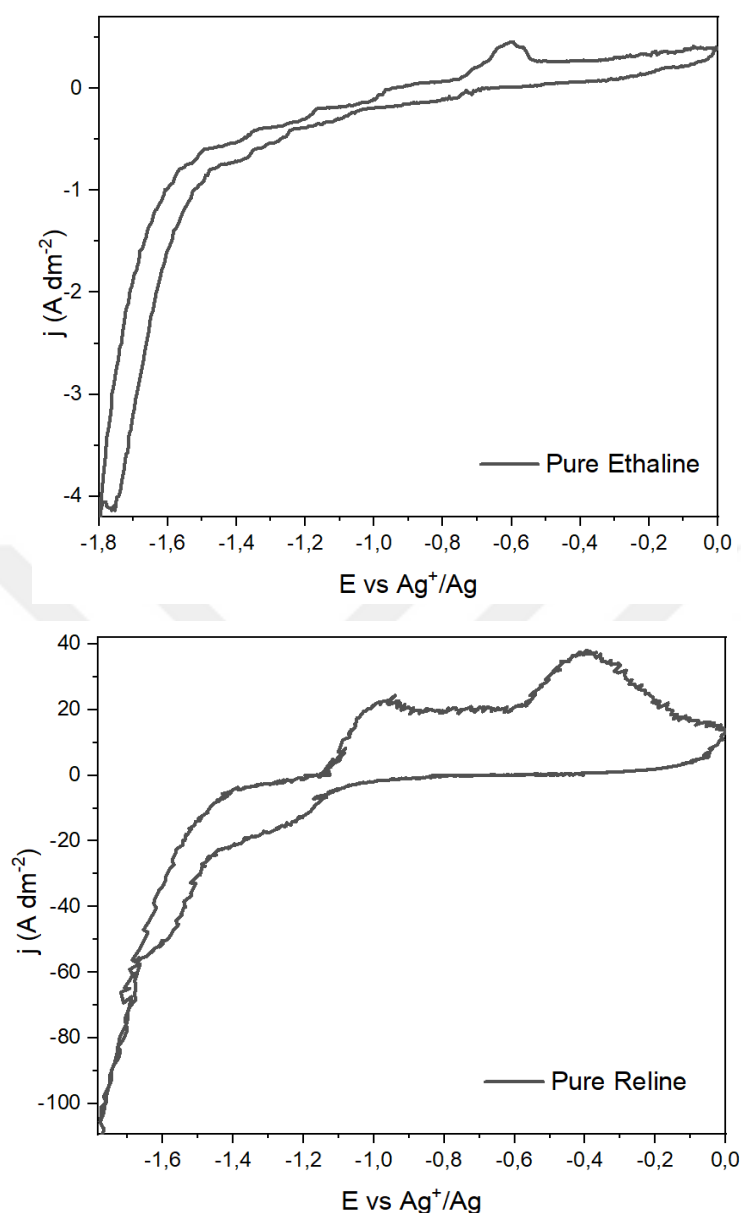


Figure 4.24. CVs of electrochemically treated ITO working electrode in different ChCl based DES namely pure reline (top) and ethaline (bottom). The applied potential at the electrode was initially scanned from -1.80 V to positive direction. Scans were recorded at a rate of 20 mV s^{-1} .

When comparing the results of the electrochemical treatment of ITO working electrodes using different solvents, such as reline and ethaline, it was observed that higher current intensities and peak intensities were obtained when using reline. This

suggests that reduction-oxidation reactions, which are important in electrochemistry, occur to a greater extent with reline than with ethaline. In addition to this, reline also exhibits faster reduction kinetics of indium compared to ethaline according to comparable CV measurements. This observation is consistent with the results obtained from XRD. Therefore, it can be concluded that reline is a better solvent for electrochemical treatment of ITO working electrodes due to its ability to facilitate reduction-oxidation reactions and faster reduction kinetics of indium. It is clear that the type and composition of the electrolyte not only affect the electrochemical processes, but also influence coupled oxidation/reduction reactions, which can lead to different product selectivity by directing the intermediates.

4.3.5 Cyclic Voltammetry Analysis on Zinc Chloride Content of Aqueous Reline

Different amounts of variations in solute concentration in reline had an impact on the electrolyte's physical characteristics, which directly affected the rate of the electrochemical process and the structure of the metal reduced on the surface. Since ZnCl_2 is soluble in choline chloride-based DES, it was considered as low-cost zinc source for zinc or zinc oxide electrodeposition. However, systematic electrochemical experiments showed that it is not possible to deposit zinc metal onto the ITO coated glass substrate by using non aqueous reline solution as electrolyte due to the distinctive ion layering mechanism between the solution and substrate during electrochemical process.

Similar to aqueous reline studies in which water molecules participated in the internal interaction network of reline, zinc and chloride ions also interact with hydrogen bonds and may alter electrochemical aspects. These ions can interact with the hydrogen bonds and affect the internal interaction network, leading to changes in the overall conductivity and current responses. Therefore, removing the ZnCl_2 from the electrolyte solution resulted in several slight differences in CV characteristics, as shown in Figure 4.25. The electrochemical behavior of the ITO electrode was studied

in 3 MR hydrated reline containing 0.1 M zinc chloride and without zinc chloride. The potential was set at 0 to -1.8 V at a test temperature of 80 °C.

For the samples treated in the electrolyte containing 0.1 M zinc chloride higher current intensity was observed from the figure. The overall increase in responses in both anodic and cathodic currents under a fixed sweep rate led to increased electronic and ionic conductivity. Furthermore, for the CV measurement performed in electrolyte containing ZnCl_2 , current decreased eventually to zero at the anodic scan with a very broad peak indicated the higher oxidation rate of indium compared to not including counterpart.

From Figure 4.25, it is clear that ZnCl_2 behaves as a supporting electrolyte, which consists of the supporting cations (Zn^{+2}) and anions (Cl^-) with practically increasing ionic conductivity of the deep eutectic solvent besides changing the physical properties of the electrolyte. This result was also discussed by Andrew P. Abbott and coworkers (2011), who were focused on the double layer effects on zinc nucleation and growth in choline chloride based DESs via electrochemical methods. They suggested that the addition of 0.1 M ZnCl_2 leads to a significant increase in molar conductivity (50 % rise) in comparison with its pure form due to the change in ionic atmosphere and diluent attitude like water.

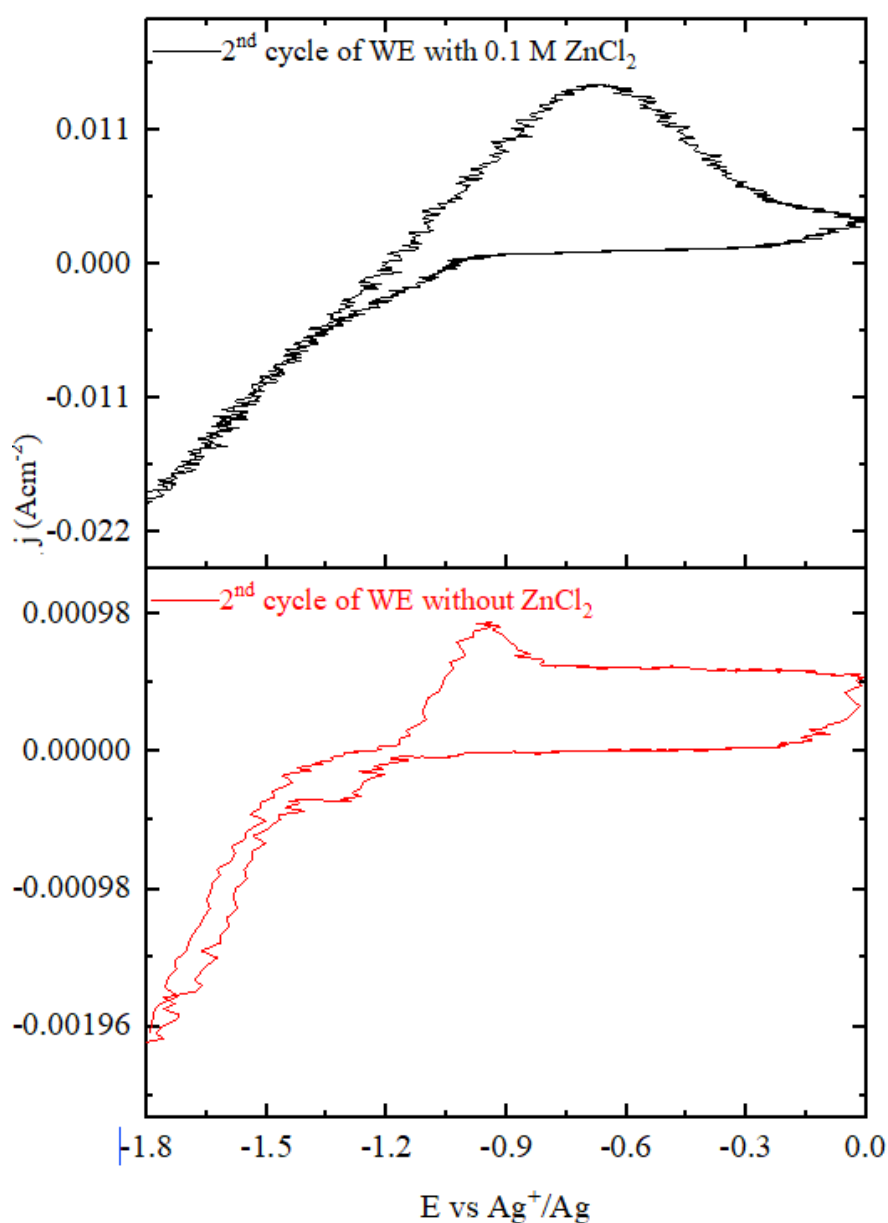


Figure 4.25. Cyclic voltammograms recorded at an ITO working electrode immersed in the 3 MR aqueous reline solution containing 0.1 M ZnCl_2 and 3 MR aqueous reline solution in the absence of ZnCl_2 . Scan rate: 50 mV/s. Number of potential cycle was indicated.

The findings suggest that the presence of zinc and chloride ions in the electrolyte solution can have a significant impact on the electrochemical behavior of the system. Moreover, the crystallographic orientation and structure of the working electrode

after electrochemical treatment in DES containing various amounts of ZnCl_2 have also been investigated for the same purpose and discussed. These ions can interact with the hydrogen bonds and affect the internal interaction network, leading to changes in the diffusion behavior between the working electrode and electrolyte. This change designates zinc chloride's purpose in the electrolyte, i.e., for higher amounts, it behaves as a zinc precursor besides supporting electrolyte since at higher amounts of ZnCl_2 , zinc deposition was observed besides indium reduction, which is also discussed in detail in the effect of zinc chloride concentration section. Therefore, it is important to carefully consider the composition of the electrolyte solution when designing and conducting electrochemical experiments.

4.3.6 Effect of pH in the Aqueous Reline Electrolyte on the Electrochemical Behavior of ITO

The pH of the electrolyte is a crucial factor in determining the properties of products formed during electrochemical reduction (Rocchetti et al., 2016). This is because pH affects the concentration of hydrogen ions, which in turn influences the electrode potential and reaction kinetics. Additionally, pH can affect the morphology and crystal structure of products by influencing nucleation and growth rates. Therefore, controlling the pH is essential for tailoring product properties, such as composition, size, and morphology. You can adjust the concentration of acid or base in the electrolyte or use buffer solutions to maintain a constant pH value.

Understanding how pH affects electrochemical metal reduction from ITO is crucial for designing efficient and selective electrochemical processes through DES. A computer-controlled Gamry Reference 600 Potentiostat/Galvanostat at Gazi University was used to examine this case. The shift in the pH near the electrode (local pH) during reduction depends on various parameters, such as the bulk pH, buffer capacity, current density, and thickness of the diffusion layer developed throughout the experiment of the electrolyte (Bollella et al., 2020).

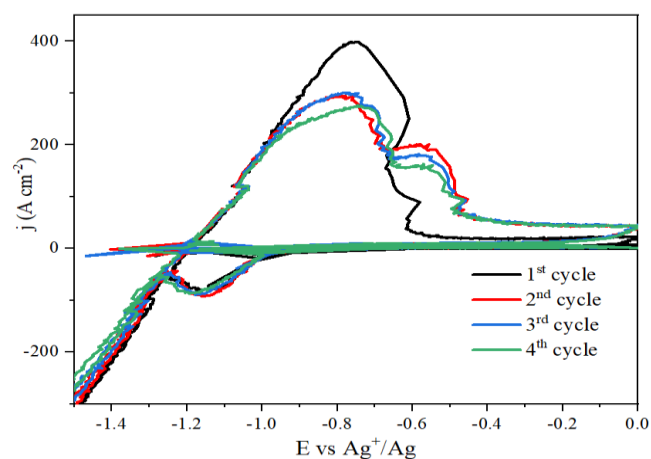
According to Shah and Mjalli (2014), an increase in water content in aqueous reline electrolyte does not significantly affect the pH value. To converge the local pH at the electrode surface through the bulk electrolyte, a small amount of glacial (anhydrous) acetic acid is used as a buffer solution. This common practice minimizes the effects of other variables and ensures consistency and accuracy in experimental results. However, excessive use of glacial acetic acid can lead to corrosion and contamination, so it is important to carefully control the amount used. The experimental section provides detailed information on how to control the amount of glacial acetic acid used in aqueous reline electrolytes to adjust pH of the solvent.

The effect of pH on the electrochemical behavior of the ZnCl_2 -ITO system was investigated at three different pH levels. The pH of the original aqueous reline solution was measured at 8 and then lowered to 6 and 5 by adding appropriate amounts of acetic acid. According to literature, the pH of 3 MR aqueous reline is reported as 10 at 30°C. However, in this study, the pH of 3 MR hydrated reline containing 0.1 M ZnCl_2 was measured as 8 at 80°C, which can be explained by the acidic nature of aqueous metal chloride solutions.

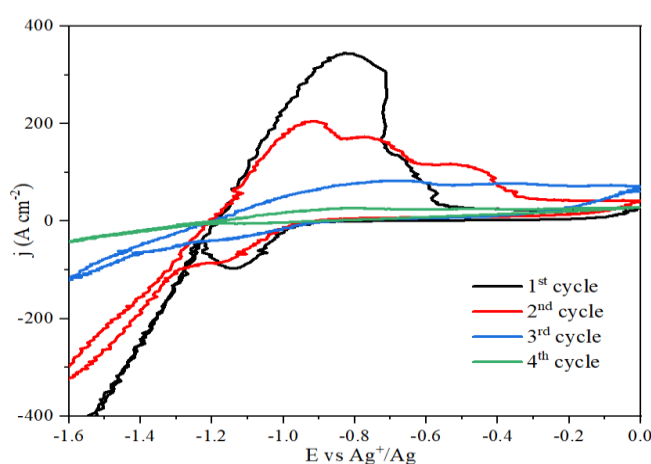
The same voltage interval and scan rate were applied, and the CV profiles obtained at different pH values are shown in Figure 4.26 (a–c). This indicates a strong effect of pH on the current and electrochemical oxidation and reduction activity. At all pH values applied, the same two-step oxidation and one-step reduction peaks were observed in the first two scans. The results of this study suggest that the electrochemical behavior of the ITO electrode in ZnCl_2 -aqueous reline solution is highly sensitive to changes in pH. The observed two-step oxidation and one-step reduction peaks were consistent across all pH values tested, but the current and overall electrochemical activity varied significantly. These findings highlight the importance of carefully controlling pH in electrochemical studies.

Both the decrease in current intensity and the peak shift can be attributed to the inhibition of the reduction of ITO in acidic conditions. This behavior may be due to the favorable electrostatic forces between the negatively charged chloride (Cl^-) ions

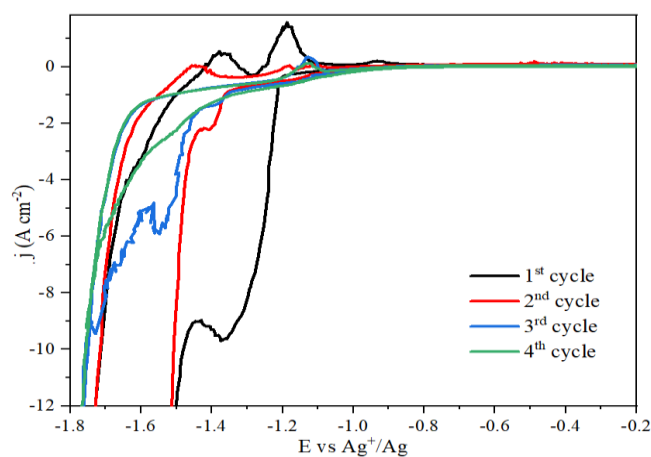
in the electrolyte and the positively charged indium ions (In^{+3} , In^{+2}) on the working electrode, resulting in the reduction of indium metals over the ITO surface. Cl^- ions adsorbed onto the surface negatively affect the oxidation and reduction mechanisms at the beginning of the electrochemical process, but the hydrogen bonding network and the ion interaction at the interface support the indium reduction in the continuation, which was observed via the shift and current density increase from cyclic voltammetry. On the other hand, a decrease in pH value and an increase in H^+ amount in the electrolyte mostly effect the local ionic network at the electrolyte-working electrode interphase cause the higher chloride ion adsorption onto the electrode, blocking the oxidation-reduction reactions and hence denaturing indium recovery.



(a)



(b)



(c)

Figure 4.26. Cyclic voltammetry of working electrode (ITO) in aqueous reline (3 MR) including 0.1 M ZnCl_2 at pH (a) 8.0 (b) 6.0 (c) 5.0 solutions. pH was adjusted by acetic acid. The applied potential at the electrode was initially scanned from -1.80 V to positive direction at a sweep rate of 50 mV s^{-1} .

The ionic behaviour of electrolyte was confirmed by performing XRD analysis of the ITO working electrodes that were electrochemically treated in 0.1 M ZnCl_2 and 3M water containing reline solution at a potential of -1.6 V for 30 minutes at three different pH values. The pH values were adjusted by adding appropriate amounts of acetic acid, as explained earlier. Figure 4.27 presents the X-ray diffractograms.

As shown in Figure 4.27, all samples obtained in alkaline (pH = 8) and acidic (pH = 6 and 5) conditions contained both indium oxide and metallic indium phases. However, the peak heights of indium peaks corresponding to (101) and (110) crystal planes, detected at 32.96° and 39.33° (2 θ), respectively, decreased significantly with decreasing pH (Figure 4.27). In contrast, In_2O_3 (222), (400), and (440) increased at 30.49° , 35.46° , and 51.04° , respectively, with decreasing pH. The higher ratio of peak height of In/ In_2O_3 for higher pH confirms that the electrochemical reduction of ITO is favored in an alkaline electrolyte. Therefore, it can be suggested that the optimum medium for indium recovery is in alkaline conditions.

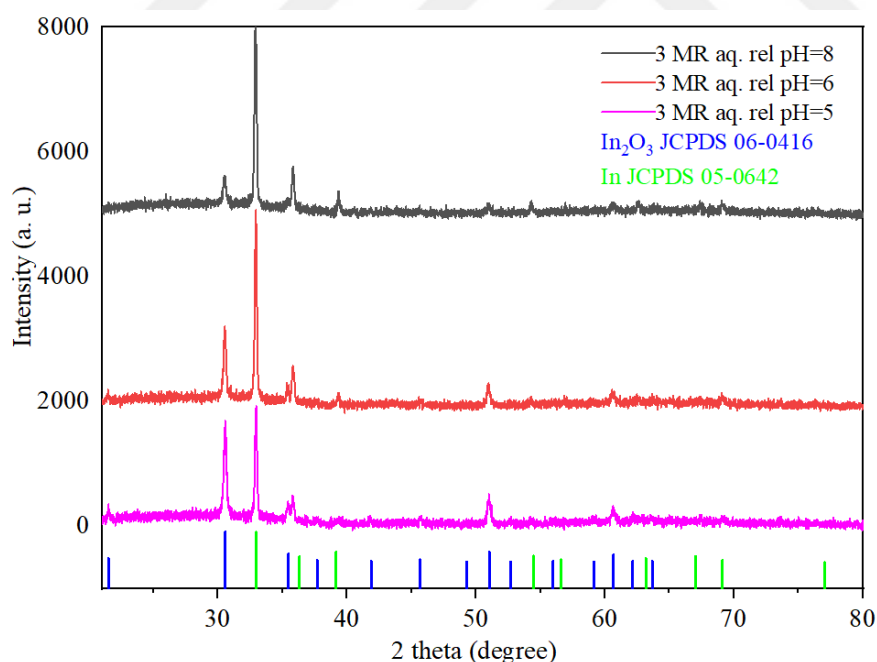


Figure 4.27. XRD patterns of ITO samples electrochemically reduced at -1.6 V for 30 minute in 0.1 mol/L ZnCl_2 supporting electrolyte containing aqueous reline solution (3 MR) at pH 8, 6, 5 by adjusting acetic acid.

In other words, the diffractograms show that the working electrode surface became covered with metallic indium when treated in 0.1 M ZnCl_2 and 3M water containing reline solution at pH 8 and 6. However, at pH 5, the diffraction peaks corresponding to indium metal were observed with significantly lower intensity, indicating a lower rate of reduced metal on the surface. This finding confirms that the reduction of ITO was inhibited at pH 5 due to the electrostatic forces between Cl^- ions and In^{+3} , In^{+2} ions. Either a decrease in current intensity or a peak shift in CV analysis and decrease in the intensity of signals associated with indium crystals in XRD could explain that a decrease in pH significantly inhibits the further reduction of ITO. To sum up, CV measurements were also in line with the XRD analysis. Finally, it should be noted that metallic tin cannot be detected by XRD in all reduced ITO samples, likely due to the low tin content of the ITO film as mentioned at crystalline analysis.

4.3.7 Cyclic Voltammetry Analysis at Various Scan Rate

The distance between the cathodic and anodic peaks of the wave can be used to determine if an electrochemical process is reversible. If the peaks are far apart, this can mean that there were problems with the electrode polishing or solution resistance compensation, or that the reaction is not electrochemically reversible. One may notice that the peak positions remain constant as the scan rates change to demonstrate reversibility. Although irreversibility can be caused by both a sluggish electron transfer and an electron transfer followed by a chemical reaction that changes the transfer's product into a different species. In conclusion, while the distance between the two peaks can provide some insight into its reversibility, it is crucial to take other parameters into account and make use of other techniques. (Pletcher, 2019)

Figure 4.28 (a) shows the 2nd cycle CVs of the ITO electrode obtained in a 3 M aqueous reline solution containing 0.1 M ZnCl_2 with various scan rates (50, 100, 200, 300, and 400 mV s^{-1}). This part of the cyclic voltammetry experiment was performed at Gazi University using a Model AFCBP1 from Pine Instrument Company. Likewise, in other CV analyses, a three electrode electrochemical cell system is used

composed of ITO coated glass, Ag^+/AgCl , and Zn wire as the working, reference, and counter electrodes, respectively.

It was hard to judge the reversibility of a metal ion/metal redox couple, possibly because of the electrolyte's dense ionic structure. The reduction waves are not clearly resolved like those previously observed with other CV analyses in ChCl based DESs due to their dense ionic structure. The scan rate affects the anodic and cathodic peak potentials, E_{pa} and E_{pc} . The difference between both the anodic and cathodic peaks, $\Delta E_p = E_{pa} - E_{pc}$, is larger as the scan rate increases, which is typical of irreversible or quasi-reversible mechanisms. In addition, the oxidation peak decreased in size as the scan rate decreased, as expected.

In cyclic voltammetry analysis, the reversibility of the electrochemical processes can be analyzed by changing the scan rate and determining half wave reduction potentials. However, as can be seen from Figure 4.28 (a), due to the high data noise and low reduction potentials, half wave potentials ($E_{1/2}$) could not be determined consistently. Instead, the change in position of oxidation peak potentials for the scan rates of 50 and 400 mV/s by 0.2 V is used to evaluate reversibility qualitatively. A similar measurement could not be made for the reduction reaction due to the uncertainty of the peak positions.

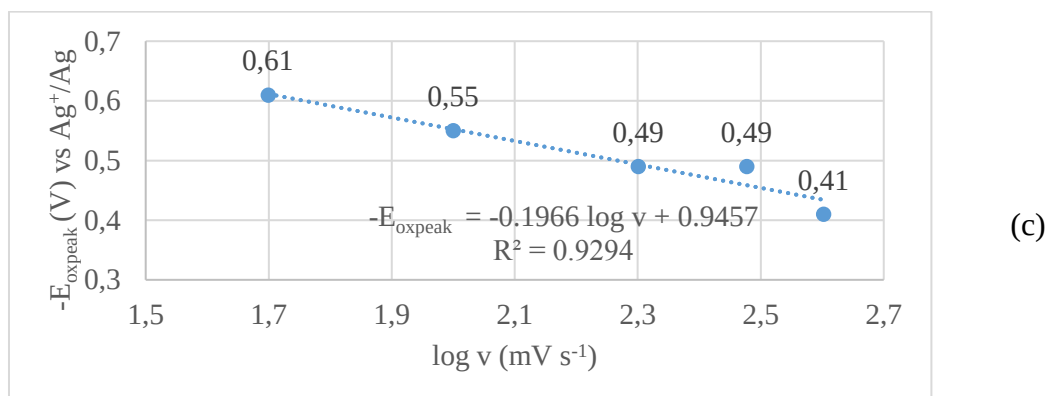
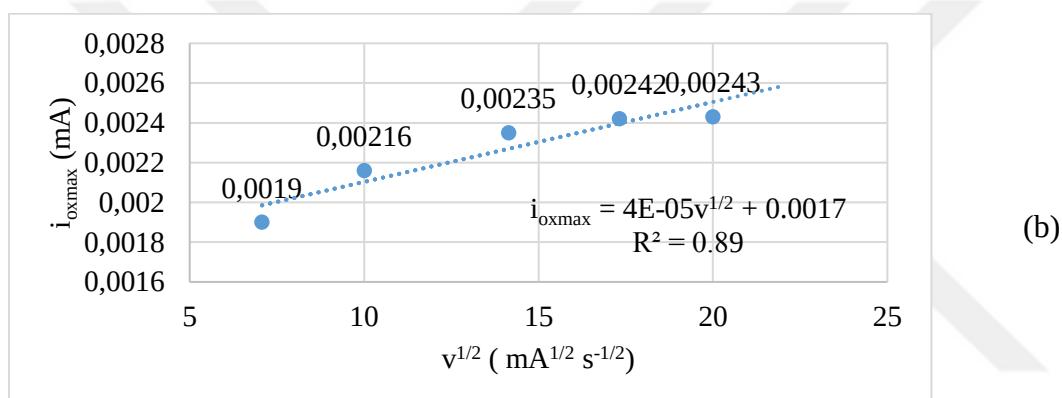
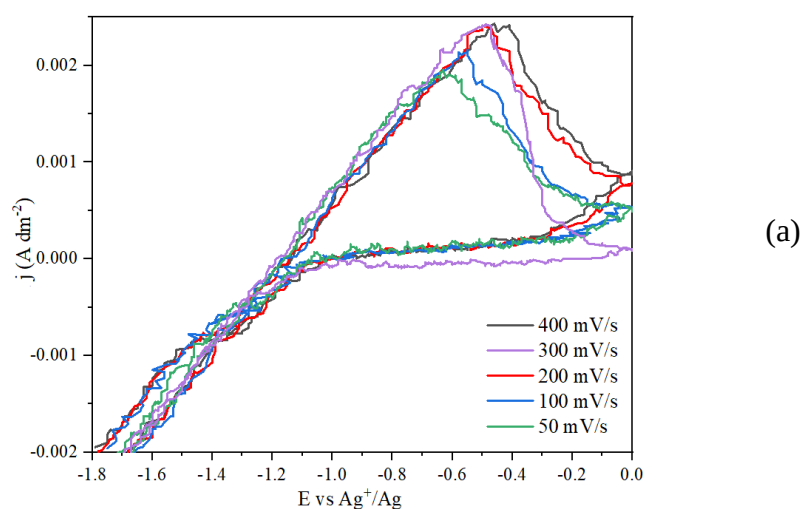


Figure 4.28. (a) CVs of electrochemically treated ITO working electrode in 3 MR water:relina electrolyte at scans(v_{scan}) recorded 50, 100, 200, 300, 400 mV s^{-1} (b) summary of data at the top: plot of peak max. current as a function of square root of the scan rate (c) plot of cathodic peak potential as a function of the scanning rate logarithms

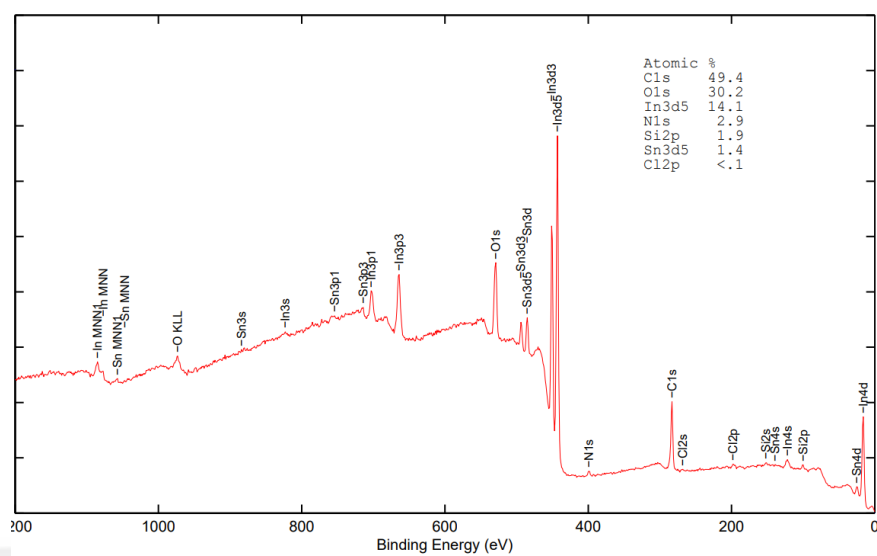
It is also worth noting that peak current varies with the square root of voltage scan rate, which is a significant analytical conclusion. This means that the redox pair is dissolved in solution instead of adsorbed on the surface of the electrode, as indicated by a linear connection among both peak current and scan rate. Therefore, this can also serve as a method to determine the reversibility of an electrochemical process in addition to changing the scan rate and examining the distance between the cathodic and anodic peaks of the wave.

In order to determine the type of indium reduction control mechanism from the ITO substrate, in Figure 4.28 (b), the maximum intensity of the anodic peak as a function of the square root of the scanning rate was plotted. Similarly, the plot of anodic peak potential as a function of the scanning rate logarithms was also observed (Figure 4.28 (c)). From the two figures, it can be seen that the i_{oxmax} peak varies linearly with $v^{1/2}$ and that the E_{oxpeak} varies linearly with $\log(v)$, characteristic of a diffusion controlled reaction (Pletcher et al., 2001). This finding may be explained due to the multi layer diffusion barrier phenomenon during electrochemical treatment and limited mass transfer property of DES with unordinary ionic structure. Plotting the graphs with the cathodic peak potential and current intensity is not possible due to indeterminate values, as shown in the figure. However, assuming similar oxidation and reduction behavior (i.e., shift in peak position and peak intensity), these plots may provide insight into the electrochemical mechanism of ITO.

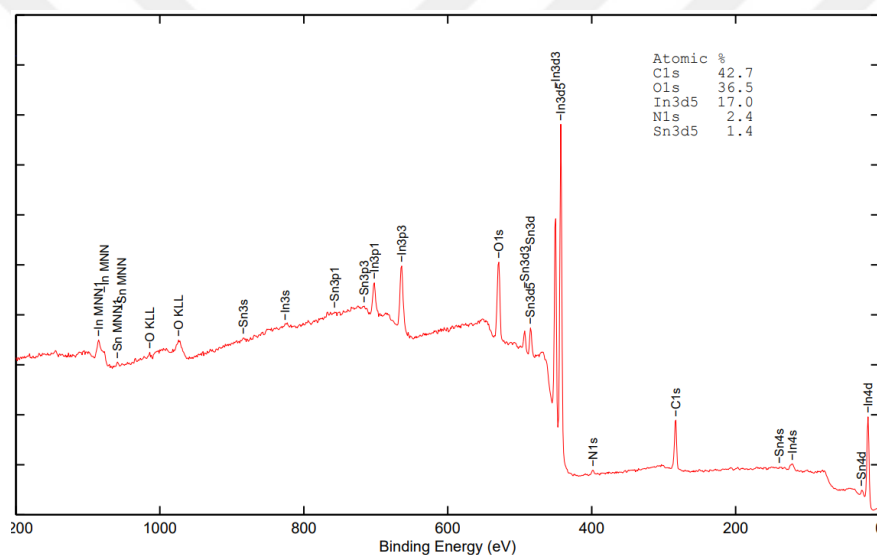
4.4 XPS Spectral Analysis

The surface composition of working electrodes that are electrochemically treated in reline and aqueous reline solutions was investigated by X-ray photoelectron spectroscopy (XPS), and the results were compared with the original ITO sample. In this part of the study, ITO samples were electrochemically processed at -1.6 V at 80 °C for 30 minutes in electrolytes having different water:reline molar ratios and containing 0.1 M ZnCl_2 . After the electrochemical treatment, the samples were rinsed with distilled water and dried.

A broad XPS survey spectrum of samples of original ITO and working electrode samples treated in pure reline depicted in Figure 4.29. In addition, XPS spectra for aqueous reline solutions containing 1 MR, 3 MR, and 9 MR of water is presented in Figure 4.30. The XPS spectra indicate the presence of indium, tin, and oxygen in all samples. In addition, Zn was detected only in the 9 MR electrolyte, which is in line with the XRD results (Figure 4.30 c). At higher water content, besides indium reduction reactions on the surface due to the H-bonding effect, zinc is also deposited onto the substrate. These initial broad spectrum findings provide valuable insights into the complex chemistry involved in electrochemical processes and highlight the importance of the selection and monitoring of electrolytes in metal recovery applications. Detailed research for all elements is needed to fully understand the relationship between electrolyte composition and element detection on the working electrode surface.

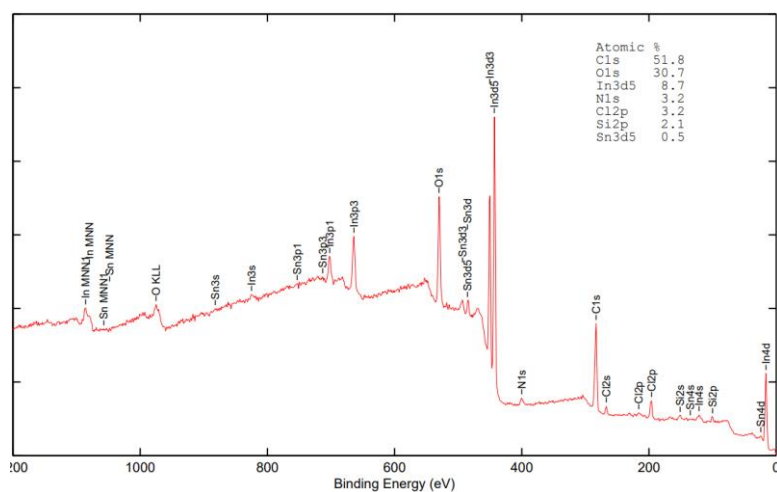


(a)
untreated
ITO (WE)

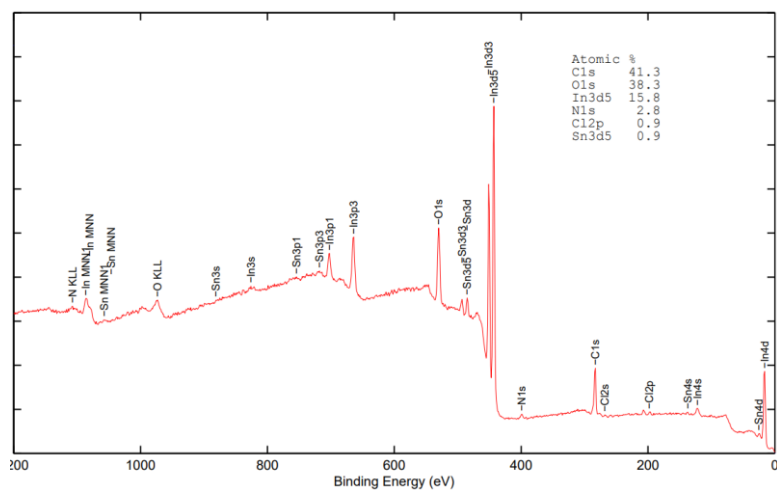


(b) WE
treated in
pure reline

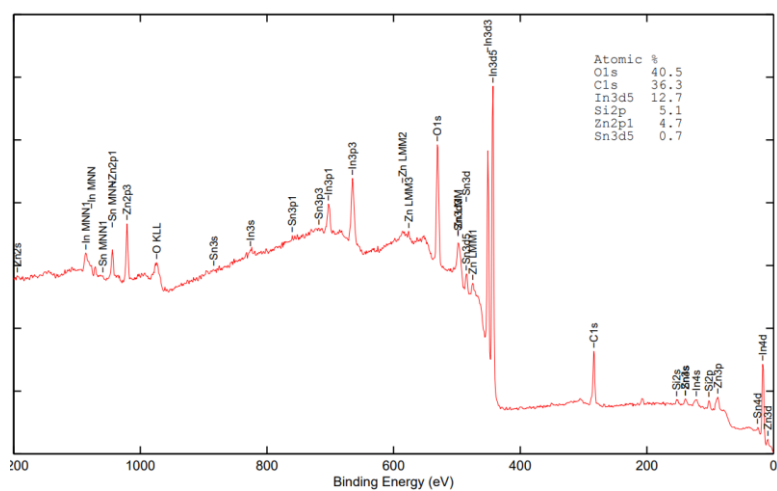
Figure 4.29. Broad XPS spectra of untreated working electrode (ITO) and electroreduced working electrode in pure reline



(a)
WE treated
in 1 MR
reline



(b)
WE treated
in 3 MR
reline



(c)
WE treated
in 9 MR
reline

Figure 4.30. Broad XPS spectra of electrochemically treated samples in aqueous reline including water at different molar ratio (a) 1 MR, (b) 3 MR and (c) 9 MR

A detailed XPS analysis was conducted for the O 1s, In 3d, and Sn 3d regions to investigate the effect of water concentration on the surface composition of working electrodes. XPSPEAK software v.4.1 was used to de-convolute the O 1s, In 3d, and Sn 3d XPS spectra. The reduction extent of indium and tin was evaluated based on spectra by calculating the contents of the compounds for samples treated in different electrolyte solutions. The relative intensity of the compounds was investigated by comparing the integrated area under the background curves of de-convoluted peaks. The results showed that the reduction extent of indium and tin varied depending on the electrolyte solution used, as discussed in different analytical observation parts of this section.

The XPS spectra were analyzed using a peak deconvolution algorithm to determine the relative amounts of each component in the sample. All peaks were fitted with a Gaussian-Lorentzian function and the Gaussian-Lorentzian ratio was optimized to achieve the experimental data are in good agreement with each other and theoretical binding energy (BE) values. The components used for fitting were assigned based on chemical reasoning. Once the initial parameters for fitting each peak were developed, these parameters were employed for subsequent peaks, with only the height of the individual components varying.

This method ensured that the binding energy difference among the components was constant and that each component's full width at half maximum (FWHM) was constant. By using a constant FWHM and binding energy separation, this technique minimized potential errors or variability that could arise from instrument calibration or other factors. This approach facilitated accurate quantification of the chemical species present in the sample, which is crucial for comprehending its properties and behavior.

Table 4.2 summarizes the high resolution of the indium, tin, and oxygen species photoemission spectra. Due to the fact that these standards may contain some other contamination by other oxide and hydroxide species, binding energy values were exhibited in two different references (Wagner et al., 2003; Donley et al., 2002).

Indium and tin 3d_{5/2} binding energy values from standards were presented in the table. During detailed XPS analysis, the In 3d_{5/2}–3d_{3/2} and Sn 3d_{5/2}–3d_{3/2} splitting values of 7.54 eV and 8.41 eV were considered (Wagner et al., 2003; Moulder et al., 1992). Moreover, as can be seen from Table 4.2, chemical state assignment for tin is difficult due to overlapping Sn 3d_{5/2} values for SnO and SnO₂. These X-ray photoelectron spectroscopy reference values provide a foundation for the accurate interpretation of XPS spectra.

Table 4.2 Standart Binding Energy (BE) values for photoemission peaks from ITO species (a) Wagner et al., 2003 and (b) Donley et al., 2002.

Species		Reference	Reference BE Values (eV)	Standart Deviation (eV)
In3d _{5/2}	In ₂ O ₃	a	444.8	0.6
		b	443.8	
In3d _{5/2}	In	a	443.8	0.3
		b	443.2	
In3d _{5/2}	In(OH) ₃	a	445.1	0.1
		b	444.8	
In3d _{5/2}	InOOH	b	444.3	
Sn3d _{5/2}	Sn	a	485	0.5
Sn3d _{5/2}	SnO	a	486.5	0.6
Sn3d _{5/2}	SnO ₂	a	486.7	0.3
O1s	metalox	b	529.5	
O1s	OH	b	531.3	

As it is presented in Figure 4.31 (a), the O 1s peak area can be successfully deconvoluted into a peak centered at the binding energy of 529.5 eV (purple line), which is assigned to In₂O₃ and SnO₂, and a peak centered at the binding energy of 531 eV (green line), which is ascribed to non-stoichiometric InO_x and SnO_x species having oxygen vacancies (Tohsophon et al., 2015). O 1s XPS spectra of working

electrodes treated in 1MR and 3MR aqueous reline solutions were also successfully deconvoluted into In_2O_3 , SnO_2 , and non-stoichiometric InO_x and SnO_x oxygen vacancies (Figure 4.31 (b) and (c)).

On the other hand, when the O 1s spectrum of the working electrode surface treated in 9MR aqueous reline solution is examined, O 1s signal can be represented by adding a third oxygen component because of the peak widening into a higher binding energy range (Figure 31 (e)). In addition to two peaks attributed to oxygen in In_2O_3 and SnO_2 (529.5 eV) and oxygen deficient non-stoichiometric species (531 eV), another peak centered at 532.5 eV is included in the analysis, which is attributed to oxygen in chemisorbed OH groups over the surface. In general, metal-OH groups are specified as indium oxyhydroxide (InOOH) or hydroxide ($\text{In}(\text{OH})_3$) since tin hydroxide is not observed in XPS tin spectral analysis (Donley et al., 2002). The lack of tin hydroxide might be due to the low tin content of ITO film, which is below the detection level.

As discussed previously, under low concentrations of water, urea-urea and cation-urea interactions get stronger, as in the case of pure reline and 1MR water content in this research. However, if water concentration is increased, reline constituents get individually hydrated and exhibit high diffusivity of water into the working electrode. Therefore, the surface OH species observed in the 9 MR aqueous solution of reline can be explained by the hydrolysis of the surface oxides, which is facilitated by excessive water and weakening hydrogen bonds between reline constituents. The hydroxide and oxy-hydroxide species, having very close standard binding energy positions, arise from the hydroxylation of the disrupted ITO lattice during electrochemical experiments in 9 MR water content reline (Donley et al., 2002):



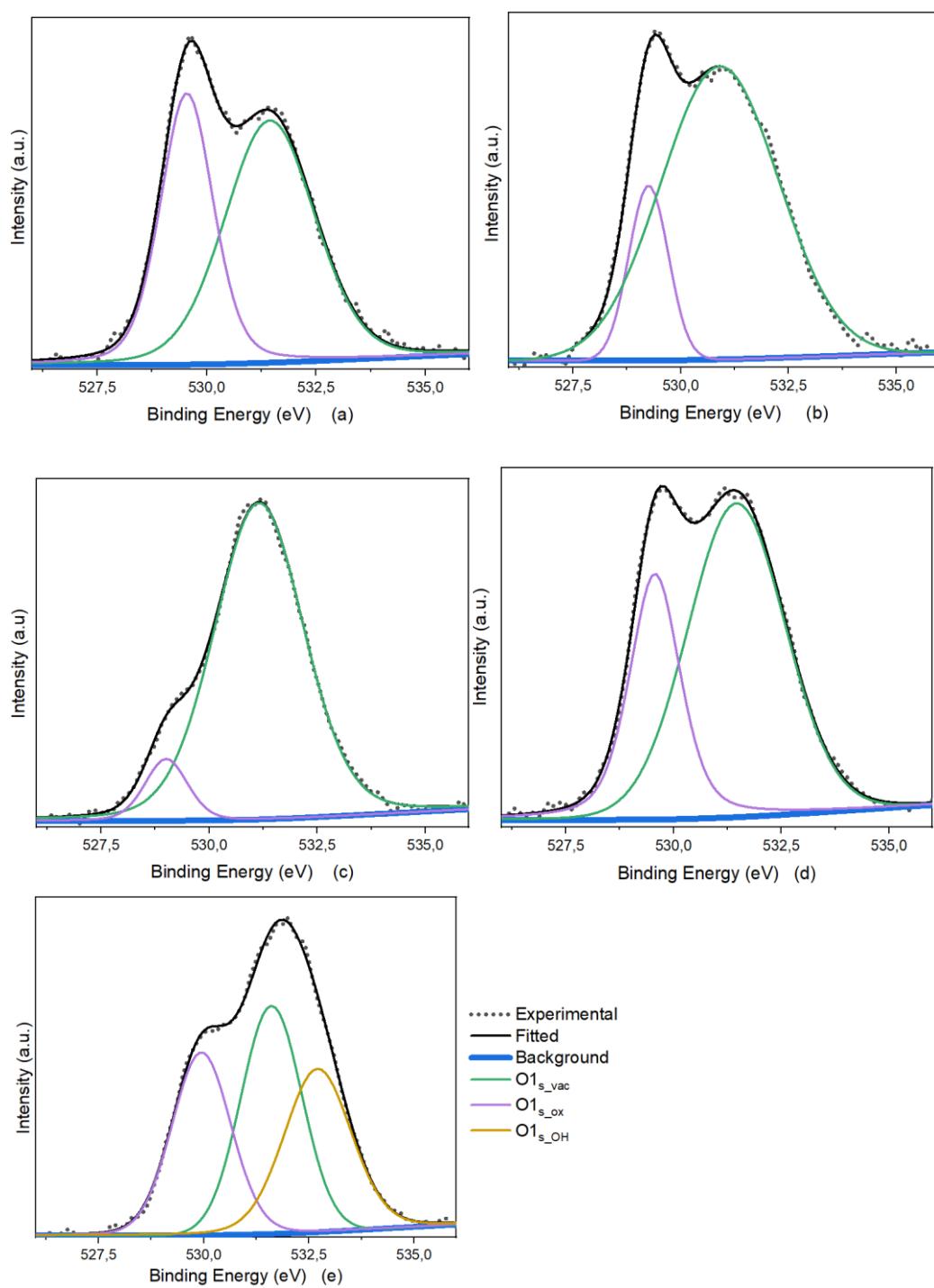


Figure 4.31. Graph fitting of O 1s XPS spectra of (a) ITO coated glass substrate (untreated WE) and electro-reduced ITO (WE) at -1.6 V at 80 °C for 30 minutes in (b) pure reline (c) 1MR hydrated reline (d) 3 MR hydrated reline (e) 9 MR hydrated reline.

Comparing the area under two peaks attributed to oxygen in metal oxides and oxygen deficiency for different samples that were not processed and electro-reduced in reline solution with varying water content, it is observed that the area under the peak relevant to metal oxide decreases in the case of pure and 1MR water content reline. The change in area related to the metal oxide is due to the recovery of indium and tin in these two electrochemically processed samples. On the other hand, an increase in the number of oxygen vacancy sites can be seen as an increase in conductivity for the sample that is electrochemically reduced in 1 MR water content reline among the reline-based electrolytes since oxygen vacancies also work as n-type dopants to enhance conductivity. Further details and numerical analysis can be found in Table 4.2.

Wide scan XPS spectra of In 3d_{5/2} and In 3d_{3/2} were analyzed for working electrode samples and compared with original ITO. Photoelectron lines 3d_{5/2} and 3d_{3/2} are observed in each sample in the binding energy range of 440–447 eV. Both 3d_{5/2} and 3d_{3/2} peaks were deconvoluted to two components as non-stoichiometric indium + indium metal and indium oxide. In 3d_{5/2}, the peak was deconvoluted, with peaks centered at the binding energies of 443.8 eV and 444.8 eV, which are assigned as In⁰+InO_x and In₂O₃, respectively. The literature value of peak splitting between In 3d_{5/2} and In 3d_{3/2} is 7.54 eV, and the same fractional area of In⁰+InO_x and In₂O₃ in both In 3d_{5/2} and In 3d_{3/2} regions is used as a constraint in peak deconvolution (Wagner et al., 2003).

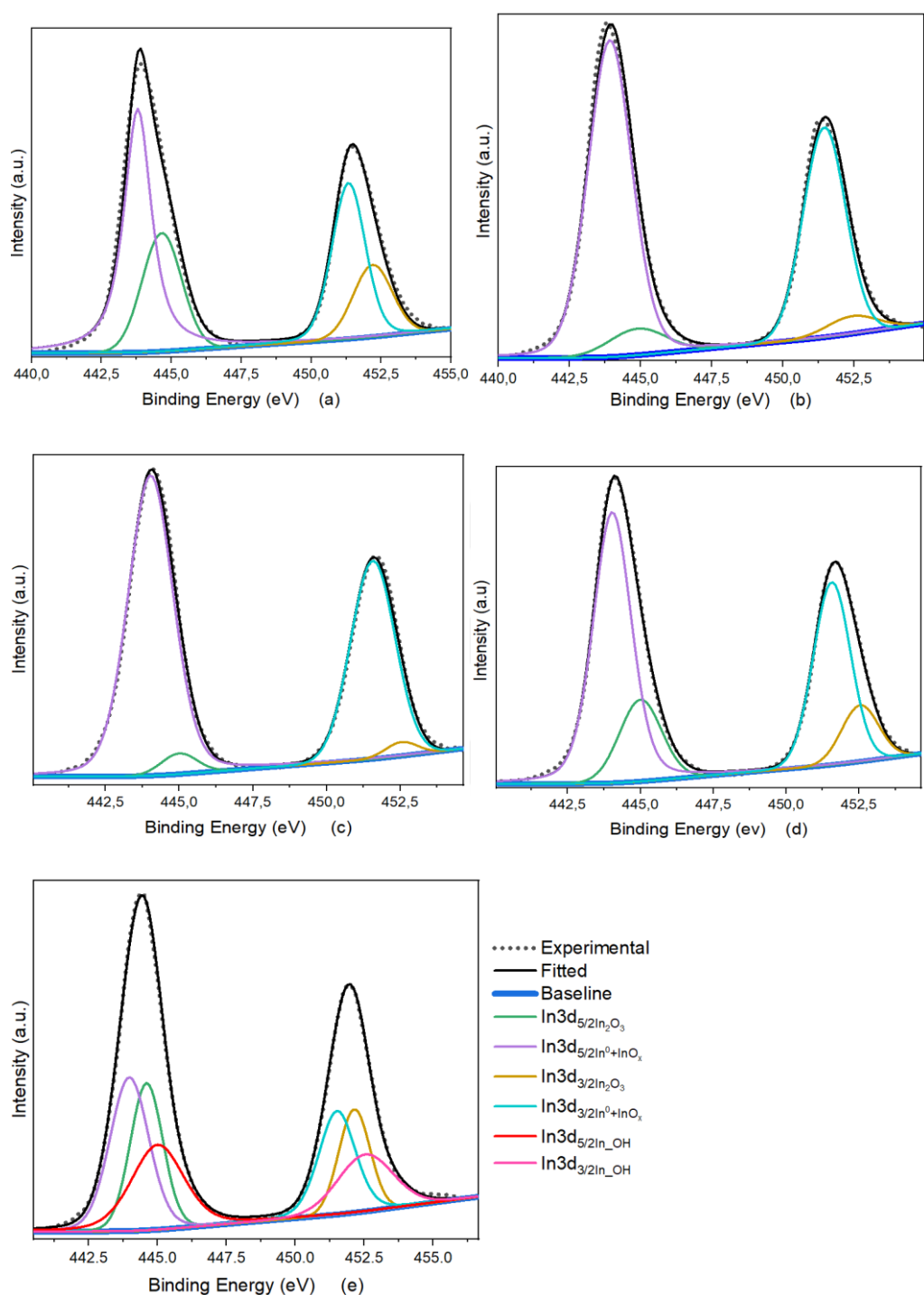


Figure 4.32. Graph fitting of In 3d XPS spectra of (a) ITO coated glass substrate (untreated WE) and electro-reduced ITO (WE) at -1.6 V at 80 °C for 30 minutes in (b) pure relin (c) 1MR hydrated relin (d) 3 MR hydrated relin (e) 9 MR hydrated relin

According to the XPS data of the ITO deposits before and after electrochemical treatment, the thin films were composed of three elements: totally oxidized indium oxide (In_2O_3), incompletely oxidized non-stoichiometric indium oxide (InO_x), and unoxidized indium (In^0) (Plumley et al., 2018). It is common to find non-stoichiometric In_2O_3 on the surface of thin films, leading to the formation of oxygen vacancies and the presence of InO_x -related species ($0 < x < 1.5$). Other studies have also reported a similar phenomenon (Plumley et al., 2018; Lu et al., 2023; Martin et al., 2016).

The lower binding energy peaks were identified as unoxidized and partially oxidized metals, using XPS reference values listed in Table 4.1. A peak at 443.8 eV in binding energy indicated the combined quantity of incompletely oxidized InO_x and In^0 in a deposit. While this peak was assigned to non-stoichiometric indium oxide for the unprocessed ITO working electrode, it was attributed to indium metal for the electrochemically processed ITO working electrode in reline and hydrated reline. Additionally, the peak at 444.8 eV binding energy for all samples indicated the extent to which indium in the thin film was in the +3 fully oxidized In_2O_3 state.

InO_x is formed suggesting that oxygen in the In_2O_3 taken away by the tin dopant or the partial reduction of In_2O_3 , which is specified as a nonstoichiometric defect due to metal deficiency. In comparison to its stoichiometric form, this non-stoichiometric form of InO_x acts as a strongly conducting semiconductor with a large optical band-gap (3.7 eV), offering great transparency in the visible light spectrum and strong reflectivity in the infrared (IR) light range (Kiriakidis et al., 2000). Therefore, this deficiency contributes to the optoelectric properties of ITO.

In order to determine the relative indium metal content of the In $3d_{5/2}$ region, the ratio of the In^0 peak area to the total area of all species under the $3d_{5/2}$ region was calculated. In other words, the extent of reduction can be evaluated by the intensity, area under each curve, and ratio of $\text{In}/(\text{In}_2\text{O}_3+\text{In})$ and $\text{In}_2\text{O}_3/(\text{In}_2\text{O}_3+\text{In})$. The comparable results obtained are summarized in Table 4.3. The higher ratio of $\text{In}/(\text{In}_2\text{O}_3+\text{In})$ and lower ratio of $\text{In}_2\text{O}_3/(\text{In}_2\text{O}_3+\text{In})$ peaks further support the idea that

electrochemical treatment leads to a more complete reduction in the related electrolyte composition.

XPS spectra for In 3d region demonstrated that reduced indium metal on the surface is not oxidized at ambient conditions. It is clearly seen that, when XPS of the In3d region of the original ITO sample is compared with the samples treated in both pure and 1 MR electrolyte solutions, the intensity of the $\text{In}^0 + \text{InO}_x$ peak at 443.8 eV increases while the intensity of the In_2O_3 peak at 444.8 decreases. These results are in good agreement with the cyclic voltametry and XRD results previously presented. When the water content in reline is further increased from 1 MR to 3 MR, the reduction of In_2O_3 is inhibited, and the In_2O_3 peak area increases with increasing concentration in water. Therefore, the maximum In^0 was observed over the electrochemically treated ITO working electrode in the 1MR water containing reline sample.

Table 4.3 XPS spectral characteristics of surface compounds

		ITO		pure reline		1M water/reline		3M water/reline		9M water/reline	
		Area	Ratio	Area	Ratio	Area	Ratio	Area	Ratio	Area	Ratio
In3d_{5/2}	In₂O₃	26658	33.33%	7921	9.09%	2325	4.76%	20339	23.08%	20782	30.19%
In3d_{5/2}	In⁰+InO_x	53317 (InO _x)	66.67% (InO _x)	79212	90.91%	46496	95.24%	67796	76.92%	26776	38.89%
In3d_{5/2}	In(OH)₃									21287	30.92%
In3d_{3/2}	In₂O₃	15530	33.33%	4722	9.09%	1382	4.76%	12155	23.08%	13508	30.19%
In3d_{3/2}	In⁰+InO_x	31059 (InO _x)	66.67% (InO _x)	47221	90.91%	27635	95.24%	40517	76.92%	17404	38.89%
In3d_{3/2}	In(OH)₃									13837	30.92%
Sn3d_{5/2}	Sn⁰+SnO	3277 (SnO _x)	33.33% (SnO _x)	2783	35.48%	1291	41.18%	1340	20.00%	663	16.67%
Sn3d_{5/2}	SnO₂	6553	66.67%	5060	64.52%	1845	58.82%	5360	80.00%	3316	83.33%
O1s	metalox	9922	40.85%	4254	16.67%	1816	8.68%	9048	32.24%	9366	30.53%
O1s	ox vac	14368	59.15%	21268	83.33%	19107	91.32%	19016	67.76%	11556	37.67%
O1s	OH									9753	31.80%

Oxygen-deficient forms of indium oxide (InO_x) can experience high levels of n-type doping as a result of intrinsic defects, specifically oxygen vacancies. From Table 4.3, it can be clearly seen that the maximum amount of reduced indium is observed over the ITO working electrode electrochemically treated in 1 MR water containing reline, while it is higher than in pure reline and other aqueous reline solutions containing more water. The peak area of non stoichiometric InO_x intensity over an untreated ITO surface is calculated to be about 66 % and results show that both InO_x and In₂O₃ are reduced in the presence of pure reline and 1 MR water in reline. This reduction in intensity suggests that the surface of the ITO film is being modified by the reline solution. At this point, the reduction mechanisms of In₂O₃ and InO_x are not clear but are suggested as follows:



In the section on CV experiments, it is noted that the reduction of indium may occur in multiple steps, which is evidenced by the presence of a broad reduction peak in the crystallograms. This suggests that the electrochemical reduction of indium in DES is a complex process that involves various reaction steps and intermediate species.

When an ITO working electrode is electrochemically treated in 9 M water containing reline, water molecules interfere, and both 3d_{5/2} and 3d_{3/2} peaks are widened to a higher binding energy range. Deconvolution constraints can be satisfied by the addition of a new peak (Figure 4.32 (e)), as in the case of O 1s discussed above. The presence of InOH species can be observed through the addition of a new peak in the deconvolution analysis of the 3d_{5/2} and 3d_{3/2} peaks. Additionally, the widening of the peaks to a higher binding energy range suggests the interference of water molecules in the electrochemical treatment process. Alongside the two peaks corresponding to In⁰ and In₂O₃ over the surface, the third peak at a binding energy

of 452.1 eV is included in the analysis and is attributed to surface InOH species, which display the interstitial settlement of water within the H-bonded network of relene components to some extent. This phenomenon suggests that the electrochemical treatment leads to the formation of InOH species on the surface of the electrode due to the interaction of water molecules with the relene component.

The Sn 3d_{5/2} envelope was able to be deconvoluted to two peaks at binding energies of 485.5 eV and 486.6 eV, which are attributed to Sn⁰+SnO and SnO₂, respectively (Figure 4.33). Similar to In 3d_{5/2} XPS spectra discussed above the peak at lower binding energy is a measure of the combined amount of reduced SnO and unoxidized Sn⁰. For the untreated and treated ITO electrodes in relene solutions, this peak at lower binding energy is associated with SnO and Sn⁰, respectively. In addition, the peak at the higher binding energy in the spectra indicated SnO₂ that was tin in the + 4 oxidation state.

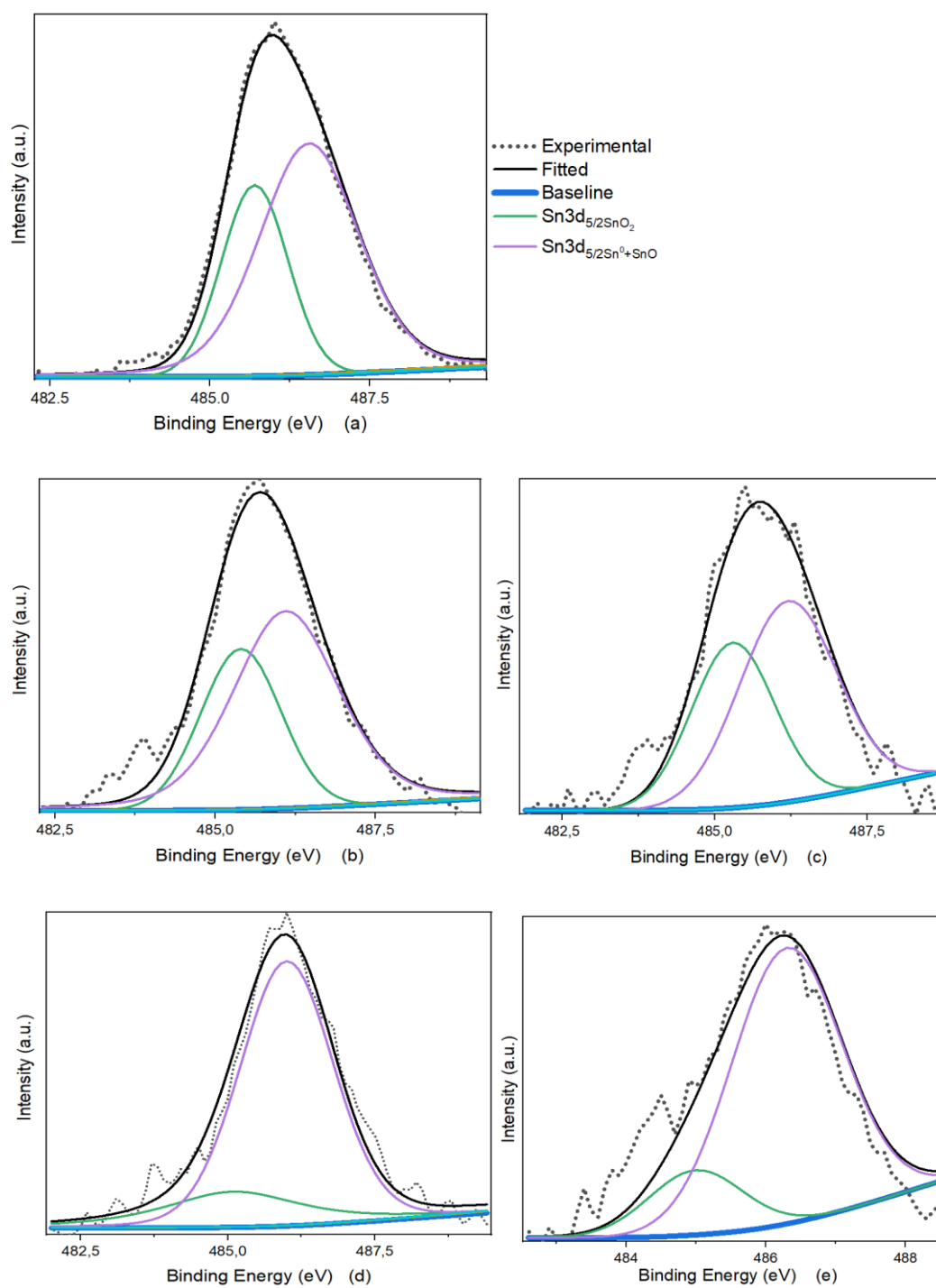


Figure 4.33. Graph fitting of Sn $3d_{5/2}$ XPS spectra of (a) ITO coated glass substrate (untreated WE) and electro-reduced ITO (WE) at -1.6 V at 80 °C for 30 minutes in (b) pure relin (c) 1MR hydrated relin (d) 3 MR hydrated relin (e) 9 MR hydrated relin.

After electrochemical treatment, the XPS survey of ITO working electrodes shows a decrease in the intensity of the SnO_2 peak while an increase in Sn^0 is observed, which is not observed in XRD analyses because the concentration of SnO_x is below the detection limit of XRD. On the other hand, XPS analysis of the sample obtained in 9 MR water content does not exhibit any shift or peak that could be attributed to the presence of tin hydroxide.

As a result, XPS analysis of working electrodes electrochemically processed in 9 MR hydrated reline confirmed the interaction of water with the hydrogen bond network of reline, which affects the electrochemical reduction of In_2O_3 and InO_x species as well as SnO_2 and SnO and the formation of In and $\text{In}(\text{OH})_x$ species over the surface. This study provides valuable insights into the behavior of In_2O_3 , InO_x , SnO_2 , and SnO under electrochemical treatment in reline and hydrated reline solutions. Additionally, these behaviors display the complex interplay between water and hydrogen bonding networks in electrochemical systems, and suggest that a more nuanced understanding of these interactions is necessary for advancing our understanding of electrochemistry.

4.5 Effect of Calcination Temperature

The results showed that the electrochemical treatment of ITO in reline facilitates the reduction of indium and its separation from ITO. This finding has significant implications for the recycling of ITO from electronic waste, as it provides a more efficient and environmentally friendly method for recovering indium. Moreover, the results of the post heat treatment investigation may further contribute to the recovery process of indium from ITO.

The reverse nature of the reduction and separation was investigated by the calcination of ITO samples obtained by electrochemical treatment in ethaline, pure reline, and aqueous reline solutions. The phase change over the sample surfaces was determined by X-ray diffraction (XRD), and the effect of calcination temperature

was studied at a 150–400 °C temperature interval under an air flow rate of 40 ml/min for 15 minutes. In addition, the textural changes that occur during calcination were analyzed by SEM imaging.

As compared with the samples calcinated at 150 oC and without calcination from Figure 4.34, there was no significant difference between the patterns except peak intensities. All peaks can be well indexed to the lattice of ITO (JCPDS No. 06-0416) and indium metal (JCPDS No. 05-0642). No significant impurities or a second phase were observed, similar to other crystallinity studies depicted above, which indicated high-purity indium output. On the other hand, the peaks became more defined and shaper for the as-reduced surfaces compared to the heat treated ones, even when calcinated at 300 oC for as little as 15 minutes.

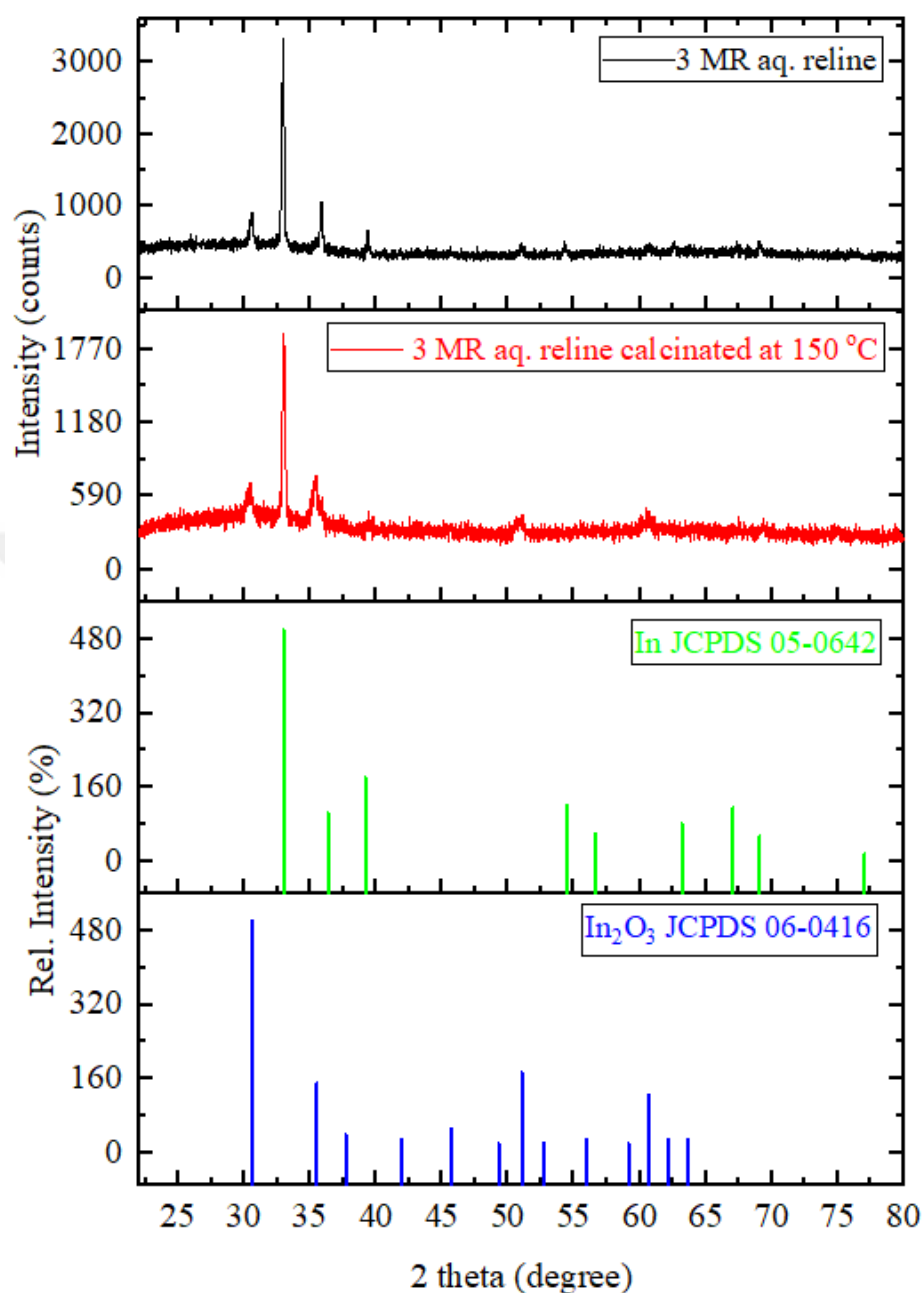


Figure 4.34. XRD patterns of the sample prepared in 3 MR water:reline solution as deposited and calcinated at 150°C .

SEM analysis revealed changes in the recovered metal structure with calcination. The morphology of the electrochemically treated samples in 3 MR aqueous reline before and after calcination was examined by scanning electron microscopy, as

shown in Figure 4.35. SEM images of electrochemically treated surfaces depict approximately spherical indium nanoparticles. The surface is covered with grains of uniform size. In addition, morphological changes can be observed for the as-treated and calcinated samples, which can be attributed to the change in relative intensities of the XRD peaks as discussed (Figure 4.34). Although the structures were still uniform after calcination, the grain size became smaller, and diagonal structures became apparent rather than spherical. These changes in morphology and crystal structure may be due to the oxidation of indium particles that were reduced during electrochemical treatment.

This suggests that annealing may have a negative effect on the electrochemical properties of the indium surface and that further investigation is needed to fully understand the implications of this finding. Therefore, various calcination temperatures were investigated to fully understand this reverse reaction in the reduction of indium.

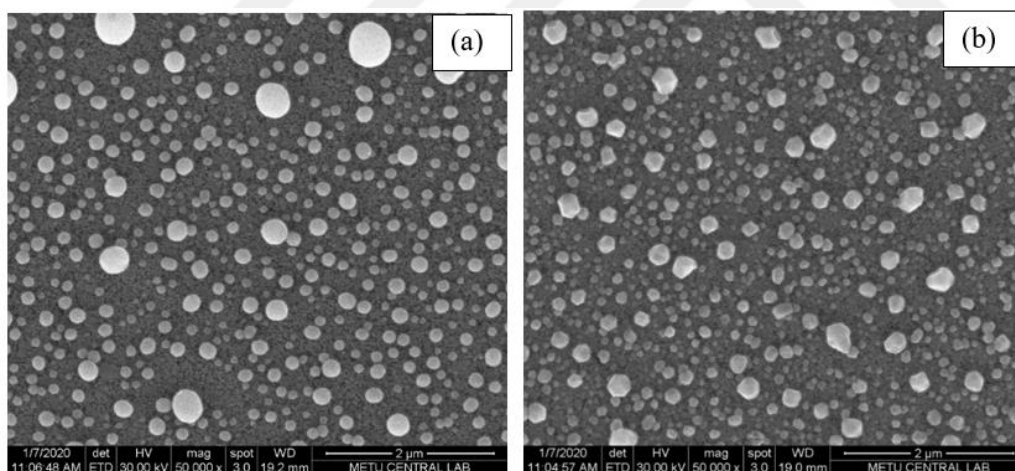


Figure 4.35. SEM image for the (a) film as-treated in 3 MR water containing reline solution (b) and after calcination at 150 °C for 15 minutes

The effect of calcination temperature and water content of the electrolyte solution on electrodeposited films is shown in Figure 4.36. ITO working electrode samples electrochemically treated in 3MR water containing reline were calcined at 150°C, 200°C, 300°C, and 400°C under 40 ml/min air flow, and X-ray

diffractograms of the samples are shown in Figure 4.36. As can be seen from the figure, the reduced indium is oxidized, and the original ITO peaks are replenished. The calcination rate increases with calcination temperature as expected, and the peaks of In_2O_3 (222) and (400) become more apparent above 300 °C.

This observation suggests that the reduction of indium is a reversible process that can be restored by oxidation with post heat treatment under air flow. The increased calcination rate with temperature indicates that higher temperatures promote the formation of In_2O_3 peaks. However, the calcination is not complete at the end of 15 minutes at 400 °C.



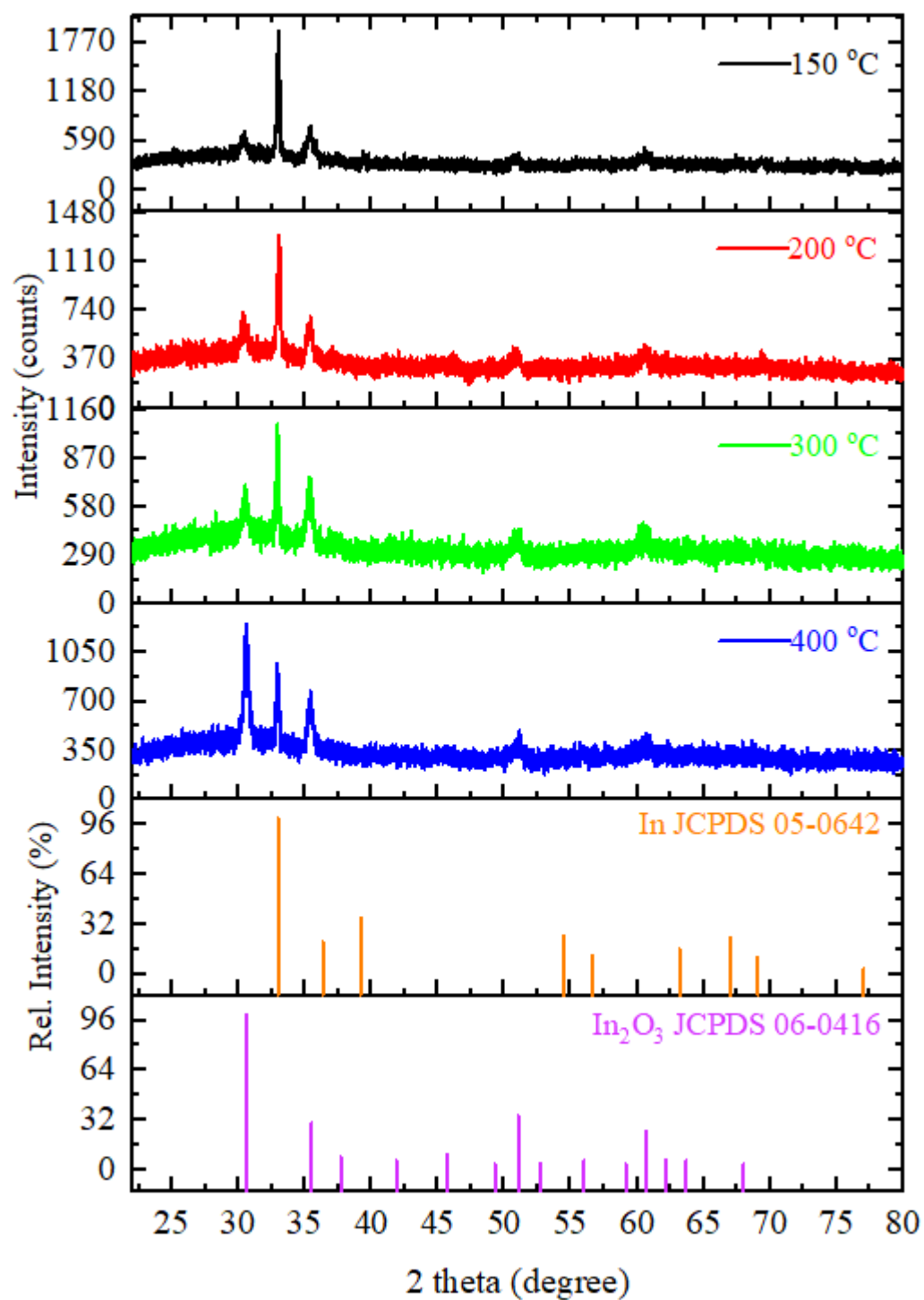


Figure 4.36. XRD patterns of the sample prepared in 3 M ratio of water/ relene solution calcinated at different temperatures (100 °C, 200 °C, 300 °C & 400 °C) for 15 minutes

For the electrochemically reduced samples in reline solution, there was a very intense and narrow peak positioned at 32.96° , which is assigned to scattering from the (101) crystal plane of indium, which decreases with increasing calcination temperature and finally disappears at 500°C (Figure 4.37). This indicates that the oxidation of the indium particles is enhanced with increasing calcination temperatures. The disappearance of the peak at 500°C suggests that the calcination is completed at this temperature in 30 minutes.

With increasing the calcination temperature, the presence of two main peaks was noticed that are expected at 2θ values of 30.58° and 35.64° degrees according to the standard JCPDS 06-0416 data. These peaks represent, respectively, the (222) and (400) planes of In_2O_3 diffraction. The effect of the calcination temperature on the film texture is assessed using the intensity difference of the (222 to 400) reflection, as indicated in Table 4.4.

Table 4.4. Calcination temperature effect on the film texture

Dataset Identifier	Peak Plane	Peak Position	Peak Height	Peak Height from Baseline	(222)/(400)
150°C	In_2O_3 (222)	30.61	696.67	310.73	0.80
150°C	In_2O_3 (400)	35.59	763.33	386.19	
200°C	In_2O_3 (222)	30.53	700.00	223.42	0.97
200°C	In_2O_3 (400)	35.57	586.67	231.01	
300°C	In_2O_3 (222)	30.56	710.00	285.32	1.47
300°C	In_2O_3 (400)	35.61	680.00	193.62	
400°C	In_2O_3 (222)	30.58	1253.33	849.83	2.60
400°C	In_2O_3 (400)	35.59	700.00	327.44	

Based on the findings of the current investigation, it was discovered that when the calcination temperature rises from 150 to 400°C , the ratio of In_2O_3 (222)/ In_2O_3 (400) increases. According to various studies, crystal formation preferentially occurs with grains that are orientated (222) when the film has enough oxygen; otherwise, crystal growth happens significantly more quickly with grains that are oriented (400).

(Bouhdjer et al., 2015). Similarly, in the relevant literature, the impact of oxygen partial pressure on altering preference orientation is discussed (Pham et al., 2014). The (222) nucleation is more advantageous when the oxygen partial pressure is high and the substrate temperature is constant.

Therefore, the findings of this texture analysis suggest that since the indium metal oxidized by calcination at higher temperatures under air flow, the resulting film contained sufficient oxygen, leading to preferential crystal growth with (222)-oriented grains. This indicates that the calcination process has a significant impact on the crystal orientation of the In_2O_3 film.



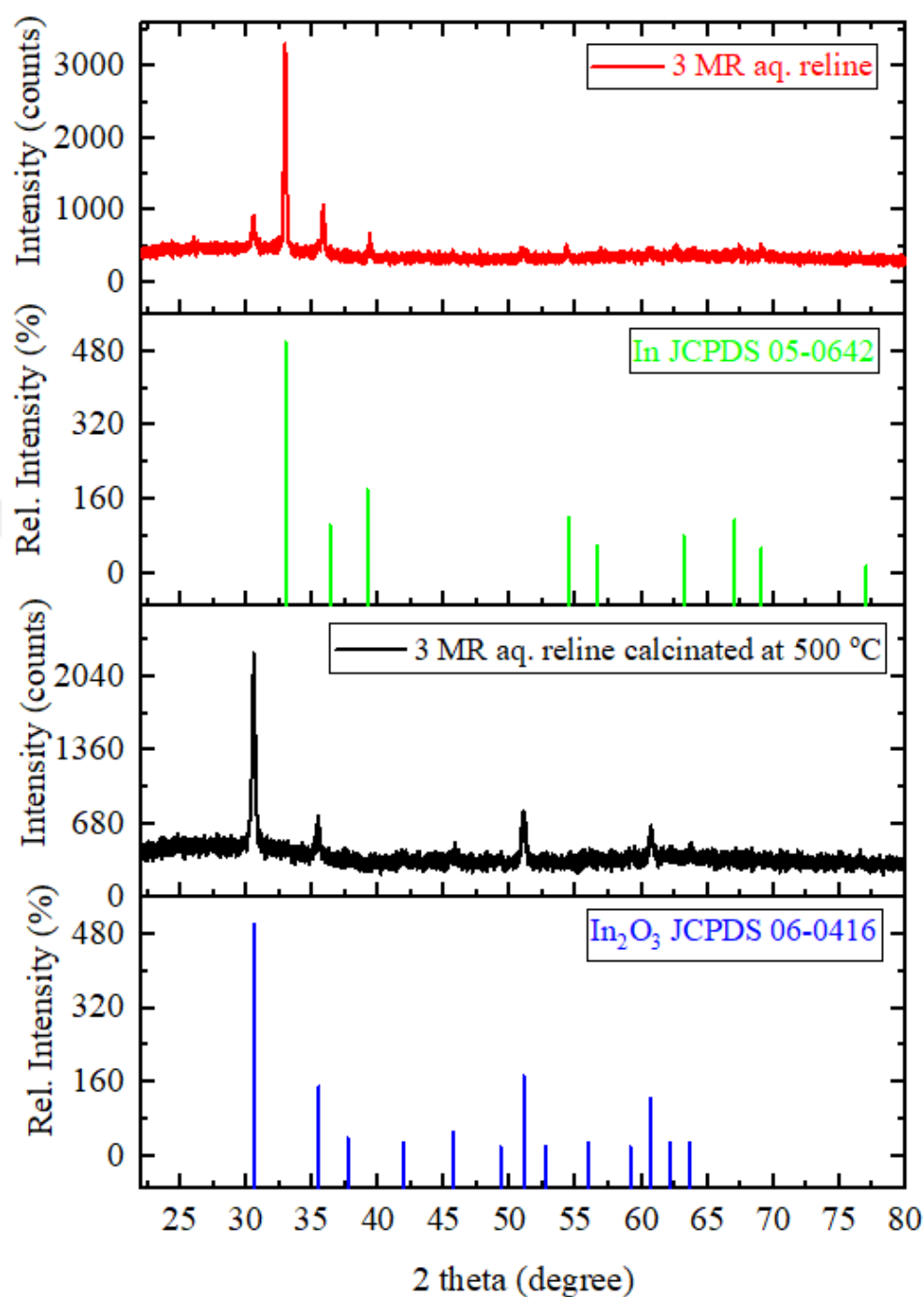


Figure 4.37. XRD patterns of the sample prepared in 3 M ratio of water/ reline solution as deposited and calcinated at 500 °C for 30 minutes.

Both electrochemically treated and unterated substrates in 3 MR hydrated reline solution and calcinated at 500 °C for 30 minutes. X-ray analysis is performed for

both. Another important detection regarding this parameter is that all peaks shift to higher 2θ positions at a calcination temperature of 500 °C as can be detected from Figure 4.38. This shift could indicate the change in the cell volume either due to the contraction in the unit cell size caused by the smaller radii of Zn^{2+} (0.74 Å) compared to In^{3+} (0.79 Å) or due to the residual compression stresses in the film. Furthermore, this shift in peak positions can also be attributed to the rearrangement of the atoms in the crystal lattice.

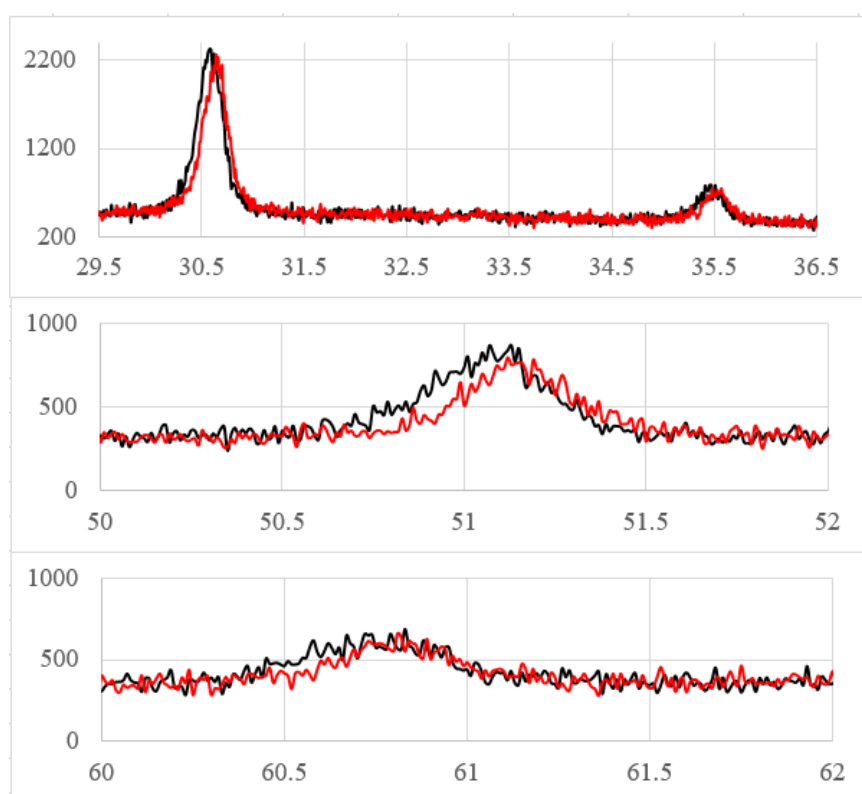


Figure 4.38. XRD pattern shift for ITO peaks between the sample prepared in 3 MR water:reline solution calcinated at 500°C for 30 minutes (red) and non-treated ITO coated glass (black).

Although it is not possible to reach a clear judgment with this study, since the change in cell volume and atomic arrangement can have significant effects on the physical and chemical properties of the material, this finding should be further investigated, as mentioned in the future work section.

XRD results for ITO working electrode samples prepared in pure and 3 MR aqueous reline solutions calcined at 300 °C for 10 and 30 minutes are shown in Figure 4.39. These patterns indicate the oxidation and conversion of indium metal to In_2O_3 over the surface. When calcination time was extended to 30 minutes, a decrease in indium peak intensities and an increase in ITO peaks were observed in both working electrodes treated in reline and 3MR aqueous reline solutions. This suggests that the longer calcination time led to a more complete conversion of indium metal to In_2O_3 and a higher formation of ITO, which could potentially indicate the reverse process on the working electrodes.

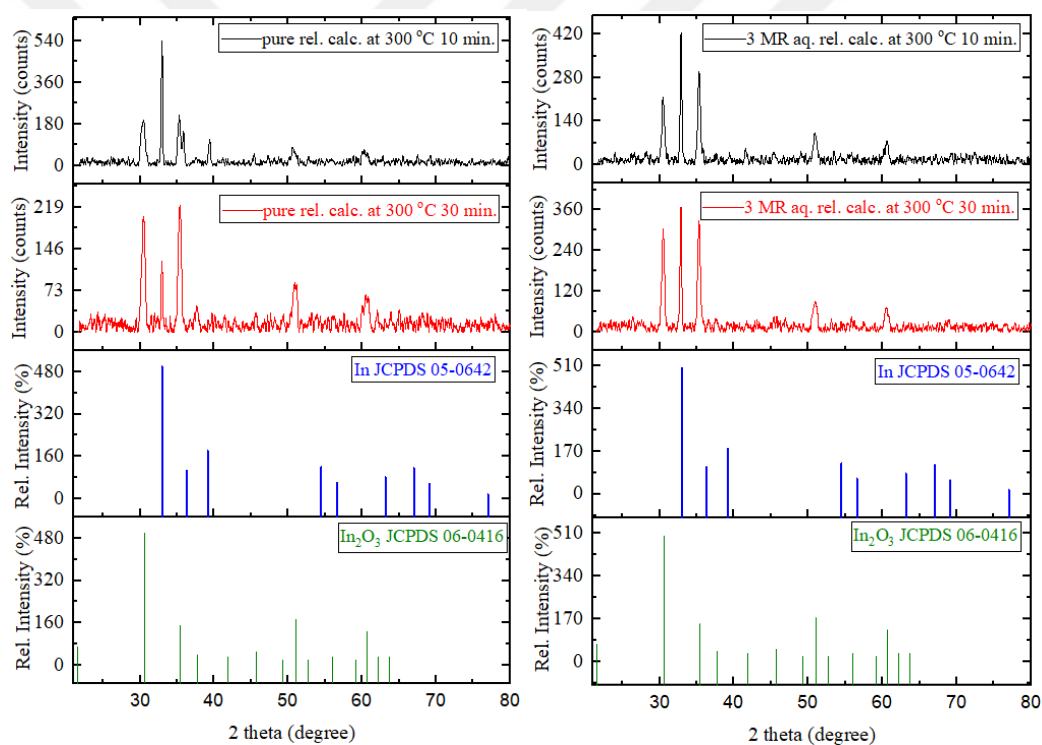


Figure 4.39. X-ray diffraction patterns for the samples prepared in reline based electrolytes calcined at different periods.

These results showed that indium oxidation takes place and more In_2O_3 forms over the surface by increasing calcination time for both pure reline and hydrated reline. The calcination effect on samples electrochemically processed in either pure or

hydrated reline was investigated to see how the oxidation of indium particles was affected by the water content. Another important finding of the Figure 4.39 is preferential growing competition between (222) and (400) planes as explained above at the calcination temperature discussion. The intensity ratio of (222)/(400) is 0.83 for the calcinated sample treated in pure reline and 0.93 for the calcinated sample treated in 3 MR reline, which is higher for the sample treated in 3 MR hydrated reline after 30 minutes of calcination at 300 °C. The findings suggest that the presence of water in hydrated reline accelerates the oxidation process of indium particles during calcination since, as explained above, adequate oxygen leads to (222)-oriented crystal growth while oxygen deficiency leads to (400) oriented film growth with very well crystallised structure.

This difference was not very strong but can be explained by the reduced particle size of indium metals on the surface as air flow rate was same, 40 ml/min, for both that was used as oxygen source during calcination. As discussed in the surface morphology of electrochemically processed ITO films in pure and aqueous reline electrolytes, reduced indium particles were smaller when treated in 3 MR aqueous reline than when treated in pure reline. This can be explained as particles with a higher diameter and denser prevent the incorporation of oxygen in the structure, leading to the preferred growth through the (400) crystal plane comparatively, as in the case of pure reline. On the other hand, the smaller size of reduced indium particles in 3 MR hydrated reline can sufficiently oxidized leading higher (222)/(400) ratio.

In addition, the (222)/(400) ratio is an important factor in determining the properties of the material, as it affects its mechanical and electrical properties. The greater values of the (222)/(400) ratio are always linked to the larger band gap values. Poor Sn^{4+} doping, decreased transmittance, and decreased carrier mobility are constant effects of (400)-oriented films. On the other hand, high Sn^{4+} doping efficiency, high transmittance, a large energy gap, and high carrier mobility are associated with (222)-oriented films (Terzini et al., 2000). The findings of this study could have implications for the development of new materials with specific properties for various applications.

4.6 Effect of the Duration of the Electrochemical Treatment

In addition to the DES type and concentration of water in the electrolyte solution, the effect of electrochemical treatment duration was also studied. In this part of the investigation, the reduction of the ITO working electrode from electrolytic solutions containing 0.1 M ZnCl_2 hydrated reline (3 MR) under electrochemical processing at different treatment durations was studied. The applied potential was -1.6 V at a bath temperature of 80 °C during different process times of 2 minutes, 30 minutes, 2 hours, and 4 hours .

XRD patterns were used to examine the ITO film's crystal structures after it had undergone various electrochemical treatments and analyses, as shown in Figure 4.40. The X-ray diffraction analysis for various treatment times of the working electrode surface reveals that the indium is undergoing a reduction reaction and forming indium metal crystal structures, which is evident from the presence of the peaks in line with the standard JCPDS 05-0642. The reduction of the working electrode is clearly seen even after the first 2 minutes over the working electrode surface as indium 101, 002, 110, and 202 crystal planes at scattering angles (2θ) of 32.96, 36.15, 39.38, and 69.31, respectively. All of these peaks can be related to the indium's body-centered tetragonal phase, indicating that the crystal structure formed on the electrode surface is consistent with the expected phase of indium under these conditions. The formation of this crystal structure occurs even in a relatively short time frame of just 2 minutes, suggesting that the reduction reaction is rapid and efficient.

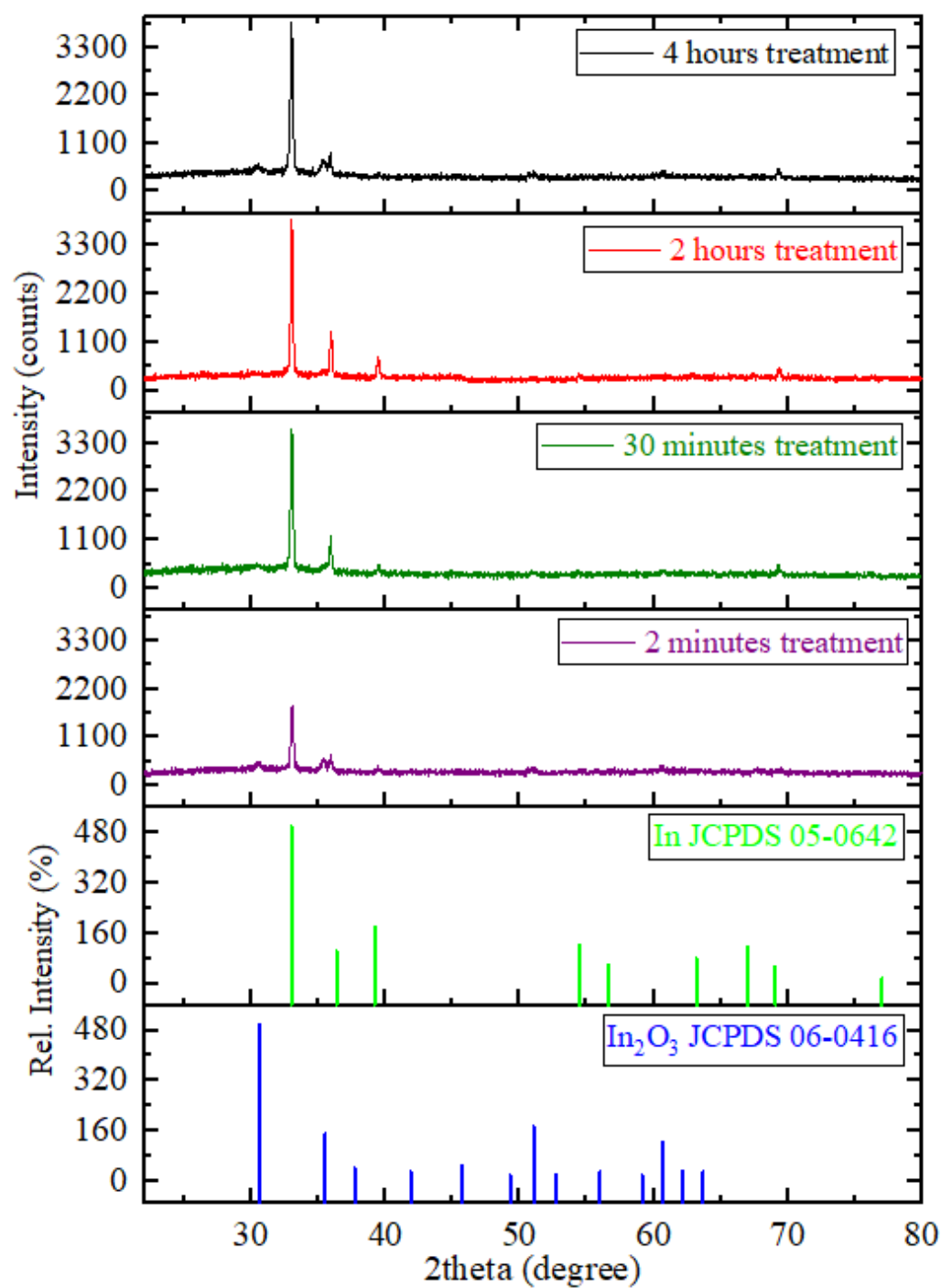


Figure 4.40. XRD patterns of ITO coated glass WE electrochemically treated at different time

The observation of these crystal planes can provide insight into the mechanism of the reduction process. The electrochemical treatment of indium has been shown to have a significant effect on the crystal planes observed at certain scattering angles. The intensity of this peak increases in the first 30 minutes, and then the peak growth slows down, which indicates the complete reduction of ITO over the working electrode surface. When the electrochemical treatment is extended to 4 hours, indium 002, 110, and 112 crystal planes observed at scattering angles (2θ) of 36.05, 39.36, and 54.51 intensity slightly decrease, which could be attributed to the disintegration of indium metal particles from the surface to the electrolyte (Figure 4.40). Overall, these findings suggest that careful consideration should be given to the duration and conditions of electrochemical treatments when working with ITO electrodes.

4.7 Effect of Zinc Chloride Concentration in the Electrolyte

Electrochemical processes are an important aspect of many industrial applications, and the concentration of electrolyte is a crucial operating parameter that affects the mass-charge transport rate in the electrolyte solution. Therefore, the effect of the concentration of ZnCl_2 in reline was also studied. The concentration of ZnCl_2 in reline is a critical factor that impacts the mass-charge transport rate in the electrolyte solution. Abbot's group extensively studied the behavior of zinc chloride in reline at different concentrations in 2011, and their published data offers useful insights into this study.

Overall, understanding how zinc chloride concentration affects electrochemical treatment of ITO is essential for developing an efficient and effective process since controlling the concentration of ZnCl_2 may have a significant impact on other electrochemical parameters. For example, the viscosity, conductivity, and pH of the electrolyte can affect the rate of electrodeposition and the quality of the resulting coatings. Increasing the concentration can result in higher current densities and faster deposition rates, but it is important to avoid going beyond the optimal range as this can lead to unwanted side reactions and reduced film quality. On the other

hand, decreasing the concentration can result in lower current densities and slower deposition rates, which can also negatively impact film quality. Therefore, finding the right balance is key to achieving optimal electrochemical performance.

Zinc chloride concentration varied from 0.1 to 0.4 M in the 1:2:3 molar ratio of choline chloride:urea:water solution. Electrolytes containing different amounts of ZnCl_2 were prepared similarly by adding powdered ZnCl_2 to the hydrated reline solution initially. ITO working electrode samples were treated in the prepared electrolyte solutions at -1.6 V for 30 minutes at 80 °C. The XRD spectrum of working electrodes treated in 3MR reline solution containing 0.1, 0.2, and 0.4 M zinc chloride is shown in Figure 4.41. As shown in the figure, very similar XRD patterns were obtained for both 0.1 and 0.2 M ZnCl_2 solutions, which indicates the reduction of ITO into indium without forming any zinc species over the surface.

When ZnCl_2 concentration is increased from 0.1M to 0.2 M, a slight increase in the peak intensity of In is observed, which indicates ITO reduction is favored by the presence of higher concentrations of Zn^{+2} and Cl^- ions in the electrolyte. Therefore, at low concentrations, ZnCl_2 , Zn^{+2} , and Cl^- ions do not interfere with the reduction of ITO and act as supporting electrolytes. However, when ZnCl_2 concentration increases to 0.4 M, Zn^{+2} ions are also reduced and deposited over the working electrode surface. This suggests that there is a threshold concentration of zinc chloride at which point zinc species begin to form on the surface during reduction.

This result can be attributed to either the increase in the monomeric ZnCl_4^{2-} ions that would be the main Zn species and increase in the conductivity of bath solution. These two cases are connected as assuming reline to behave like a true molten salt, during electrodeposition zinc chloride would be achieved with the complete formation of ZnCl_4^{2-} through the reaction:



which also trigger to increase in conductivity as at the beginning of the experiment for 0.1-0.2 M ZnCl_2 the current was measured around 20 mA and when the amount increased up to 0.4 M current raised to 40 mA (Abbott et al., 2011).

The formation of ZnCl_4^{2-} ions during electrodeposition is an important process that is closely linked to the increase in conductivity of the bath solution. Moreover, these ions are the main species of zinc that are present during electrodeposition in reline including zinc chloride. The effect of the presence of ZnCl_2 on ChCl/urea has been investigated by Abbott et al. (2011), who reported the apparent change in DES's properties such as viscosity, conductivity, and density by the addition of solute. The decrease in viscosity and hence increase in conductivity observed in the experiment were attributed to the higher concentration of ZnCl_2 . According to Abbott's findings, as the concentration increased from 0.1–0.2 M to 0.4 M, the current also increased from 20 mA to 40 mA. This can be explained by the fact that higher concentrations of ions in a solution lead to a greater number of charge carriers, resulting in higher conductivity. The phenomenon is also known as an increase in electrolyte strength, which is a measure of the ability of an electrolyte to conduct electricity and hence transfer ions between electrodes.

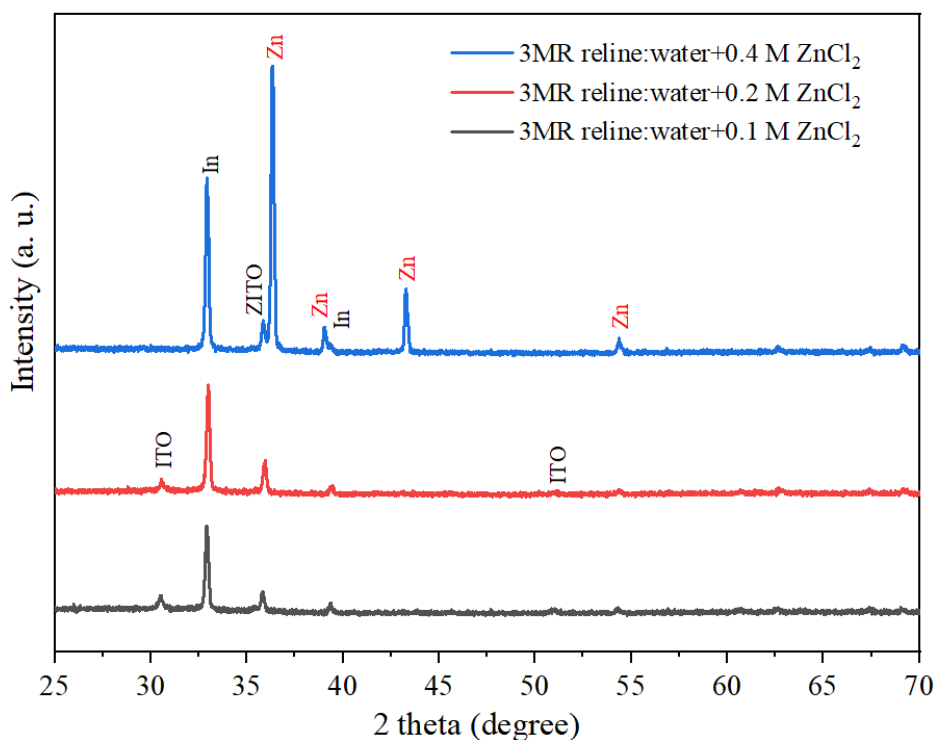


Figure 4.41. XRD patterns of the working electrode electrochemically treated in 3 MR water:reline solution at different ZnCl_2 precursor amount.

The effect of solute (zinc chloride) concentration on viscosity and conductivity is crucial when studying mass transport in electrolytes. XRD results, as shown in Figure 4.41, indicate that an increase in ZnCl_2 concentration in the electrolyte can lead to changes in reduction and deposition processes. These changes may be attributed to differences in mass transport, speciation, and layering mechanisms during electrochemical treatment. Addition of the physical properties of reline significantly change by the increase rate of ZnCl_2 associated with the addition of water, which similarly may cause the weakening of the hydrogen bonding network in reline. This disruption of the bonding structure increases the average void magnitude between the reline components and hence promotes the mass transport of zinc ions. Therefore, at higher concentrations of zinc chloride, such as 0.4 M, it is possible to deposit zinc onto surfaces through indium reduction, which is similar to that observed in 9 MR hydrated reline.

4.8 Transmission Electron Microscopy Analysis

The solid particles formed on the working electrode surface are also analyzed by transmission electrode microscopy (TEM), and high-resolution transmission electrode microscopy (HRTEM) and selected area electron diffraction (SAED) analysis. In this part of the study, the solid particles are sampled from the surface of the working electrode prepared in a 3 MR water:reline solution containing 0.1 M ZnCl_2 at -1.6 V and 80 °C by scraping the surface slightly with a razor blade into ethanol.

As shown in the Figure 4.42, when the ITO-coated glass surface was electrochemically processed in reline at a potential of -1.6 V and a temperature of 80 °C, indium particles formed as a white layer on the transparent surface after 30 minutes. In addition, indicated in the figure, these particles can be collected using a slightly sharp tool without applying significant mechanical force.

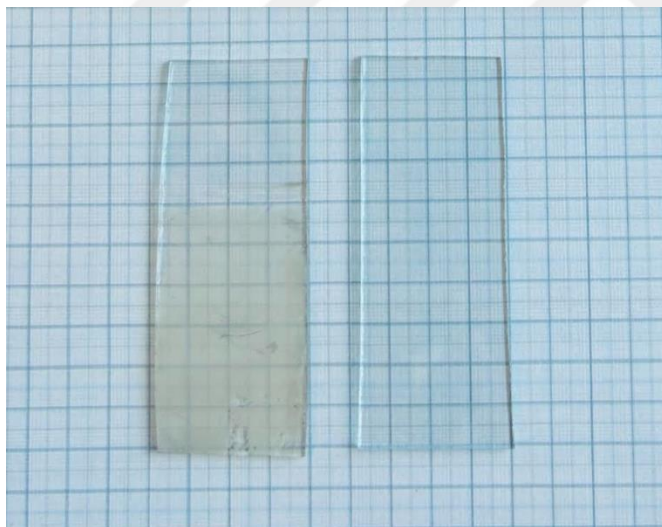


Figure 4.42 The surface of ITO WE before (right) and after (left) electrochemically treated in reline a potential of -1.6 V and a temperature of 80 °C for 30 minutes time

These processes include the measurement of particle size and shape, surface area, and pore size distribution. Additionally, the chemical composition and crystal structure of the particles are analyzed, with a focus on identifying any impurities or

defects that may be present. Through these comprehensive analyses, a more thorough understanding of the physical and chemical properties of the reduced indium can be achieved.

TEM samples are prepared by transferring one drop of solid particles suspended in ethanol into a copper grid. The TEM image of particles (Figure 4.43 (a)) shows that the synthesized nanoparticles are mostly spherical. The particle size distribution is between 50 and 300 nm, and the average particle size was determined to be 140nm (Figure 4.43 (b)) that was measured by the help of Image J software. The TEM image of the particles revealed their spherical shape, confirming the success of the synthesis process. These results suggest that the synthesis process was successful and yielded indium nanoparticles.

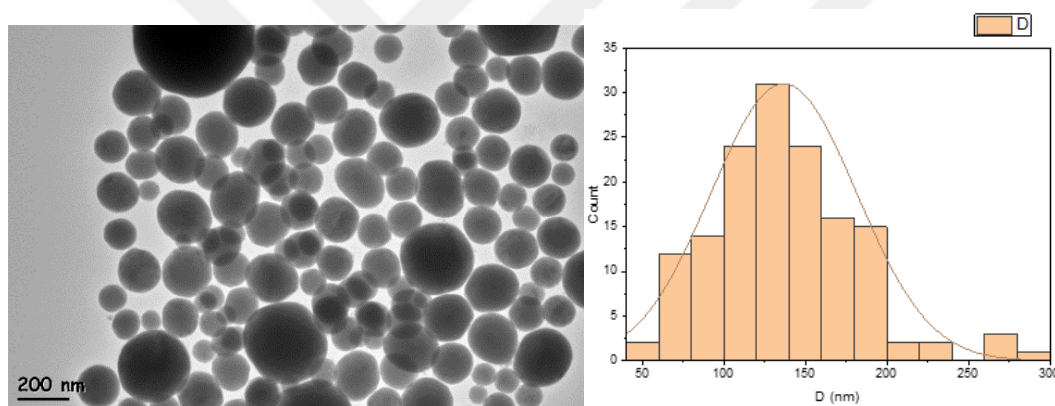


Figure 4.43. TEM images and histograms of particle size distribution for indium particles obtained in 3 MR hydrated reline electrolyte

The values obtained from XRD data with a TEM SAED pattern can provide valuable insights into the crystal structure and properties of materials. The advantage of TEM SAED is the smaller spot size of the analysis. Therefore, the background signal in the XRD spectrum obtained by powder diffraction can be eliminated, and impurities in the crystal structure can be identified with SAED.

The d-spacing calculation obtained from an X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda=1.54051 \text{ \AA}$) is compared with the d-spacing calculations for the TEM SAED pattern (Figure 4.44). This value is a measure of the distance between adjacent planes

of atoms within the crystal lattice. The SAED image obtained in Figure 4.44 provides valuable information about the crystal's composition and quality. By analyzing the diameter of each diffraction ring from the central spot using Image J software, the crystal's d-spacing can be determined.

Since nanoparticles can be polycrystalline and comprise numerous crystalline domains, the size of the crystalline domain does not always correlate to the size of the particle. Particles can be considered single crystals if the Scherrer equation's prediction of the crystalline domain size agrees with the average diameter of the particles as measured by TEM imaging. Diffraction from a single crystal causes the formation of SAED patterns, whereas many crystals cause the formation of rings. It can be seen from the SAED pattern in Figure 4.44. The sample involves either single or polycrystalline crystals since there are combinations of spots and rings. The SAED pattern of the particles contains seven rings, each corresponding to specific crystal planes (Figure 4.44). These rings can be observed from the SAED pattern indicated to multiple crystals.

Moreover, by measuring the angles at which X-rays are diffracted by a crystal, we can calculate the spacing between planes in the crystal lattice. Each peak in an x-ray diffractogram also corresponds to a specific d-spacing which can be identified using Bragg's law (Pope, 1997):

$$d = \frac{n\lambda}{2\sin\theta} \quad (34)$$

where d is the spacing between planes, λ is the wave length of X-ray equal to 0.154 nm, θ is the angle at the maximum point of the peak in the spectra, and n is a whole number that represents the order of diffraction, taken as 1 in our calculations.

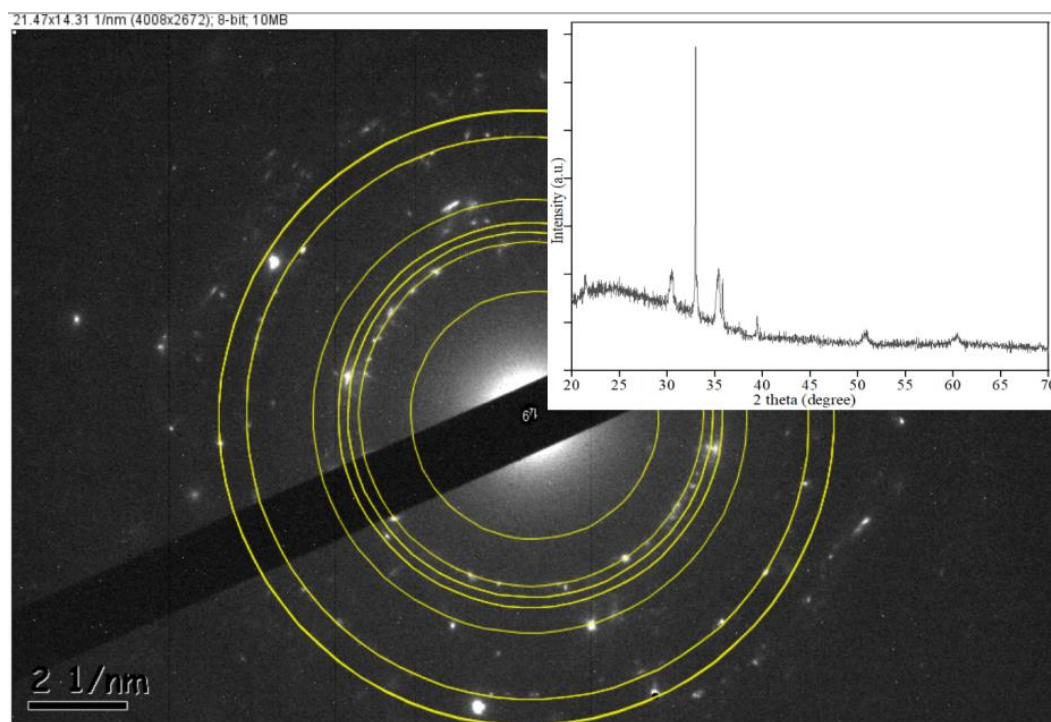


Figure 4.44. XRD and SAED patterns for electroreduced particles obtained in 3 MR hydrated reline electrolyte

The d-spacing values corresponding to the diameter of the rings in the SAED image are compared with the XRD spectrum of the working electrode sample (Table 4.5). Each ring on the SAED pattern corresponds to a specific set of lattice planes. In the XRD pattern, there are 7 major peaks corresponding to In_2O_3 (211), In_2O_3 (222), In (101), In_2O_3 (400), In (110), In_2O_3 (440), and In_2O_3 (622), respectively. As can be seen from the table, the d-spacing values of the derived diffraction planes from rings 1 to 7 are in good agreement with XRD diffraction patterns. The In_2O_3 and In data were analysed using JCPDS 06-0416 and 05-0642 standards, respectively.

Table 4.5 D-spacing values obtained from SAED and XRD patterns.

	XRD data		TEM data	
	2θ (deg)	d-spacing ($\text{\AA}^\circ$)	$1/2r$ (1/nm)	d-spacing ($\text{\AA}^\circ$)
1	22.189	3.999	5.096	3.925
2	31.176	2.866	7.087	2.822
3	32.983	2.713	7.515	2.661
4	35.389	2.534	7.916	2.527
5	39.451	2.282	8.923	2.241
6	50.722	1.798	11.585	1.726
7	60.328	1.533	12.666	1.579

The agreement between the derived diffraction planes from rings 1 to 7 and the XRD diffraction patterns is a strong indication that the crystal structures were successfully indexed to ITO coming from the substrate and that In was recovered from ITO after electrochemical treatment. This suggests that the electrochemical treatment was effective and that the crystal structures are stable. Furthermore, the absence of impurities on the surface of the crystals is also a positive sign. This could indicate that the crystal growth was relatively clean and free of contaminants, which is important for ensuring that the electrolyte perform optimally during electrochemical applications. Additionally, this suggests that the quality of the reduced indium crystals is high, which could have implications for their use in recovery applications as secondary raw material. Therefore, these findings are significant for understanding the behavior of ITO crystals during electrochemical applications in reline, as well as for exploring their potential use in other areas, such as optics and electronics.

Comparing the d-spacing values obtained from XRD and SAED results with the reported d-spacing values can determine the phase purity of indium and indium oxide materials. This finding is crucial for reusing the recovered material in the production of ITO thin film on glass or other transparent substrates. Several fabrication methods can be used to grow ITO thin film layers, such as spray pyrolysis (Brinzari et al., 2014), thermal evaporation (Pan et al., 2013), the sol-gel process (Wang et al., 2014), magnetron sputtering (Heo et al., 2015), and vapor deposition (Maruyama & Fukui, 1991). Each technique has its advantages and disadvantages, but they all use common target materials, such as In_2O_3 and SnO_2 , or indium or tin ingots. Therefore, the recovered indium and indium oxide, whose purity has been clarified in this study and can be easily separated from the surface, may be reused on the substrate surface in ITO deposition or synthesis without any purification process.

4.9 Current Measurement Analysis in 2-Electrode System

The use of a reference electrode is typical for electrochemical experiments. The cost of the reference electrode has been reduced, and the potential for contamination of the electrolytic solution by leakage or frit from the reference electrode has been avoided, thanks to the two electrode structure. A straightforward two-electrode deposition setup was adopted in the current work due to these factors and the fact that minor adjustments in deposition voltage do not significantly affect deposition experiments in DES electrolyte.

By using a two-electrode configuration, it was possible to investigate the effects of electrolyte temperature, time for deposition, pH, the electrodes used, ion concentration in the electrolytic bath, and applied voltage on the electrochemical conditions in a deep eutectic solvent. To characterize such non-uniform electrochemical processes, another electrochemical parameter which was electrodeposition currents have been measured during the process. Currents in the electrotreatment circuit were read by a digital multimeter which was connected in series to the circuit. Current change according to time for deionized water, reline and

ethaline solutions can be seen in Figure 4.45. Moreover, the detail of this modification were also referred at the Appendix B of this thesis.

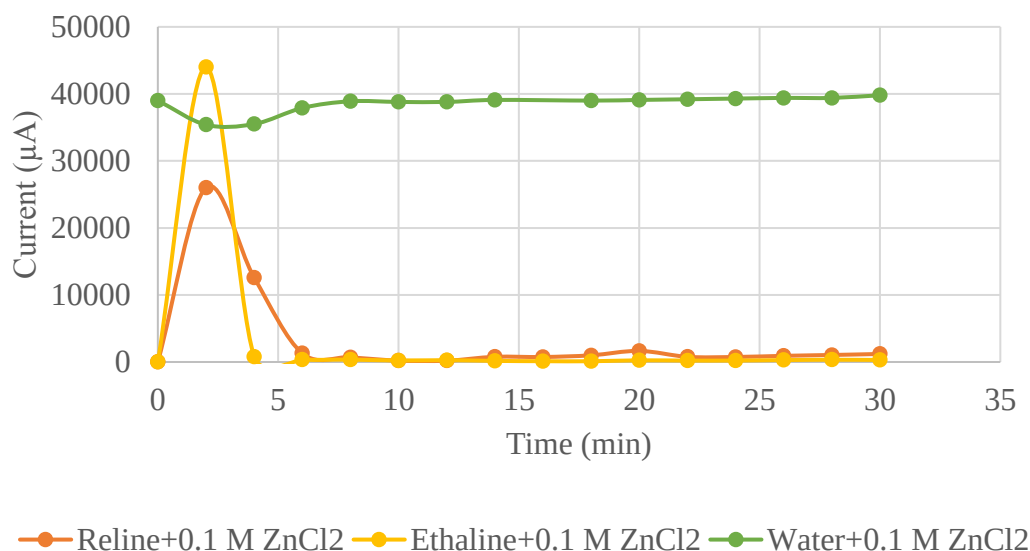


Figure 4.45 Current measurements in 2-electrode electrochemical setup in various electrolytes

Current transition measurements were made primarily in aqueous media, as in all other trial sets. It was observed that the current increased by 7 milliamperes in a minute caused by a low level of 2 mA in the electrodeposition experiments performed in pure water retention. Following this observation, the current values were fixed within 2-3 minutes and this value remained in the range of 10-13 mA throughout the experiment as can be seen in Figure 4.45.

On the other hand, current measurements in DES exhibited completely different observations. In the electrochemical treatment carried out in ethaline, the current observed in the order of about 40 milliamperes followed by a rapid decrease in the scale of microamperes within an average of 2 minutes time (Figure 4.45). In addition to this rapid decrease, the current was very variable in the 6-12 minutes of the experiment which increased to 800 μ A and decreased to 200 μ A within seconds.

In the experiments with pure reline solution bath, the 30 mA current level was measured initially which has been chased to microampere rates within 5-6 minute. When these two ChCl based DESs were compared, the current values were found to be relatively higher throughout the electrochemical process as well as the decline in the current was longer for reline.

The significant inequality in current behavior between water and DES based electrolytes was due to different electrochemical mechanism and ion attitude generating double/multi layers between electrode and electrolyte interface. All systematical analysis results suggested that cation and anion properties in electrolyte possessed important effect on the electrostatic interactions which directed the mechanism and hence determined the final structure. In addition, electrode surface was another crucial identifier for determining the behavior of ions amongst the substrate and solution. Therefore, the use of surfaces with different properties may reveal different interactions and arrangements of the anions and cations relevant for the structure of the ion layering capacity. Finally, both electrolyte and electrode selection may enhance the electrochemical properties and consequently industrial applications of the product.

Besides, the difference in current measurements for reline and ethaline which are belonging to the ChCl based DES group can be attributed to the role of the chloride ion in their content. As explained in the CV analysis part of this thesis, even very few publications exist on the electrochemical behavior of ionic liquids, it should be mentioned that both anions and cations take action at the interface region. Hence for either ChCl based DESs, chloride ion involved at the interface affecting the electrochemical mechanism by adsorbing onto the electrode and blocking the reduction process. Similar to cyclic voltammetry studies, rapid drop in current could be associated with chloride anion adsorption onto the ITO coated glass substrate. In addition, it has been suggested that the activity of the chloride anion is comparably higher in the ethaline solution than reline which may leading rapid fall at less time according to current measurements depicted in the Appendix B.

4.10 Electrical and Optical Properties of Indium Tin Oxide Working Electrode Processed under Different Conditions

ITO thin films on glass have high optical transmittance and low electrical sheer resistance, making them suitable for use in optoelectronic applications as discussed in the study's literature section. As a part of this study, it is expected that electrical and optical properties will not improve because phase separation and metal reduction occur on the WE surface instead of zinc deposition. However, before and after the electrochemical process, it is necessary to comperably examine how and to what extent these changes are reflected in both electrical and optical properties on the sample surface.

By utilizing ohmic contacts spaced by 2 mm, the Van der Pauw four point probe method was used to test the resistivity of the thin films under investigation (Ramadan et al., 1994). The shear resistance of the samples is listed in Table 4.6. However, due to phase separation and changes in intrinsic and extrinsic defects caused by electrochemical treatment in reline and hydrated reline solutions, the shear resistivity increase from 20.4 Ω/sq to 50 Ω/sq when the water content in reline increases. Moreover, with the electrochemically treated sample in 9 MR hydrated reline for 30 minutes process time, it is not possible to measure shear resistivity due to the deterioration of the homogeneous structure resulting from the elevation difference of the zinc metal deposited on the surface. Consequently, the measurement of shear resistivity becomes unreliable and cannot be used as a reliable indicator of the electrochemical properties of the sample processed in higher water content reline.

Table 4.6 Comparison of electrical properties of ITO working electrode (WE) electrochemically processed in various electrolyte solutions

Process Type	Electrolyte	Process Time	Sheer Resistance (ohm/sq)
Untreated ITO WE	-	-	20.4
Electrochemically treated ITO WE	Pure reline including 0.1 M ZnCl ₂	30 min	34
Electrochemically treated ITO WE	1 MR hydrated reline including 0.1 M ZnCl ₂	30 min	32
Electrochemically treated ITO WE	3 MR hydrated reline including 0.1 M ZnCl ₂	30 min	38
Electrochemically treated ITO WE	9 MR hydrated reline including 0.1 M ZnCl ₂	15 min	50
Electrochemically treated ITO WE	9 MR hydrated reline including 0.1 M ZnCl ₂	30 min	-

Figure 4.46 (a) shows the transmittance and reflectance spectra of ITO on a glass substrate working electrode before the electrochemical process. The maximum value for optical transmission in the visible range is 81 % at 595 nm, and for reflection, the maximum value is 15 % at about the same range. The maximum transmittance of the uncoated glass substrate is only 90.98% (at 500 nm) because to reflection losses (Gonçalves et al., 2007). As expected, the ITO layer shows high transmittance and low reflection in the visible spectrum.

In addition, the transmittance and reflectance spectra of ITO coated glass electrodes processed in various reline based electrolytes containing 0.1 M zinc chloride and various amounts of water are also shown in Figure 4.46 (b)–(f). The maximum transmittance decreases to 55–60% and is observed at higher wavelengths, at about 850 nm, treated in either pure reline or 1MR hydrated reline solutions. Moreover, the highest transmission value was observed at about 47 % again in the near IR range for the samples electrochemically treated in 3 MR hydrated reline for 30 minutes and 9 MR hydrated reline for 15 minutes. The wavelength range change at which the

maximum transmittance is achieved may be associated with the change in the ITO working electrode film thickness due to the reduced indium nanoparticles formed on the surface with a particle size distribution between 50 and 300 nm, as discussed above. On the other hand, the reflectance spectrum did not significantly change for the electrochemically treated samples, and no oscillation was observed in the transmission or reflectance spectra for these samples.

The optical transmission spectra of the processed ITO WE film in 9 MR hydrated reline solution indicate significant decreases in transmission, as well as an increase in reflectance values in the visible region (see Figure 4.46 (f)). Additionally, oscillation in the near-infrared radiation is observed from the transmission and reflection spectra, suggesting surface plasmon resonance (SPR). For the samples electrochemically treated in 9 MR hydrated reline for 30 minutes, XRD and EDS analysis reveal the deposition of zinc metal in addition to indium reduction on the ITO working electrode. This results in two separate absorption bands related to indium and zinc metals. The low transmittance of this sample in the visible region further suggests that the working electrode is largely covered by zinc particles, which can cause both SPR absorption and visible light reflection.

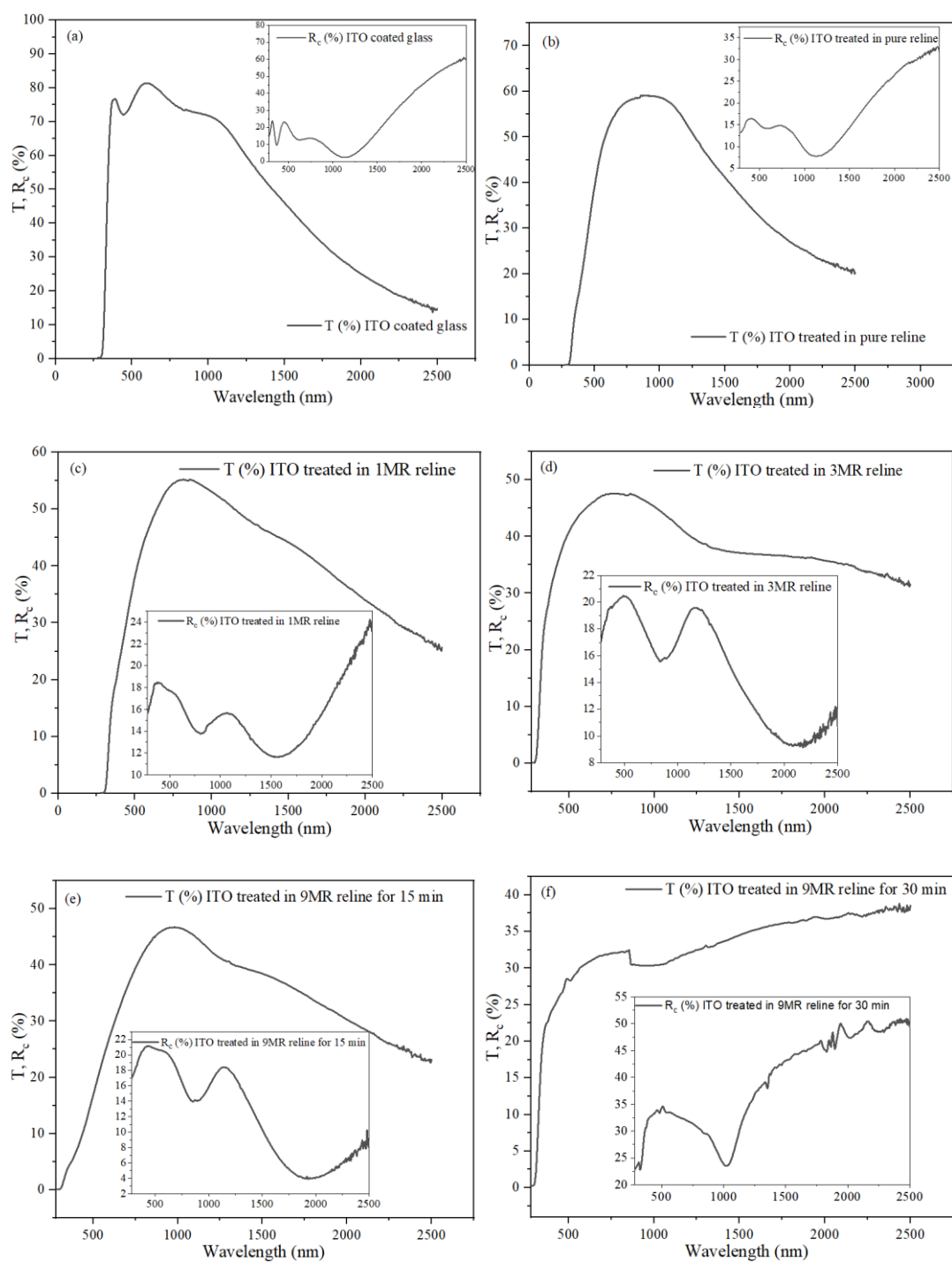


Figure 4.46 Transmittance and reflectance spectra for ITO working electrode (a) unprocessed and processed in pure and hydrated reline containing 0.1 M ZnCl_2

In short, the ITO coated glass working electrode had a resistance of 20.4 Ω/sq and an optical transmittance of 81% at 595 nm before the electrochemical treatment. Surface roughening caused by aggregation of recovered indium metal during the electrochemical treatment resulted in increased dispersion of incoming light and a decrease in transmittance. The increased surface scattering effect also increased sheet resistance. For the electrochemically processed samples in reline, the decrease in electrical conductivity properties is also attributed to the decrease in nonstoichiometric In_2O_3 and hence oxygen vacancies, which have a significant influence on the electronic properties.





CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

Significant interest has been shown in DESs because of their physical and thermodynamically properties. Therefore in this study, it was aimed to use DESs synthesis/shape control of particles during electrochemical process. While the number of articles of DESs have grown in last few years, knowledge about their functionalization and behavior during electrodeposition still remains unclear. This is an active research gap where it is needed to better understand the fundamental properties of DESs and how to best utilize them in various electrochemical applications.

This work aims to investigate the electrodeposition of zinc on the indium tin oxide (ITO) electrode and the resultant surface modifications in ChCl based DESs. To achieve this, a two-electrode electrochemical system was utilized. Unlike traditional electrochemical experiments in aqueous media, changes in the ITO surface structure were observed in DES, instead of the expected zinc deposition. Interestingly, the indium from the ITO was reduced in the DES, which presents a novel outcome in the electrochemical reduction of ITO. The zinc deposition mechanism was found to be entirely related to the hydrogen bonds in the DES structure.

To achieve the goal, a series of systematic studies were conducted on the electrochemical recovery of ITO on glass. By carefully controlling the electrodeposition parameters and thoroughly understanding the relationship within these parameters and the properties of the electrode surface, we were able to gain valuable insights into the electrochemical mechanism of an ITO electrode from ChCl-based DES. This represents the first comprehensive study of its kind,

investigating the effect of parameters on the electrochemical mechanism of an ITO electrode from ChCl-based DES. Moreover, we investigated the correlation between electrodeposition parameters and the resulting metal properties, which include morphology, efficiency, crystallinity, and other essential characteristics.

The investigated electrochemical process parameters are the electrolyte content such as anion-cation content or supporting electrolyte amount, pH of the reaction medium, and electrochemical process time. XRD, EDX mapping analysis, SEM, TEM and XPS used to characterize films, all of which revealed the presence of DES compounds in the solution totally change the mechanism of the electrodeposition and hence structures formed on the substrate. This research allowed us to develop a more profound knowledge on the factors that impact the properties of the electrode surface, and we were able to identify significant findings that can be used to steer future studies in this field.

5.2 Conclusions

The physicochemical behaviors and surface morphology of an electrode, after electrochemical treatment, can vary significantly depending on several factors. These include the electrolyte used (including the concentration of the metal source or supporting electrolyte, pH, presence of anions/cations, and additives), changes in electrodeposition parameters (such as current density, temperature, and potential), the type of working electrode/counter electrode, and their pretreatment conditions.

In this work, the effect of electrochemical parameters on the electrodeposition of zinc on the ITO substrate and the electrochemical reduction of indium from the ITO electrode were systematically investigated. Deep eutectic solvents, including ZnCl_2 , were used as electrolytes rather than conventionally used water solutions. Besides pure form, the electrochemical behavior of hydrated DES with various amounts of water and ZnCl_2 concentrations has been explored. In addition, electrolyte pH,

electrodeposition time effects on surface morphology, crystal structure, and electrochemical behavior were studied.

The thorough investigation has been conducted on how the type and concentration of electrolyte affect the electrodeposition of zinc on the ITO substrate and the electrochemical reduction of indium from the ITO electrode. The main goal was to explore whether deep eutectic solvents (DES) including ZnCl_2 could be a viable alternative to the more commonly used water solutions. To achieve this, we used various electrolytes with different amounts of water and ZnCl_2 concentrations. The electrolyte pH and electrodeposition time also varied to observe their effects on surface morphology, crystal structure, and electrochemical behavior.

During this study, a significant discovery was the structural change of ITO during cathodic treatment in DES, which resulted in indium reduction. Therefore, the structural change of ITO on the substrate surface as well as the deposition of zinc ions in the DES electrolyte on the substrate surface during electrochemical experiments were carefully observed and analyzed. The findings of this comprehensive study led us to systematically explore the details of these two independent mechanisms, including the ionic structure and the hydrogen bonding network of DES, and the relationship of these properties with various electrochemical parameters.

It has been mostly studied on electrolyte solution to understand the structure formed onto the substrate during electrodeposition. For this reason ChCl based DESs that are reline, ethaline, their binary mixtures and their aqueous solutions were used. It can be suggested that reline shows higher polarizability thus reline exhibits faster reduction kinetics of indium compared to ethaline. The composition of the electrolyte should also be taken into account since it may have an impact on the charge passed during indium oxidation and reduction. Ion interaction and the hydrogen bonding network are likely to play a role in this.

The proposed alternative electrolyte bath, called reline, consists of aqueous reline mixtures with varying water rates up to 9 MR water content. By analyzing the

existing hydrogen bonding between reline components, the interaction energies between them, and the polarization properties, it was found that these factors mostly influence the mechanism of zinc electrodeposition and indium reduction that was observed on the ITO working electrode surface. In deep eutectic solvents (DES), the electrochemical mechanisms function differently from those in the aqueous solution. Bulky asymmetric components DES act as ligands for the metal species in the electrolyte, and these ions may also adsorb onto the electrode surface, changing the traditional electrochemical double layer to multilayering that blocks the zinc ions in the electrolyte from reaching the electrode surface. These characteristic DES behaviors directly affect the conventional electrodeposition mechanism by inhibiting metal nucleation onto the electrode surface and initiating surface modification.

The effect of water in the DES electrolyte on zinc electrodeposition and indium electroreduction can be classified into three groups depending on the water content. At low water content, with ChCl:urea:water at a molar ratio of 1:2:1, water exhibited a favorable contribution to the reduction mechanism. When the water molar fraction increased to 3 MR, the reduction of indium was still observed, but its rate decreased, which was associated with the decrease in the hydrogen bonding interaction. This suggests that the presence of a low amount of water has a positive effect on the reduction mechanism, but an excess amount can have a negative impact on the reaction rate. At higher water fractions (9 MR), reline is hydrated with water molecules, which cause a change in the solution's properties such as viscosity and conductivity. This property change leads to the formation of indium hydroxide reactions and the deposition of zinc metal during electrochemical processes on ITO substrates. It is worth noting that the formation of indium hydroxide can lead to a decrease in the efficiency of the electroreduction process.

The surfaces of all electrolyte types and the amount of water in them were extensively examined using XRD, SEM, EDS mapping, and XPS analyses. As discussed in detail, the sample obtained in 1 MR reline showed the most intense peaks of the indium crystal, while the area under the peak of the indium metal was relatively higher than on other sample surfaces in the XPS results. Additionally, the

increase in the amount of water in hydrated reline resulted in the detection of peaks of the Zn crystal structure in the XRD spectrum as well as in the elemental analysis performed with EDS. In fact, the EDS mapping analysis showed that the indium metal was reduced before the ITO on the electrode surface, after which zinc was deposited mainly around the reduced metal. Taken together, these results provide valuable insights into the mechanism and process of the electrolyte properties. Although different test and analysis methods were used, they all provided consistent results, which enabled us to make holistic observations about the properties of the samples.

Additionally, the analysis results are linked to the properties of deep eutectic solvents (DES) obtained from theoretical and experimental studies reported in the literature. These observations reveal that DES components are interrelated, and the hydrogen bonding network based on this relationship affects indium reduction. In addition to DES ion interactions, these ions have complicated, uneven, and large structures. Because of this, denser multi-layers form instead of the double layer formation at the electrode and electrolyte interphase, which is seen in traditional electrochemical experiments. This unique layering composition completely alters the deposition of zinc by preventing the zinc ions in the electrolyte from reaching the electrode surface.

To investigate the electrochemical mechanism of metal deposition and reduction in reline and reline-water mixtures at different ratios, cyclic voltammetry (CV) was performed using a 3-electrode system with an Ag/AgCl reference electrode. This technique revealed interesting findings, including the observation of two oxidation peaks in the anodic scan. These peaks were attributed to the electrochemical oxidation of In^0 to In^+ and the oxidation of In^+ to In^{3+} . The oxidation peak positions and relative area under these curves changed with water content. In voltammograms of 1 MR reline solution, where the highest reduction efficiency is obtained, the highest area under the anodic peak of In^+ to In^{3+} oxidation belongs to the In (III) valence, which is the basis for the reduction mechanism. Additionally, it was observed that the shifts in peak positions were related to the intermolecular

relationship of reline components and strength of the hydrogen bonds between them. The difference between the peak position potentials was the highest for the 1 MR hydrated reline with the strongest hydrogen bonding network, indicating that samples treated in it has the highest indium recovery rate.

Additionally, a cathodic peak was detected, which was attributed to the reduction of indium and appeared at approximately -1.2 V for all samples analyzed in pure and hydrated reline solutions. Although a single reduction peak was observed in cyclic voltammetry (CV) experiments, this peak was observed within a wide range. As the standard reduction potentials of indium ions with different valences were close to each other, this broad peak may be attributed to multiple reduction steps. CV results were consistent with the XRD, SEM, EDS and XPS data.

Moreover, the amount of ZnCl_2 that is assumed to be the supporting electrolyte, in the reline solution has been investigated. The addition of ZnCl_2 to the DES has a clear effect on the viscosity and conductivity, which have a similar effect as the water by altering the hydrogen bonding network. The base ZnCl_2 amount in the reline solution was 0.1 M. When ZnCl_2 concentration increases to 0.4 M, besides the phase separation reaction that arises on the surface, zinc crystals are deposited onto the substrate, which can be attributed to an increase in current density and a change in the hydrogen bonding network strength that was found to play a crucial role in the phase separation reaction.

Although not well understood, this mechanism may account for the behavior related to water addition. In the electrodeposition of zinc from 3 MR hydrated reline solution, a relatively high critical ZnCl_2 concentration was required. In other words, at higher water or zinc chloride content, zinc metal deposition occurred in addition to indium reduction. The higher concentration of ZnCl_2 led to the diffusion of ions into the reline compounds. Due to the fact that the diffusion of ions weakens the molecular interactions between reline compounds, as in the case of water molecules, this supported the deposition of zinc crystals onto the substrate. It is clear that

understanding molecular interactions and current density is crucial for discussing zinc deposition and indium reduction.

In this study, the effect of electrolyte pH on the electrochemical reduction of ITO and metal electrodeposition was investigated. The results show that the pH of the electrolyte significantly affects the electrochemical processes in reline, as demonstrated by XPS and XRD analysis. Specifically, the reduction is inhibited when the pH of the solution decreases, which may be attributed to the effect of chloride ions on the oxidation of indium from ITO under acidic conditions.

Further electrochemical studies with various pH ranges suggested that, at lower pH, the indium reduction decreases with the increase in H^+ ions in the electrolyte. This can be attributed to the penetration and absorption effect of chloride ions onto the working electrode surface, which diminishes the contact between the working electrode and electrolyte. Although the adsorption of chloride ions onto the surface did not totally inhibit the metal reduction, it significantly affected the oxidation step and hence decreased the reduction rate. Moreover, as the cycling continues, more chloride ions penetrate, causing oxidation and reduction peaks to disappear and leading to a decrease in the overall electrochemical activity of the electrode at lower pH according to CV studies.

Experimental parameters, such as the type, composition, and pH of the electrolyte, were varied to observe the chemical balance. It was also advised to deposit at different time periods to measure the growth maturity of the microstructure. Experiments were repeated for 2 minutes, 30 minutes, 2 hours, and 4 hours. The results showed that, even at 2 minutes, a film was deposited on the substrate. With increasing time intensities, film deposition also increased, indicating that the microstructure reached a certain growth maturity.

When the results of samples electrochemically processed in hydrated reline with $ZnCl_2$ for 30 minutes were compared to those of 2-hour and 4-hour samples, peak positions and intensities were parallel. This suggests that 30 minutes is an efficient time for completing the growth mechanism and forming the desired nanostructure.

A slight decrease in peak intensities of indium metal in the surface XRD spectrum of the 4-hour process period was observed. This decrease was attributed to the dissolution of the indium metal in the electrolyte or its detachment from the electrode surface. However, further analysis revealed that the formation of the desired nanostructure was still in progress after 4 hours of processing.

To observe the structural evolution of electrochemically treated samples, post-treatment processes were applied. Various calcination temperatures up to 500 °C were studied under air flow for the optimum design and characterization of coatings. The findings showed an opposite effect even at low temperatures and short times, such as 300 °C for 10 minutes. This suggests that calcination had a significant negative impact on the structural evolution of the recovered indium metal. Therefore, no post-deposition heat treatment was performed on the samples reported in this study before characterization.

It was observed that as the calcination temperature increased, the reduced indium peak intensities decreased, and the peaks of the ITO crystal structure increased. This result shows that indium metal reduction from ITO with electrochemical treatment is oxidized again when temperature is applied under air flow, even becoming fully oxidized at 500 °C calcination. Moreover, as the indium metal was oxidized by calcination at higher temperatures under air flow, In_2O_3 (222)/ In_2O_3 (400) increased with increasing calcination temperature, attributed to the fact that the calcination film contained sufficient oxygen, leading to preferential crystal growth with (222)-oriented grains.

5.3 Achievements

As a result of this extensive research, important insights into the use of DES as an alternative electrolyte to water solutions in the electrodeposition of zinc and electrochemical reduction of indium have been discovered. By exploring the various

factors that impact the electrochemical behavior of DES, it is possible to gain a more comprehensive understanding of the mechanisms involved in these processes.

The main achievements of this study can be summarized as follows:

- During the experiments, ITO was utilized as a working electrode. ITO surfaces contain defects such as oxygen vacancies, substitutional Sn^{4+} or interstitial In, grain boundary orientations, and different In:Sn ratios. Studies have revealed that these complex non-stoichiometric microstructure variations and defects impact the ITO electrochemical response. The investigations have shown that the cathodic treatment in DES induces structural changes in ITO, resulting in the appearance of a structure distinct from ITO's original structure. This new structure has been associated with the metallic phase of indium metal.
- Electrodeposited ITO at different pH values showed that the onset potential shifts negatively as the pH of the electrolyte decreases. This indicates that reduction is more favorable in a basic environment than in an acidic medium. This finding suggests that the difference in mechanism at different H^+/OH^- ratio, may be due to the specific adsorption of chloride on the electrode surface, blocking indium recovery on the surface.
- Zinc chloride was used as a zinc precursor in ChCl:Urea based DES. However, it was observed that ZnCl_2 functions as a supporting electrolyte in the solution during electrochemical processes. Furthermore, it was found that the electrochemical structural change of ITO depends heavily on the anions of the electrolyte. Metal reduction is significantly inhibited under acidic conditions due to the absorption of Cl^- ions onto the surface at the applied voltage.
- The analysis of the ChCl based DES electrolyte indicated that the electrochemically processed samples in reline had a higher reduction rate than those in ethaline, which was attributed to the higher polarizability of reline. In addition this finding also associated with the hydrogen bonds as

highest number of HBs is observed between urea–urea because the oxygen in urea is a stronger HB acceptor.

- The influence of electrolysis on the ITO structure in hydrated reline was investigated. According to the results of the study, it was found that when the water compositions were at a low level of 1MR, there was an increase in the molecular interactions of urea-based compounds, such as urea-urea and choline-urea. These interactions consequently resulted in an increase in the recovery rate of indium. Moreover, at a higher water composition (9MR), the reline constituents are individually hydrated, which results in a higher diffusivity of the DES in water. This enables zinc deposition and subsequently indium reduction onto the working electrode surface.
- The physical properties of reline significantly change with the increase in ZnCl_2 concentrations associated with the weakening of the hydrogen bonding network in reline. The hydrogen bonding network in reline plays a crucial role in promoting the mass transport of zinc ions. As in the case of water addition, besides disrupting this bonding structure, which leads to an increase in the average void magnitude between the reline components, the effect of ZnCl_2 concentration on the viscosity and conductivity of reline further enhances the mass transport of zinc ions. Therefore, at higher zinc chloride amounts, at 0.4 M ZnCl_2 , both indium recovery and zinc deposition were observed on the working electrode processed in 3 MR reline.
- According to XRD analysis, peaks corresponding to scattering from the indium crystal planes decreased in the electrochemically processed films when exposed to hydrated reline solution. At the same time, peaks corresponding to standard In_2O_3 crystals increased as the calcination temperature rose. These peaks even disappeared at 500 °C. This observation suggests that the electrochemically reduced indium metal was reoxidized during post-heat treatment under air, which caused a reversal of the reduction mechanism. This finding suggests that the reoxidation of indium metal could be a potential issue to be addressed in further studies.

- In a comparison of the *d*-spacing between TEM/SAED and X-ray diffraction patterns of the sample treated in 3 MR hydrated reline, the crystalline phase was assigned to indium metal and indium oxide. This could indicate that the crystal growth was relatively clean and free of contaminants, which is important for ensuring that the electrolyte performs optimally during electrochemical applications on behalf of the indium recovery. The comparative *d*-spacing is another important achievement of this study since indium ingots or indium oxide solid sources are used during ITO coating onto the glass substrate. This finding of this study highlights that it is possible to directly use the easily detached material from the working electrode after electrochemical treatment as a source for ITO in different coating methods

This study proposes that zinc electrodeposition is inhibited on an ITO-coated glass substrate in ethylene glycol and urea-based ChCl DES instead. This inhibition is associated with both the hydrogen bonding structure of the electrolyte and ZnCl₂ concentration. This work represents the first example of recovering indium from ITO as a working electrode using mild electrochemical reducing conditions at a -1.6 V cathodic potential in reline, a natural DES, with very high reduction efficiency. XPS analysis was used to compare the indium removal efficiency of untreated and electrochemically treated ITO surfaces, showing a reduced metal ratio for the latter. It was assumed that the indium metal did not dissolve in reline or separate from the surface while washing with distilled water after electrotreatment.

In view of the systematic studies explained above, the highest recovery of indium detected from comparable XPS analysis and the crystallinity rate identified from XRD with the electrochemical parameters were specified as follows:

Substrate (Working Electrode): ITO

Supporting Electrolyte: 0.1 M ZnCl₂

Electrolyte Solution: 1:2:1 molar ratio of Choline Chloride:Urea:Water

Applied Voltage: -1.6 V

Electrodeposition Time: 30 minutes

Counter Electrode: Zinc Wire

Electrodeposition Temperature: 80 °C

This study systematically investigated the modifications and evolutions of the ITO layer on the electrode surface during zinc electrodeposition in DES under different electrochemical conditions. In addition to the thorough and efficient metal recovery studies, a significant contribution of this study to the literature is the finding that ITO-coated glasses do not require purification processes that are physically or financially intensive before or after electrochemical treatment. Furthermore, even after the electrochemical experiment, the electroreduced indium metal on the electrode surface did not contain any impurities, even when the surface was only washed with pure water and dried. Additionally, reduced indium metals on the glass surface can be easily removed using a flat and fine apparatus such as a razor or knife. This study provides a new process route for ITO recycling that is efficient, simple, sustainable, and environmentally friendly. With further developments, this process can be extended to large-scale production.

5.4 Recommendations

This thesis highlights the importance of designing a sustainable method to recover and reuse indium and tin from used ITO. Indium's strategic scarcity, excellent conductivity, and light transmittance make it widely used to prepare ITO targets. While some open questions remain, as mentioned in various parts of this thesis, several recommendations can be made for future research directions.

This study exploited an electrolysis method in deep eutectic solvent to recover and reuse used ITO targets, providing a novel way to recycle valuable resources. Moreover, there are limited publications on the use of DES in electrochemistry studies and the electrochemical behavior of these solutions, as well as the

experimental procedures and results of this study. Therefore, there are some areas open to improvement due to the importance of the topic and the scarcity of studies.

In the scope of this study, XPS analyses were conducted to compare the proportional stoichiometric calculations of the elements on the surface and the relative intensities of the XRD peaks, and the best conditions were discussed in line with these inferences. However, further studies are necessary to conclude the efficiency of the reduced metals. A detailed XRD study could be done to measure metal recovery efficiency.

Furthermore, although ChCl-based DES used in the study can be prepared with a cost-effective and easy procedure when compared to other ionic liquids, it is necessary to investigate the usability of DES prepared for larger sizes and sustainable applications with the same effect in how many experiments. Therefore, further studies are required to investigate for how many cycles DES-based electrolytes can be used without decomposition electroreducing effects as an electrolyte solution.

Moreover, exploring heat treatment after electrodeposition is another part of such a comprehensive study. It was discussed that after the electrochemical process, the reduced metals were deoxidized with calcination under high temperatures on the electrode and returned to the ITO structure. However, there were shifts examined in the XRD peaks compared to its untreated conjugate, which were attributed to the replacement of tin and zinc metals that were reduced and deposited on the electrode surface during the electrochemical experiment, respectively. Although the negative effect of calcination on the recovery of indium metal was discussed, XRD peak shifts should be investigated further in depth. Similarly, ZITO structure, which was addressed in the study between zinc and indium oxide crystal peaks, should also be further understood due to the fact that the Zn-In-Sn-O system is an attractive system for replacement of ITO.

Additionally, studying the effects of other important processing parameters, such as electrodeposition temperature and cyclic voltammetry, could lead to a better

understanding of the nucleation and growth mechanisms involved in either metal recovery or ZITO crystallization.



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APPENDICES

A. JCPDS Reference Data

Indium Oxide			Indium		
JCPDS 06-0416			JCPDS 05-0642		
h k l	Standard 2 θ (°)	Standard intensity (%)	h k l	Standard 2 θ (°)	Standard intensity (%)
In ₂ O ₃ (211)	21.497	14	In(101)	32.963	100
In ₂ O ₃ (222)	30.581	100	In(002)	36.325	21
In ₂ O ₃ (400)	35.464	30	In(110)	39.167	36
In ₂ O ₃ (411)	37.684	8	In(112)	54.473	24
In ₂ O ₃ (332)	41.884	6	In(200)	56.589	12
In ₂ O ₃ (431)	45.689	10	In(103)	63.199	16
In ₂ O ₃ (521)	49.266	4	In(211)	67.029	23
In ₂ O ₃ (440)	51.039	35	In(202)	69.11	11
In ₂ O ₃ (433)	52.712	4	In(004)	77.038	3
In ₂ O ₃ (611)	55.988	6	In(220)	84.164	5
In ₂ O ₃ (541)	59.133	4	In(213)	89.884	12
In ₂ O ₃ (622)	60.678	25	In(301)	93.362	4
In ₂ O ₃ (631)	62.163	6			
In ₂ O ₃ (444)	63.683	6			
In ₂ O ₃ (721)	68.024	4			
In ₂ O ₃ (651)	73.656	4			
In ₂ O ₃ (800)	75.019	4			
In ₂ O ₃ (741)	76.366	4			

Zinc Oxide			Zinc		
JCPDS 36-1451			JCPDS 04-0831		
h k l	Standard 2 θ (°)	Standard intensity (%)	h k l	Standard 2 θ (°)	Standard intensity (%)
ZnO(100)	31.76	57	Zn(002)	36.295	53
ZnO(002)	34.42	44	Zn(100)	38.991	40
ZnO(101)	36.25	100	Zn(101)	43.23	100
ZnO(102)	47.53	23	Zn(102)	54.333	28
ZnO(110)	56.6	32	Zn(103)	70.053	25
ZnO(103)	62.86	29	Zn(110)	70.657	21
ZnO(200)	66.37	4	Zn(004)	77.024	2
ZnO(112)	67.96	23	Zn(112)	82.098	23
ZnO(201)	69.09	11	Zn(200)	83.761	5
ZnO (004)	72.57	2			
ZnO(202)	76.949	4			
ZnO(104)	81.364	1			

B. Current Measurements

Electrolyte Concentration: 0.1 mol ZnCl_2 + Reline (1 mol ChCl + 2 mol ethylene glycol)

Electrotreatment Temperature: 80 °C

Electrotreatment Potential: -1.6 Volt

Initial Resistance: 70.5 Ω

Final Resistance: 15 Ω

Time (min)	Current (mA)
0	26
2	12.6
4	1.3
Time (min)	Current (μA)
6	702
8	213
10	198
12	768
14	747
16	998
18	1655
20.5	771
22	750
24	921
26	1047
28	1200
30	579

Electrolyte Concentration: 0.1 mol ZnCl_2 + Ethaline (1 mol ChCl + 2 mol ethylene glycol)

Electrotreatment Temperature: 80 °C

Electrotreatment Potential: -1.6 Volt

Initial Resistance: 70.5 Ω

Final Resistance: 52 Ω

Time (min)	Current (mA)
0	44
2	0.8
Time (min)	Current (μA)
4	340
6	351
8	220
10	270
12	166
14	120
16	112
18	252
20	207
22	213
24	286
26	336
28	303
30	274

Electrolyte Concentration: 0.1 mol ZnCl₂ + Pure Water

Electrotreatment Temperature: 80 °C

Electrotreatment Potential: -1.6 Volt

Initial Resistance: 70.4 Ω

Final Resistance: 0.54 Ω

Time (min)	Current (mA)
0	39.0
2	35.4
4	35.5
6	37.9
8	38.9
10	38.8
12	38.8
14	39.1
18	39.0
20	39.1
22	39.2
24	39.3
26	39.4
28	39.4
30	39.8

Electrolyte Concentration: 0.1 mol ZnCl_2 + Ethaline (50%) and Reline (50%) mixture in mole

Electrotreatment Temperature: 80 °C

Electrotreatment Potential: -1.6 Volt

Initial Resistance: 69.5 Ω

Final Resistance: 49 Ω

Time (min)	Current (mA)
0	31
2	13.2
4	4.1
Time (min)	Current (μA)
6	174
8	151
11	143
12	126
15	130
16	124
18	126
21	104
23	96
24	102
26	104
28	97
30	87

Electrolyte Concentration: 0.1 mol ZnCl_2 + Ethaline (90%) and Reline (10%) mixture in mole

Electrotreatment Temperature: 80 °C

Electrotreatment Potential: -1.6 Volt

Initial Resistance: 69 Ω

Final Resistance: 55.8 Ω

Time (min)	Current (mA)
0	34.5
2	0.82
Time (min)	Current (μA)
4	230
6	380
8	88
10	628
12	184
14	88
16	77
18	80
20	73
22	83
24	68
26	57
28	75
30	67

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name: Koç Haskılıç, Burcu

EDUCATION

Degree	Institution	Year of Graduation
MS	METU Mikro Nanotechnology	2009
BS	METU Chemical Engineering	2004
High School	Gazi Anadolu High School, Ankara	1999

FOREIGN LANGUAGES

Advanced English

PUBLICATIONS and THESIS

Master Thesis: Production of Titanium Dioxide Thin Films with Improved Photocatalytic Activity: The Use of Bacteria as 3D Templates

Chief Expertise Thesis: R&D Studies and TEYDEB Supports for Thin Film Coating Technology in the Last 10 Years

Expertise Thesis: A Study on the Companies Executing National and International Projects in the Materials, Metallurgy and Chemical Technologies Group