

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**DEVELOPMENT OF ELECTRODES & ELECTROLYTES FOR HIGH
PERFORMANCE AND LONG LIFE SUPERCAPACITORS**



Ph.D. THESIS

Mert Umut ÖZKAYNAK

Department of Materials Science and Engineering

Materials Science and Engineering Programme

APRIL 2025

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**DEVELOPMENT OF ELECTRODES & ELECTROLYTES FOR HIGH
PERFORMANCE AND LONG LIFE SUPERCAPACITORS**

Ph.D. THESIS

**Mert Umut ÖZKAYNAK
(521042004)**

Department of Materials Science and Engineering

Materials Science and Engineering Programme

**Thesis Advisor: Prof. Dr. F. Seniha GÜNER
Thesis Co-Advisor: Prof. Dr. Nilgün KARATEPE YAVUZ**

APRIL 2025

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**YÜKSEK PERFORMANSLI VE UZUN ÖMÜRLÜ SÜPERKAPASİTÖRLER
İÇİN ELEKTROT VE ELEKTROLİT GELİŞTİRİLMESİ**

DOKTORA TEZİ

**Mert Umut ÖZKAYNAK
(521042004)**

Malzeme Bilimi ve Mühendisliği Anabilim Dalı

Malzeme Bilimi ve Mühendisliği Programı

**Tez Danışmanı: Prof. Dr. F. Seniha GÜNER
Eş Danışman: Prof. Dr. Nilgün KARATEPE YAVUZ**

NİSAN 2025

Mert Umut ÖZKAYNAK, a Ph.D. student of ITU Graduate School, student ID 521042004 successfully defended the thesis entitled “DEVELOPMENT OF ELECTRODES & ELECTROLYTES FOR HIGH PERFORMANCE AND LONG LIFE SUPERCAPACITORS”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. F. Seniha GÜNER**
Istanbul Technical University

Co-advisor : **Prof. Dr. Nilgün KARATEPE YAVUZ**
Istanbul Technical University

Jury Members : **Prof. Dr. Metin GENÇTEN**
Yıldız Technical University

.....
Prof. Dr. Ali GELİR
Istanbul Technical University

.....
Assist. Prof. Dr. Osman EKSİK
Gebze Technical University

.....
Assoc. Prof. Dr. Melih Beşir ARVAS
Istanbul University

.....
Assoc. Prof. Dr. Mehmet Suha YAZICI
Istanbul Technical University

Date of Submission : 10 January 2025

Date of Defense : 29 April 2025



FOREWORD

This dissertation stands on the steadfast guidance of my advisor, Prof. Dr. F. Seniha GÜNER, and co-advisor Prof. Dr. Nilgün KARATEPE YAVUZ, whose rigorous insight, steady encouragement, and exacting standards shaped every stage of this work. I am equally indebted to my thesis committee—Prof. Dr. Metin GENÇTEN, Prof. Dr. Ali GELİR, and Assist. Prof. Dr. Osman EKSİK—for their time, discerning critique, and constructive counsel.

My sincere gratitude extends to Prof. Dr. Ömer DAĞ for his generous collaboration, as well as to Dr. Yurdanur TÜRKER, Dr. Koray Bahadır DÖNMEZ, Dr. Banu KOCAAĞA, Dr. Zehra ÇOBANDEDEDE, Selin DAĞLAR, and Merve Metin ÇELENK, whose expertise proved indispensable.

This research further benefited from the facilities of the Materials Science and Engineering, Chemical Engineering, and Energy Institute laboratories; Sabancı University Nanotechnology Research and Application Center (SUNUM); Bilkent University National Nanotechnology Research Center (UNAM); and the Bilkent University Department of Chemistry.

January 2025

Mert Umut ÖZKAYNAK



TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	vii
TABLE OF CONTENTS	ix
ABBREVIATIONS	xi
SYMBOLS	xiii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
SUMMARY	xix
ÖZET	xxi
1. INTRODUCTION	1
2. HIGH-MOLE-RATIO PA/NI LIQUID CRYSTAL GEL ELECTROLYTES FOR ADVANCED SUPERCAPACITORS	3
2.1 Experimental Part	5
2.1.1 Materials	5
2.1.2 Preparation of PA-NI LC gels	5
2.1.3 Synthesis of rGO	6
2.1.4 Fabrication of symmetric rGO-PA-NI LC gel supercapacitor	6
2.1.5 Materials characterization	7
2.1.6 Electrochemical characterization	7
2.2 Results and Discussion	8
2.3 Conclusions	25
3. UNDERSTANDING THE ROLE OF WATER IN THE LYOTROPIC LIQUID CRYSTALLINE MESOPHASE OF HIGH-PERFORMANCE FLEXIBLE SUPERCAPACITOR ELECTROLYTES USING A RHEOLOGICAL APPROACH	27
3.1 Experimental Part	30
3.1.1 Materials	30
3.1.2 Preparation of electrolytes	30
3.1.3 Structural characterization	31
3.1.4 Rheological characterization	31
3.1.5 Dynamic oscillatory measurements	32
3.1.6 Time and temperature dependence	32
3.1.7 Thixotropic oscillation strain test	32
3.1.8 Creep-recovery analysis	32
3.1.9 Electrochemical characterization	33
3.2 Results and Discussion	33
3.2.1 Structural characterization	34
3.2.2 Rheological characterization	35
3.2.3 Strain sweep analysis	36
3.2.4 Frequency sweep analysis	37
3.2.5 Shear thinning property	39

3.2.6 Time sweep	39
3.2.7 Temperature sweep.....	39
3.2.8 Self-Healing property	40
3.2.9 Creep recovery	42
3.2.10 Zero-shear viscosity	45
3.2.11 Stress relaxation	45
3.2.12 Electrochemical performance.....	46
3.3 Conclusions	52
4. MOLTEN SALT ASSISTED ASSEMBLY (MASA) OF NOVEL MESOPOROUS $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ FOR HIGH-PERFORMANCE ASYMMETRIC SUPERCAPACITORS	55
4.1 Experimental Part	58
4.1.1 Synthesis of mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , MnCo_2O_4	58
4.1.2 Synthesis of activated carbon	58
4.1.3 Preparation of active carbon coated carbon foam	58
4.1.4 Preparation of active mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ coated Nickel Foam.	59
4.1.5 Characterization of materials	59
4.1.6 Electrochemical measurements	59
4.1.7 Assembly of asymmetric supercapacitor	60
4.1.8 Calculation methods	60
4.2 Results and Discussion.....	61
4.3 Conclusions	75
5. CONCLUSION	77
6. FUTURE WORK.....	83
REFERENCE	85
CURRICULUM VITAE	101

ABBREVIATIONS

AC	: Activated Carbon
BET	: Brunauer–Emmett–Teller
Cdl	: Double-Layer Capacitance
CE	: Confinement effect
Cs	: Specific capacitance
CV	: Cyclic voltammetry
E	: Specific energy density
Ea	: Activation Energy
EDLC	: Electric double-layer capacitor
EIS	: Electrochemical impedance spectroscopy
FTIR	: Fourier transform infrared spectroscopy
GCD	: Galvanostatic charge/discharge
GO	: Graphene Oxide
LC	: Liquid Crystal
LLC	: Lyotropic liquid crystalline
LVE	: Linear Viscoelastic Range
MASA	: Molten Salt Assisted Assembly
NI	: Non-ionic Surfactant
NMP	: N-Methyl-2-Pyrrolidone
P	: Power density
PA	: Phosphoric Acid
POM	: Polarized optical microscopy
R_{ct}	: Charge Transfer Resistance
rGO	: Reduced Graphene Oxide
R_s	: Ohmic Resistance
SEM	: Scanning Electron Microscopy
TEM	: Transmission Electron Microscopy
TMO	: Transition metal oxide
W	: Warburg Element
XRD	: X-ray diffractometry



SYMBOLS

Ea	: Activation energy
G'	: Elastic modulus
G''	: Viscous modulus
Gf	: Flow point
Yf	: Strain amplitude at the flow point
G'LVE	: Storage modulus at the critical point
<i>J_{max}</i>	: Maximum deformation
tan δ	: Damping factor
<i>Tanβ</i>	: Slope of the creep curve
η0	: Zero-shear viscosity
T	: Characteristic relaxation time
τ_k	: Shear stress



LIST OF TABLES

	<u>Page</u>
Table 2.1: Ohmic and charge transfer resistance of supercapacitor cells.....	17
Table 2.2: Performance comparison of different carbon-based electrodes.....	23
Table 3.1: Formulation of gel structures.	30
Table 3.2: Experimental setup for rheological characterization.	31
Table 3.3: γ_f , G'_{LVE} and G''_f , damping factor ($\tan \delta$), temperature-induced gel point, and recovery (RS) of the elastic modulus after high strain of the gels.	36
Table 3.4: Maximum deformation corresponding to the compliance value $J_{max,25}$ at 25 Pa, Creep recovery percentage at 25 ($RC_{25} \%$) and 10 ($RC_{10} \%$) Pa, Zero shear viscosities at 25 and 10 Pa, and Activation Energies of the formulations.	44
Table 4.1: Specific capacitance data calculated by GCD and CV.....	67
Table 4.2: Equivalent-circuit parameters extracted from fitting the EIS data.....	72
Table 4.3: Comparison of the electrochemical performance of $Ni_{0.5}Mn_{0.5}Co_2O_4//AC$ and similar devices.	74
Table 5.1: Key achievements.....	79
Table 5.2: Electrochemical performance metrics	80



LIST OF FIGURES

	<u>Page</u>
Figure 2.1: XRD patterns of (a) graphite and (b) graphene oxide (c) rGO	9
Figure 2.2: Raman spectra of the graphite and the reduced graphene oxide.....	10
Figure 2.3: XRD patterns of (a) PA-NI60, (b) PA-NI80, and (c) PA-NI100. (d) Polarized optical microscopy images of all ratios of LC gels.....	10
Figure 2.4: FTIR spectra of PA-NI60, PA-NI80, and PA-NI100	11
Figure 2.5: Hydrogen-bonding network.....	12
Figure 2.6: LC gel electrolyte split cell.....	13
Figure 2.7: (a) Cyclic voltammograms of the LCs and pure PA in different molar ratios at a scan rate of 1mV s ⁻¹ . (b) Electrochemical performance of LC gel prepared with the 80:1 PA:NI mole ratio measured at various scan rates (c) Cyclic voltammograms obtained in a three-electrode measurement configuration	13
Figure 2.8: Electrochemical impedance spectra of LCs and pure PA at different molar ratios in the frequency range of 100 000 to 0.01 Hz and the elements in the equivalent electrical circuit model for the supercapacitor	16
Figure 2.9: Nyquist plot of the rGO 85 wt % H ₃ PO ₄ rGO cell with extended-Randles fit; Rs-(Cdl (Rct+Ws))-C accurately captures charge transfer and proton diffusion.	18
Figure 2.10: (a) GCD profiles of supercapacitor cells containing pure PA, PA-NI60, PA-NI80, and PA-NI100. (b) GCD profile of PA-NI80 measured at various current densities. (c) Energy density, power density, and specific capacitance obtained at different current densities from the system with PA-NI80 electrolyte. (d) Cycling stability of supercapacitor cell prepared with PA-NI80 electrolyte. (e) Discharge curves and voltage drop for supercapacitor cells containing pure PA, PA-NI60, PA-NI80, and PA-NI100.....	20
Figure 3.1: 5.63 LiCl:C12E23:1.125 g H ₂ O sample: aging-time-dependent XRD patterns (inset: plot of d-spacing versus hkl relation for cubic phase)....	35
Figure 3.2: Oscillatory analysis of structures. (a)damping factor at various angular frequencies, (b)complex viscosity analysis, and (c)damping factor analysis related to the time sweep. (d)Damping factor analysis related to temperature sweep. (e)Visual observations further support temperature-induced gelation;at 25°C, they were able to hold their weight in the inverted vial at a particular angle, and at 60°C, all the samples exhibited flowable characteristics.	38
Figure 3.3: Rapid self-healing determination of (a) LC _{0.875} (H ₂ O) (b) LC _{1.000} (H ₂ O), (c) LC _{1.125} (H ₂ O), and (d) LC _{1.250} (H ₂ O) formulations by oscillation strain steps	42

Figure 3.4: (a) Creep curves of $\text{LC}_{1.000}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$. Stress relaxation test of (b) $\text{LC}_{1.000}(\text{H}_2\text{O})$, (c) $\text{LC}_{1.125}(\text{H}_2\text{O})$, (d) $\text{LC}_{1.250}(\text{H}_2\text{O})$ formulations.	44
Figure 3.5: Cyclic voltammograms of (a) $\text{LC}_{1.000}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolytes, (b) $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolyte at different scan rates in the voltage window of 0-0.5 V, and (c) electrochemical impedance spectra of the $\text{LC}_{1.000}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolytes in the frequency range of 0.1 Hz to 100.000 Hz.	49
Figure 3.6: (a) Galvanostatic charge-discharge curves of the $\text{LC}_{1.125}(\text{H}_2\text{O})$ electrolyte at different current densities (inset is specific capacitance versus current density) and (b) variation of coulombic efficiency (%) and capacity retention (%) depending on the number of cycles.	51
Figure 3.7: Schematic Li^+/Cl^- transport pathways and restrained convective flow within the bicontinuous-cubic $\text{C}_{12}\text{E}_{23}\text{-LiCl-H}_2\text{O}$ gel electrolyte.	51
Figure 4.1: Schematic illustration of the fabrication routes of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$	58
Figure 4.2: XRD patterns of (a) NiCo_2O_4 fresh samples, (b) MnCo_2O_4 fresh samples (c) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ fresh samples; high angle XRD pattern after calcination at 400 °C; (d) NiCo_2O_4 (e) MnCo_2O_4 (f) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, POM images for (g) NiCo_2O_4 (h) MnCo_2O_4 (i) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$	62
Figure 4.3: (77 K) N_2 adsorption-desorption isotherms, (a) and pore-size distribution plots, (b) of (I) NiCo_2O_4 , (II) MnCo_2O_4 and (III) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$	63
Figure 4.4: SEM images of (a) NiCo_2O_4 , (b) MnCo_2O_4 and, (c) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, and TEM images of (d) NiCo_2O_4 , (e) MnCo_2O_4 , (f) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$...	64
Figure 4.5: (a) CV curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams in 6 M KOH (Reference Electrode: SCE), (b) CV curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ coated Ni foam at a scan rate of 1, 5, 10, 20, 50, 100, 250, and 500 mV.s^{-1} (Electrolyte: 6 M KOH, Reference Electrode: SCE), (c) Nyquist plots of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams in 6 M KOH (Reference Electrode: SCE), (d) GCD curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams in 6 M KOH (Reference Electrode: SCE, Current Density at 5 mA.cm^{-2}), (e) GCD curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ at a current density of 5, 10, 15, 20, 25, and 50 mA.cm^{-2} (Electrolyte: 6 M KOH, Reference Electrode: SCE), (f) Areal specific capacitance at various current densities	66
Figure 4.6: Charge transfer mechanism of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode in $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{KOH}/\text{active carbon}$ asymmetrical device (charging mechanism of asymmetric device)	71
Figure 4.7: (a) GCD curves of the device at different current densities (b) CV measurements performed with separate half-cells of the anode and cathode (Red/electrolyte 6 M KOH, scan rate: 1 mV.s^{-1} , Black/electrolyte: 6 M KOH, scan rate 1 mV.s^{-1}), (c) Nyquist plot of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{Active Carbon}$ device, (d) Areal capacitance at various current densities (e) Long term cycling stability of the asymmetrical device	73

DEVELOPMENT OF ELECTRODES & ELECTROLYTES FOR HIGH PERFORMANCE AND LONG LIFE SUPERCAPACITORS

SUMMARY

This study enhances supercapacitor technology through three primary advancements: First, it introduces a phosphoric acid-based liquid crystal gel electrolyte with enhanced specific capacitance. Second, it examines how water influences the lyotropic liquid crystalline (LLC) mesophase characteristics of C12E23-LiCl-H₂O gel electrolytes, revealing their self-healing properties with optimized features for the first time. Lastly, it develops mesoporous Ni_{0.5}Mn_{0.5}Co₂O₄ electrodes for the first time utilizing the Molten Salt Assisted Assembly technique. These innovations address the shortcomings of traditional supercapacitors, paving the way for adaptable, high-efficiency energy storage solutions suitable for wearable electronics and electric vehicles.

In the first part of the thesis study, a novel liquid crystal (LC) gel electrolyte by combining phosphoric acid (H₃PO₄, PA) and a non-ionic surfactant (NI), optimized at a PA:NI mole ratio of 80:1 (PA-NI80) was developed. A bicontinuous LC mesophase with a lattice distance of 3.9 nm was observed at all mole ratios between 60:1 and 100:1, as confirmed through X-ray diffraction and optical microscopy.

The PA-NI80 LC gel achieved a specific capacitance (*C_s*) of 1128 F g⁻¹ at 0.1 A g⁻¹ using reduced graphene oxide (rGO) symmetric electrodes. Results highlight the pivotal role of the LC gel mesophase in achieving high electrolyte performance. The high viscosities and stable mesophase structures make the PA-NI LC gels suitable for use in flexible and high-performance supercapacitors.

The mesophase structure facilitated controlled ion transport via the Grotthuss mechanism, where hydrogen hopping through hydrogen bonds contributed to the gel's high ionic conductivity and superior electrochemical performance.

In the second part of this thesis, we systematically investigated the role of water in shaping the lyotropic LC mesophase properties of C12E23-LiCl-H₂O gel electrolytes, with a focus on their mechanical and electrochemical performance in supercapacitors. XRD and POM data confirmed the formation of a cubic mesophase at all water concentrations. Rheological analysis suggested quantitative information about gel strength, gelation point, and structural recovery changed with water content and LiCl concentration. The storage modulus increased with decreasing water content, attributed to variations in the quantity and average size of junction points due to system entanglement. The study revealed that excess water molecules break down micellar connections, weakening the gel. Conversely, at low water concentrations, the micellar domains entangle, displaying viscoelastic behavior similar to that of a transitory polymer network. The gel structures exhibited self-healing properties, attributed to their shear-thinning behavior. This property allows the gels to flow under shear stress and self-recover once the stress is removed. By varying water content while maintaining a 5.63:1 LiCl-to-C12E23 molar ratio, we observed that reduced water content significantly enhanced gel rigidity, as evidenced by an increase in storage

modulus (G') from 82 Pa for $LC_{1.125}(H_2O)$ to 113 Pa for $LC_{0.875}(H_2O)$. Structural analyses using XRD revealed cubic mesophases with a unit cell parameter of 13.2 nm across all formulations. Rheological measurements highlighted the gels shear-thinning behavior and self-healing capability, with $LC_{1.125}(H_2O)$ achieving full recovery after strain-induced rupture. Electrochemical tests further demonstrated that $LC_{1.125}(H_2O)$ displayed a specific capacitance of $316 \text{ F} \cdot \text{g}^{-1}$ at $0.25 \text{ A} \cdot \text{g}^{-1}$ and retained 80% capacity over 1500 cycles, indicating its suitability for robust energy storage systems.

In the last part of this study, to complement the electrolyte, we synthesized mesoporous $Ni_{0.5}Mn_{0.5}Co_2O_4$ electrodes using the Molten Salt Assisted Assembly (MASA) method, marking the first application of MASA for ternary metal oxides. This approach enabled the creation of nanoscale active sites and ensured the formation of mesoporous $Ni_{0.5}Mn_{0.5}Co_2O_4$, $NiCo_2O_4$, and $MnCo_2O_4$ with relatively high surface areas. By simply altering the salt type and composition in the initial clear solutions used to prepare the LLC mesophases and applying calcination, MASA facilitated precise control over the electrode material properties. The MASA method allowed for the synthesis of mesoporous $Ni_{0.5}Mn_{0.5}Co_2O_4$ with high surface area and enhanced redox behavior. The method involves using metal nitrate salts precursors assembled with non-ionic and ionic surfactants in their lyotropic liquid crystalline phase, followed by high-temperature calcination.

Among the synthesized materials, the $Ni_{0.5}Mn_{0.5}Co_2O_4$ electrode showed the highest specific capacitance ($11.51 \text{ F} \cdot \text{cm}^{-2}$) and exhibited superior electrochemical activity, with the lowest charge transfer resistance compared to $NiCo_2O_4$ and $MnCo_2O_4$.

The asymmetric supercapacitor, assembled with $Ni_{0.5}Mn_{0.5}Co_2O_4$ utilizing the positive electrode and employing activated carbon for the negative electrode, achieved an energy density of 79.52 Wh kg^{-1} . The device exhibited excellent performance, with a low ohmic resistance of $2.348 \text{ } \Omega$ and a charge transfer resistance of $0.672 \text{ } \Omega$. Additionally, it maintained high capacitance even at elevated current densities. The study emphasizes $Ni_{0.5}Mn_{0.5}Co_2O_4$, crafted using the MASA technique, as a highly efficient material for asymmetric energy storage devices, attributed to its remarkable specific capacitance, low resistance, and excellent energy density.

YÜKSEK PERFORMANSLI VE UZUN ÖMÜRLÜ SÜPERKAPASİTÖRLER İÇİN ELEKTROT VE ELEKTROLİT GELİŞTİRİLMESİ

ÖZET

Bu araştırma, süperkapasitör teknolojisinde üç temel yenilik sunmaktadır: Özgül kapasitansı artırılmış fosforik asit bazlı sıvı kristal jel elektrolit sentezlenmiş, C12E23-LiCl-H₂O jel elektrolitlerin liyotropik sıvı kristal mezofaz özellikleri ve suyun bu özelliklere etkisi incelenerek optimize edilirken kendini iyileştirme özellikleri ortaya ilk kez çıkarılmıştır, ayrıca Eriyik Tuz Yardımı ile Kendiliğinden Oluşma (EYKO) tekniği kullanılarak ilk kez mezogözenekli Ni_{0.5}Mn_{0.5}Co₂O₄ elektrotlar geliştirilmiştir. Bu yenilikler, geleneksel süperkapasitörlerin eksikliklerini gidererek giyilebilir elektronikler ve elektrikli araçlar için uyarlanabilir, yüksek verimli enerji depolama çözümlerinin önünü açmaktadır.

Bu çalışmanın ilk bölümünde, fosforik asit (H₃PO₄, PA) ve iyonik olmayan bir yüzey aktifin (NI) birleştirilmesiyle oluşturulan ve 80:1 PA:NI mol oranında (PA-NI80) optimize edilen yeni bir sıvı kristal (SK) jel elektrolit geliştirilmiştir. X-ışını kırınımı ve optik mikroskop analizleri sonucunda, 60:1 ve 100:1 arasındaki tüm mol oranlarında 3,9 nm kafes mesafesine sahip kararlı bir SK mezofaz gözlemlenmiştir.

PA-NI80 SK jel, indirgenmiş grafen oksit (rGO) simetrik elektrotlar kullanılarak 0,1 A g⁻¹'de 1128 F.g⁻¹'lik bir spesifik kapasitansa (Cs) ulaşmıştır. Sonuçlar, yüksek elektrolit performansı elde etmede SK jel mezofazının önemli rolünü vurgulamaktadır. Yüksek viskoziteler ve kararlı mezofaz yapıları, PA-NI SK jelleri esnek ve yüksek performanslı süperkapasitörlerde kullanıma uygun hale getirmektedir.

Mezofaz yapısı, hidrojen bağları yoluyla hidrojen atlamasının (hopping) jelin yüksek iyonik iletkenliğine ve üstün elektrokimyasal performansına katkıda bulunduğu Grotthuss mekanizması aracılığıyla kontrollü iyon taşınmasını kolaylaştırmıştır.

Bu tez çalışmasının ikinci bölümünde, C12E23-LiCl-H₂O jel elektrolitlerinin liyotropik sıvı kristal (LSK) mezofaz özelliklerini şekillendirmede suyun rolünü sistematik olarak araştırılmıştır. XRD ve POM verileri, tüm su konsantrasyonlarında kübik bir mezofazın oluşumunu doğrulamıştır. Reolojik analizler; jel dayanımının, jelleşme noktasının ve yapısal geri kazanımın, su ve LiCl miktarına göre değiştiğini gösterdi. Jeldeki su miktarı azaldıkça, misellerin birbirine dolaşmasıyla oluşan bağlantı noktalarının sayısı ve/veya boyutu artmış, bu da jelin depolama modülünün yükselmesine neden olmuştur. Çalışma, fazla su moleküllerinin misel bağlantılarını bozarak jeli zayıflatıldığını ortaya koymuştur. Düşük su konsantrasyonlarında ise, misel alanları dolaşır ve geçici bir polimer ağına benzer viskoelastik davranış sergiler. Jel yapıları, kesme inceltme davranışlarına atfedilen kendi kendini iyileştirme özellikleri sergilemiştir. Bu özellik, jellerin kesme gerilimi altında akmasına ve gerilim kaldırıldığında kendini toparlamasına olanak tanır. 5,63:1 LiCl-C12E23 molar oranını korurken su içeriğini değiştirerek, azalan su içeriğinin jel katılığını önemli ölçüde artırdığı gözlemlenmiştir. Bu durum, depolama modülünün (G') LC_{1.125}(H₂O) için 82

Pa'dan $LC_{0.875(H_2O)}$ için 113 Pa'ya yükselmesiyle doğrulanmıştır. XRD kullanılarak yapılan yapısal analizler, tüm formülasyonlarda 13,2 nm'lik bir birim hücre parametresine sahip kübik mezofazları ortaya koymuştur. Reolojik ölçümler, jellerin kayma incelenmesi davranışını ve kendi kendini iyileştirme yeteneğini öne çıkartmıştır, $LC_{1.125(H_2O)}$ gerilim kaynaklı kopmadan sonra tam geri kazanım sağlamıştır. Elektrokimyasal testler ayrıca, $LC_{1.125(H_2O)}$ 'nin $0,25 A \cdot g^{-1}$ 'de $316 F \cdot g^{-1}$ 'lik bir spesifik kapasitans sergilediğini ve 1500 döngü boyunca %80 kapasiteyi koruduğunu göstermiş, sonuç olarak yüksek performanslı enerji depolama sistemleri için uygun bir aday olduğunu göstermiştir.

Bu tez çalışmasının son bölümünde, elektroliti tamamlamak için, Eriyik Tuz Yardımı ile Kendiliğinden Oluşma (EYKO) yöntemini kullanarak mezogözenekli $Ni_{0.5}Mn_{0.5}Co_2O_4$ elektrotları sentezlendi ve EYKO'nun üçlü metal oksitler için ilk uygulaması gerçekleştirildi. Bu yaklaşım, nanometre ölçekli aktif bölgelerin oluşturulmasına olanak sağlamış ve nispeten yüksek yüzey alanlarına sahip mezogözenekli $Ni_{0.5}Mn_{0.5}Co_2O_4$, $NiCo_2O_4$ ve $MnCo_2O_4$ sentezlenmesini mümkün kılmıştır. LSK mezofazlarını hazırlamak için kullanılan başlangıç tuz türünü ve bileşimini basitçe değiştirerek ve kalsinasyon uygulayarak, EYKO elektrot malzeme özelliklerinin hassas kontrolünü kolaylaştırmıştır. EYKO yöntemi, yüksek yüzey alanına ve gelişmiş redoks davranışına sahip mezogözenekli $Ni_{0.5}Mn_{0.5}Co_2O_4$ sentezlenmesine olanak tanımıştır. Yöntem, liyotropik sıvı kristal fazlarında iyonik olmayan ve iyonik yüzey aktiflerle bir araya getirilen metal metal nitrat tuzlarının prekürsör kullanılmasını ve ardından yüksek sıcaklıkta kalsinasyon yapılmasını içerir.

Sentezlenen malzemeler arasında, $Ni_{0.5}Mn_{0.5}Co_2O_4$ elektrot en yüksek spesifik kapasitansı ($11,51 F \cdot cm^{-2}$) göstermiş ve $NiCo_2O_4$ ve $MnCo_2O_4$ 'e kıyasla en düşük yük transfer direncine sahip üstün elektrokimyasal aktivite sergilemiştir.

Pozitif elektrot olarak $Ni_{0.5}Mn_{0.5}Co_2O_4$ ve negatif elektrot olarak aktif karbon kullanılarak oluşturulan asimetrik süperkapasitör, $79,52 Wh kg^{-1}$ enerji yoğunluğuna ulaşmıştır. Sistem, $2,348 \Omega$ düşük omik direnç ve $0,672 \Omega$ yük transfer direnci ile mükemmel performans sergilemiştir. Ayrıca, yüksek akım yoğunluklarında bile yüksek kapasitansı korumuştur. Bu bulgular, EYKO yaklaşımıyla sentezlenen $Ni_{0.5}Mn_{0.5}Co_2O_4$ 'ün yüksek spesifik kapasitansı, düşük direnci ve üstün enerji yoğunluğu nedeniyle asimetrik enerji depolama sistemleri için oldukça umut verici bir malzeme olduğunu göstermiştir.

Bu tez çalışmada, yeni geliştirilen PA–NI çift sürekli jel elektrolit ve mezogözenekli $Ni_{0.5}Mn_{0.5}Co_2O_4$ elektrotları temel alan çok yönlü bir enerji depolama platformu sunulmuştur. İncelenen sistem, yüksek kapasitans ve enerji yoğunluğuna sahip olup hibrit çalışma rejiminde etkin performans sergileyerek özellikle elektrikli araçlarda hafif ve verimli tamponlama uygulamalarına yönelik önemli avantajlar sağlamaktadır. Geliştirilen jel elektrolit yüksek sıcaklık kararlılığına, mekanik stres altında şekil değiştirme ve hızlı kendini onarma özelliklerine sahip olmasıyla cilt teması gerektiren giyilebilir cihazlardan, biyomedikal implantlara ve esnek IoT sistemlerine kadar geniş bir kullanım alanına sahiptir. Ayrıca solvent içermeyen yapısı ve nano kanallı düzenli morfolojisi sayesinde mikro elektronik sistemlerde ve havacılık uygulamalarında kullanıma uygundur. Öte yandan, yüksek kapasitans değeri ve düşük yük-transfer direncine sahip mezogözenekli elektrotlar, yenilenebilir enerji sistemlerinde enerji depolama ve tamponlama uygulamalarına ek olarak bifonksiyonel katalitik özellikleri ile enerji depolama ve enerji dönüşümünü tek bir yapı içinde bütünleştirme potansiyeli

göstermektedir. Bu kapsamda tez, enerji depolama teknolojilerinde çok disiplinli bir yeniliđi ortaya koyarak gelecekteki uygulamalara önemli bir temel oluşturmaktadır.



1. INTRODUCTION

Energy storage systems are at the forefront of technological innovation, driving advancements in fields such as consumer electronics, electric vehicles, and renewable energy integration. As the demand for compact, efficient, and sustainable energy storage devices continues to grow, supercapacitors have emerged as a critical solution. Supercapacitors boast remarkable characteristics including elevated power density, fast charge and discharge rates, and long-lasting durability [1], [2], [3]. However, the evolution of flexible electronics and wearable technologies has introduced new challenges, requiring supercapacitors to deliver not only high performance but also mechanical adaptability and durability [4], [5], [6].

The development of next-generation supercapacitors necessitates breakthroughs in both electrolyte and electrode technologies. Electrolytes, which facilitate ionic conduction between electrodes, are essential to the functionality of supercapacitors. Although traditional liquid electrolytes offer excellent ionic conductivity, they are susceptible to leakage and evaporation, which restricts their use in flexible and portable systems. [6], [7], [8], [9]. Gel and solid-state electrolytes have emerged as promising alternatives, offering structural stability and compatibility with flexible designs [10], [11], [12]. Among these, proton-conducting gel electrolytes, particularly those based on phosphoric acid ($\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, PA), have demonstrated exceptional ionic conductivity and electrochemical performance [10], [13], [14]. However, confining PA within a structured matrix, such as a liquid crystal (LC) gel, is necessary to optimize its properties for enhanced energy storage [11], [14], [15].

LC gels have garnered attention for their ability to form highly ordered mesostructures, which enhance ionic conductivity and mechanical stability [16], [17], [18]. By incorporating PA into a non-ionic surfactant matrix, LC gels with tailored viscosities and mesophase structures can be achieved [14], [15], [19]. Such characteristics enhance not only the electrochemical efficiency of the electrolyte but also make it suitable for application in flexible devices [20], [21], [22]. Despite these advancements, challenges remain in optimizing the LC gel's rheological and

electrochemical features to meet the demands of next-generation applications [23], [24], [25].

Simultaneously, the materials used for electrodes are crucial in influencing the energy density, power density, and overall efficiency of supercapacitors. Transition metal oxides (TMOs) have emerged as a leading class of electrode materials due to their high theoretical capacitance and redox activity [26], [27], [28]. Mesoporous structures further enhance the performance of TMOs by increasing the ion-accessible surface area and facilitating efficient charge transfer [28], [29]. Among TMOs, nickel manganese cobaltite ($\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$) offers unique advantages owing to its synergistic redox activity and structural stability. However, conventional synthesis methods often fail to achieve the desired mesoporosity and compositional precision required for optimal performance [29], [30], [31].

MASA method represents a novel approach to synthesizing mesoporous TMOs. By leveraging a molten salt medium and liquid crystal templates, the MASA method enables the formation of highly ordered mesoporous structures with enhanced redox behavior [1], [32], [33]. This study explores the first application of MASA for synthesizing $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ and assesses its effectiveness as a robust electrode constituent for non-symmetric supercapacitors [29], [30], [31]. Combined with the optimized PA-based LC gel electrolyte, the resulting supercapacitor system demonstrates exceptional energy and power densities, along with mechanical flexibility [33], [34], [35].

This thesis addresses the critical challenges in the design and development of supercapacitors for flexible applications. The research focuses on combining rheology-adjusted LC gel electrolytes with mesoporous electrodes derived from MASA to thoroughly explore the material characteristics and their influence on the performance of devices. The findings contribute to the advancement of sustainable, adaptable, and superior energy storage systems, paving the way for future innovations in wearable and portable technologies.

2. HIGH-MOLE-RATIO PA/NI LIQUID CRYSTAL GEL ELECTROLYTES FOR ADVANCED SUPERCAPACITORS ¹

Supercapacitors can benefit greatly from the use of proton-conducting gel electrolytes. Phosphoric acid ($\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, PA)) stands out among various acids due to its superior proton conductivity, making it a promising electrolyte for these devices. When paired with a symmetric electrode made of reduced graphene oxide, PA exhibited a notable specific capacitance of 620 F g^{-1} at a current density of 0.1 A g^{-1} , outperforming traditional acidic and basic electrolytes such as H_2SO_4 and KOH . The efficacy of the PA electrolyte was further augmented by its integration into a liquid crystal (LC) gel matrix. This was achieved by creating LC gels using PA and a non-ionic surfactant with PA:NI molar ratios ranging from 60 to 100:1. Notably, when tested with an rGO symmetric electrode at 0.1 A g^{-1} , the LC gel electrolyte delivered an impressive performance of 1128 F g^{-1} . To thoroughly investigate the LC-gel mesophase at every PA:NI proportion, methods such as X-ray diffractometry (XRD), Fourier-transform infrared spectroscopy (FTIR) and polarized optical microscopy (POM) were applied, confirming that the mesostructure contributed to the enhanced specific capacitance and overall device energy performance.

Electrochemical behavior was evaluated using multiple electrochemical techniques and galvanostatic cycling analyses. Additionally, considering the requirement for enhanced energy density in supercapacitors, particularly for automotive applications, this LC gel electrolyte shows potential for utilization in asymmetric pseudocapacitor configurations.

The swift development of the consumer electronic technology, automobiles, and aerospace markets has led to a continuous rise in demand for energy storage devices. To address this need, supercapacitors are being developed as advanced

¹ This chapter was published in “Özkaynak, M. U., Türker, Y., Dönmez, K. B., Karatepe, N., & Güner, F. S. (2022). High-performance supercapacitor electrolytes based on high-mole-ratio phosphoric acid/lauryl ether surfactant liquid crystalline gel. *International Journal of Energy Research*, 46(14), 19980-19991.”

energy storage devices that can charge/discharge quickly, have a long life cycle life, and provide high power density [1], [2], [3].

The lithium ion batteries power density is 100 times lower than that of supercapacitors, so they have been integrated with batteries to assist start- stop and regenerative braking in cars [36], [37], [38].

In addition, a long cycling stability and low weight are significant advantages of supercapacitors in the fields of automobile and aerospace applications [39], [40], [41].

To design a top-tier supercapacitor, it is needed to further improve both the electrodes and electrolytes. Hence, the choice of electrolyte is vital for the progress of energy storage devices for future technological applications [10], [13], [42]. For this reason, paramount importance has been given to developing a highly conducting electrolyte for robust supercapacitors [15], [19], [43], [44]. Among various viable aqueous electrolytes, concentrated acids such as H_2SO_4 and concentrated bases such as KOH have commonly been used as electrolytes for supercapacitors, and can be used alone or inside a hydrogel [45], [46]. In comparison to electrolytes such as H_2SO_4 and KOH, phosphoric acid ($\text{H}_3\text{PO}_4\text{-H}_2\text{O}$; PA) delivers superior proton conductivity and impressive specific capacitance when utilized with a symmetrical electrode composed of reduced graphene oxide (rGO) [47], [48]. However, solid-state and gel-type electrolytes have recently been used in supercapacitors to prevent liquid leakage during cycling [24], [49]. Therefore, highly conducting PA must be confined in a matrix, such as a hydrogel, to sustain high ionic conductivity [45], [50], [51]. However, although PA has very high ionic conductivity, it does not provide high specific capacitance in a supercapacitor because the charge/discharge times are too short, due to rapid ion transport through the electrolyte, and must be confined to a well-ordered matrix. For this reason, Dag et al showed that PA forms highly ordered mesostructured liquid crystal (LC) gels at certain mole ratios with a non-ionic surfactant, lauryl ether ($\text{C}_{58}\text{H}_{118}\text{O}_{24}$) [52]. These LCs can be potentially used as electrolytes [52], [53], [54], [55]. However, the mole ratio of PA:NI was limited to 20:1, at which point the viscosity of the LC hydrogel was still too high to be processed as a supercapacitor electrolyte; therefore, electrochemical tests could not be conducted [52]. Furthermore, they applied the LC mesostructured PA-NI electrolyte to an optical

modulator in a supercapacitor structure, but they did not perform electrochemical tests.

Therefore, in this study, an LC gel electrolyte was reformulated to achieve an optimal viscosity for easy use as a supercapacitor electrolyte. Based on structural characterization by XRD, FTIR, and POM, the mole ratio of PA:NI was optimized over a wide range (60-100:1). Such mole ratios led to the formation of an LC mesophase, and the low viscosity of the LC gel allowed electrochemical tests to be performed. The PA:NI mole ratios of 60:1, 80:1, and 100:1 gave the viscosity measurements of 5309, 3678, and 868 mPa s, respectively, at a shear rate of 100 s^{-1} . To the best of our knowledge, ours is the first study to use such high mole ratios for PA-NI gels as supercapacitor electrolytes. The LC mesophase did not form at mole ratios above 100:1. In this study, rGO was used as an electrode in combination with carbon black to get proper mechanical integrity and conductivity and polyvinylidene fluoride as a binding agent. The electrochemical performance of the supercapacitor cells was assessed based on their capacitive properties.

2.1 Experimental Part

2.1.1 Materials

Phosphoric acid ($\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$; PA) with a purity of 99.99% was purchased from Sigma Aldrich with 85% weight concentration. Lauryl ether ($\text{C}_{12}\text{H}_{25}[\text{OCH}_2\text{CH}_2]_{10}\text{OH}$) was purchased from JK Scientific with a purity of 100% and used as a non-ionic surfactant (NI). The molecular weight of the NI was $1199.90\text{ g mol}^{-1}$. Commercial graphite foam current collectors were cleaned with water and ethanol to remove any industrial residue or dust particles. *N*-methyl- 2-pyrrolidone (NMP) was bought from Aldrich Chemical Inc. and used as received. All other chemicals were bought from Sigma Aldrich and used without further modification. Carbon black was purchased from the Fuel Cell Store and was used without any treatment.

2.1.2 Preparation of PA-NI LC gels

The LC gel phases were prepared by mixing 1.0 g of NI, which was heated above its melting point of 50°C , and the required amount of PA in a 20 mL glass vial. This mixture was homogenized at 80°C for 15 minutes. For example, to obtain an

80:1 mol ratio of PA:NI, 7.6 g of % 85.0 wt/wt PA was mixed with 1.0 g of NI. Various PA:NI ratios (60-100:1) were evaluated to optimize the mole ratio to achieve LC gels with optimal viscosity for use as supercapacitor electrolytes. Henceforth, the samples are referred to as PA-NI60, PA-NI80, and PA-NI100 to indicate the mole ratios of 60:1, 80:1, and 100:1, respectively.

2.1.3 Synthesis of rGO

GO was prepared using the modified Hummers method. Typically, a solution of graphite powder (1.5 g, 325 mesh), $K_2S_2O_8$ (2.5 g), P_2O_5 (2.5 g), and H_2SO_4 (12.0 mL) was prepared, which was then brought to 80°C by agitating for 5 hours. Subsequent cooling to 25°C was achieved by dilution with 500 mL deionized water. A 0.2- μ m syringe filter was used to filter the final product and then allowed to dry. Pretreated graphite powder was cooled in 120 mL of concentrated H_2SO_4 in an ice bath; then, 15 g of $KMnO_4$ was mixed slowly under vigorous stirring at 35°C for 4 hours. Subsequently, 250 mL of deionized water was mixed at a temperature below 50°C. Exactly 700 mL of deionized water was added and then 20 mL of 30% H_2O_2 was added dropwise. To eliminate metal ions from the media, the product was purified, washed with an HCl aqueous solution (1:10, 1 L) and water, and led to dry at 60°C for 4 hours.

Further, rGO was produced from GO by thermal reduction. In this method, the dry GO powder was exposed to high temperature (1050°C) in a $N_{2(g)}$ atmosphere for 60 seconds to eliminate oxygen and produce graphene with an open pore structure.

2.1.4 Fabrication of symmetric rGO-PA-NI LC gel supercapacitor

In a typical experiment, 35 mg of rGO, 5 mg of PVDF, and 5 mg of carbon black were slowly dispersed in a 1.5 mL NMP (*N*-methyl-2-pyrrolidone) with ultrasonic treatment and kept until the solution became completely dispersed. Then, the dispersion was dropped onto graphite foam and left at 70°C overnight to remove the excess water on the electrode. A 1.2-cm-diameter filter membrane was soaked in the LC gel for 30 seconds, and then the filter membrane was assembled between the rGO electrodes. A symmetrical supercapacitor cell was prepared from two 1.1cm diameter rGO-coated graphite foam electrodes.

2.1.5 Materials characterization

Powder XRD was performed using a Philips PW-3710 with a CuK α radiation source ($\lambda = 0.15406$ nm). Raman spectroscopy was studied using Renishaw in-via microscope Raman system equipped with 532 nm laser source.

FTIR spectroscopy was performed using Thermo Scientific Nicolet IS10. Polarized optical microscopy (POM) was performed using Zeiss POM equipped with a 10X optical lens and polarizer. The viscosity of the LC gel was determined with Brookfield DVIII+.

2.1.6 Electrochemical characterization

To test the supercapacitor performance of the gel electrolyte with rGO electrodes, electrochemical tests were performed in a two-electrode configuration under ambient conditions using an electrochemical working station (PARSTAT MC 1000). The membrane filter was dipped in gel electrolyte, sandwiched between two identical electrodes, and placed in a split cell. CV tests of LC-combined supercapacitors (LCs) were performed at various scanning rates between 0 and 1 V. Two-electrode CV was performed using LC gel and bare PA electrolytes, operating scan rates of 1, 10, 50, and 100 mVs⁻¹. GCD tests were performed at 0.1, 0.25, 0.5, 0.75, and 1 Ag⁻¹ to evaluate the response of the LCs at diverse current densities. Ten charge-discharge cycles were performed at specific currents. EIS tests of the LCs were performed between 100 000 Hz and 0.01 Hz, and the amplitude of the AC voltage was 10 mV.

The gravimetric specific capacitance (C_s , F g⁻¹), specific energy density (E , Wh kg⁻¹), and power density (P , W kg⁻¹) of the supercapacitor were determined from the GCD curves using the following equations:

$$C_s = \frac{4I\Delta t}{m\Delta V} \quad (2.1)$$

$$E = \frac{C_s \Delta V^2}{28.8} \quad (2.2)$$

$$P = \frac{3600E}{\Delta t} \quad (2.3)$$

The variable m (g) denotes the aggregate mass of active material present on both working and counter electrodes, while I (A) represents the GCD current density. Additionally, Δt (s) indicates the duration of discharge, and ΔV (V) specifies the operational voltage range within the Δt period. In Equation (2.2), In a two-electrode system, C_s represents the specific capacitance of an individual electrode, while V (V) denotes the voltage at which the system operates.

The C_s calculated over the area of the voltammograms $C_{s(CV)}$ was determined using the following equation:

$$C_{s(CV)} = \frac{1}{m(WE)k(V_b - V_a)} \int_{V_a}^{V_b} IdV \quad (2.4)$$

where $m_{(WE)}$ (g) represents the quantity of active substance applied to the working electrode; k denotes the rate at which the scan is conducted during CV measurements; and V_a and V_b indicate the minimum and maximum voltage values, respectively, within the range utilized for calculating C_s [23], [55]. All voltammograms were normalized according to the amount of the total active material used.

2.2 Results and Discussion

Powder XRD was used to determine the degree of oxidation of the produced GO. The interlaminar microenvironment, structure, and oxidation state of the layered materials determine the final XRD patterns. Therefore, differences in the interlayer spacing can indicate variations in the functional groups containing oxygen bound to the graphite sheet. The peak around 25° to 26° (Figure 2.1a) is characteristic of graphite, giving an inter-layer spacing of 3.7 to 3.8 Å. After oxidation by the modified Hummers method, a characteristic peak of GO was observed at 11° (Figure 2.1b), which gave a 8.3 Å interlayer spacing. This increase in the interlayer spacing after oxidation indicates the presence of oxygenated groups between the graphite layers. Following the reduction treatment, the XRD pattern (Figure 2.1c) displays a reduced GO (001) reflection at $\sim 10^\circ 2\theta$, the graphitic (002) peak at $24-26^\circ$, and comparatively weaker in-plane (100) and (101) reflections at $\sim 42^\circ$ and $\sim 44^\circ$, respectively.

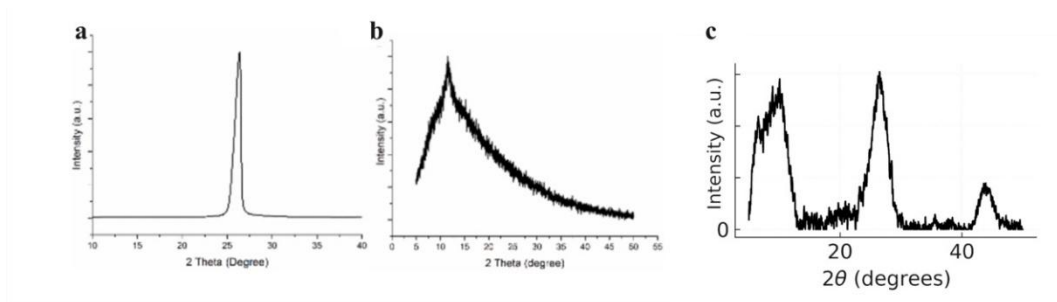


Figure 2.1: XRD patterns of (a) graphite and (b) graphene oxide (c) rGO

Raman spectroscopy is a strong tool for exploring the binding assets of various carbon materials. Hence, to further characterize the graphite reduction reaction and explore the nature of the sp^2 domains, Raman analysis of the rGO are shown in Figure 2.2. D and G peaks centered around 1300 and 1600 cm^{-1} , respectively, were observed in the spectra. The G band appeared due to the graphite optical mode of the C-C bonds in plane stretching. In addition, the A_{1g} breathing mode at the Brillouin zone boundary K results in the D band. The area under this peak is related to the number of defects in the graphene plane, since the thermal exfoliation of graphite oxide defines the intensity of the D band. An overtone of the D peak reveals around 2700 cm^{-1} as the 2D band (or the G^0 band), which is initiated with a double-resonance process as in the case of the D peak but necessitates the scattering of two phonons with opposite wave vectors to confirm momentum preservation and its initiation. It is assigned as the 2D band since it comprises two same phonons responsible for the D band. Opposite to the D band, the 2D band does not necessarily involve imperfections to satisfy the momentum conservation law, and consequently, it appears in the graphene' second-order Raman spectra. BET analysis showed that rGO had an area of $597\text{ m}^2\text{g}^{-1}$ and it has a total pore volume of 1.176 ccg^{-1} and an average pore diameter of 94.84 Å .

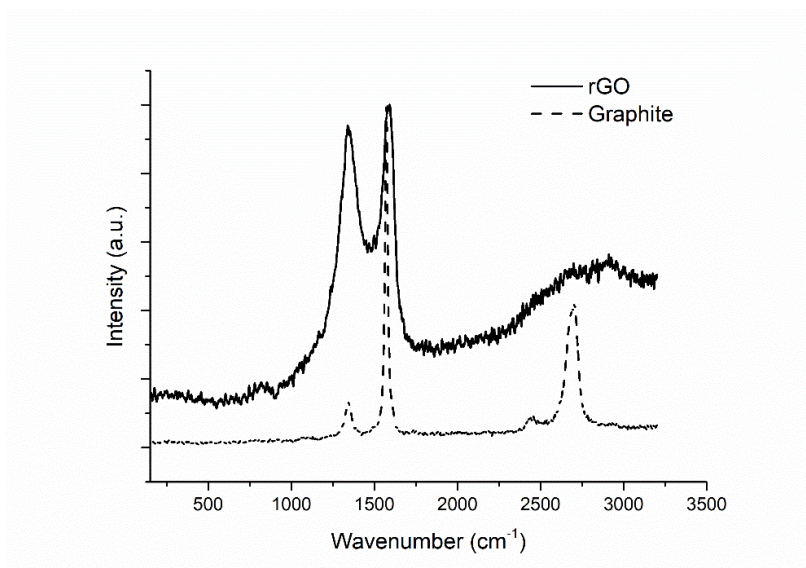


Figure 2.2: Raman spectra of the graphite and the reduced graphene oxide

PA and the NI were used to form an LC gel without the addition of any solvent. The 60 to 100:1 mol ratios of PA:NI were evaluated, which correspond to the range of 85% to 90% w/w of PA. XRD analysis showed that an LC gel mesophase formed for mole ratios of 60 to 100:1, but not above 100:1.

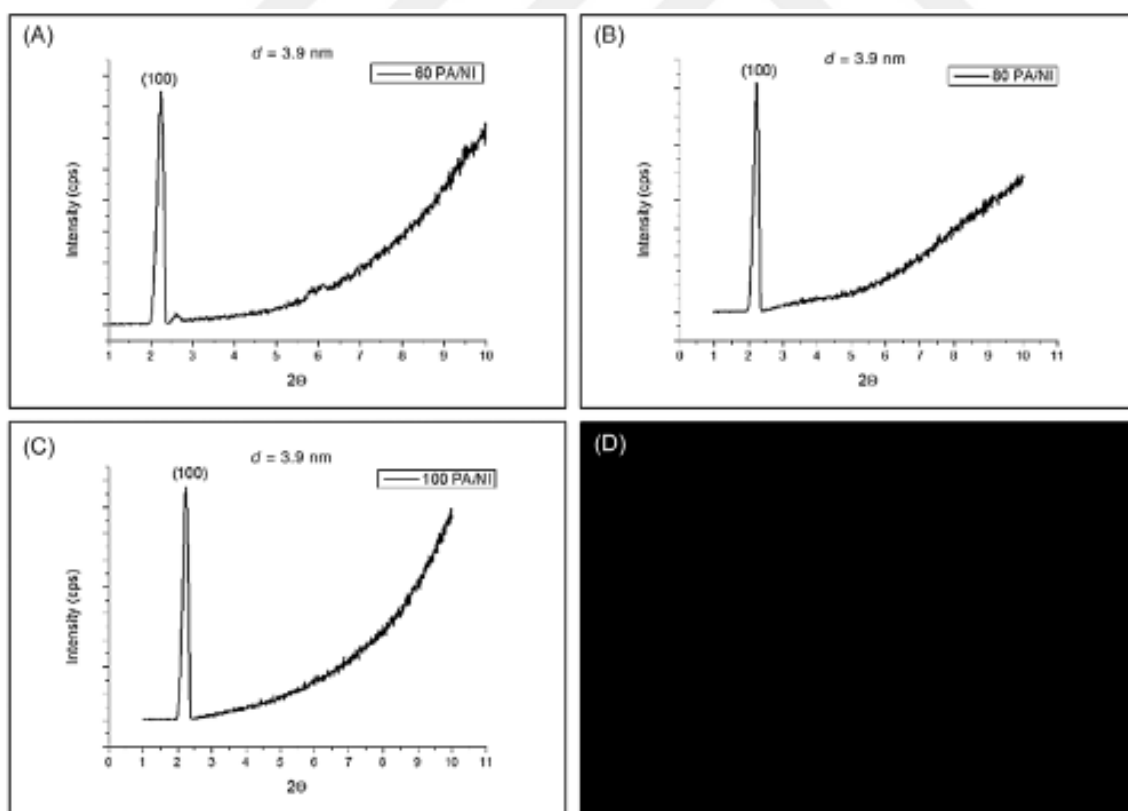


Figure 2.3: XRD patterns of (a) PA-NI60, (b) PA-NI80, and (c) PA-NI100. (d) Polarized optical microscopy images of all ratios of LC gels

The LC mesophase gel exhibited optimal working viscosity in the mole ratio of 60 to 100:1. Below the 60:1 mol ratio, the gel is too viscous to be used as an LC gel electrolyte. Moreover, based on the XRD pattern of the LC mesophases displayed in Figure 2.3, the LC gel forms a bicontinuous cubic phase at mole ratios of 60 to 100:1. The PA-NI samples diffracted at small angles, which is characteristic of LC gel formation. The mesophase was firm up to a PA:NI mole ratio of 100:1. The bicontinuous cubic mesophase had a lattice parameter of $d = 3.9$ nm, which was calculated using Bragg's law: $n\lambda = 2d\sin\theta$, where $\lambda = 0.15406$ nm, $\theta = 2.23$, and $n = 1$. The formation of a bicontinuous cubic mesophase for all mole ratios of the LC gel was confirmed by POM (Figure 2.3d).

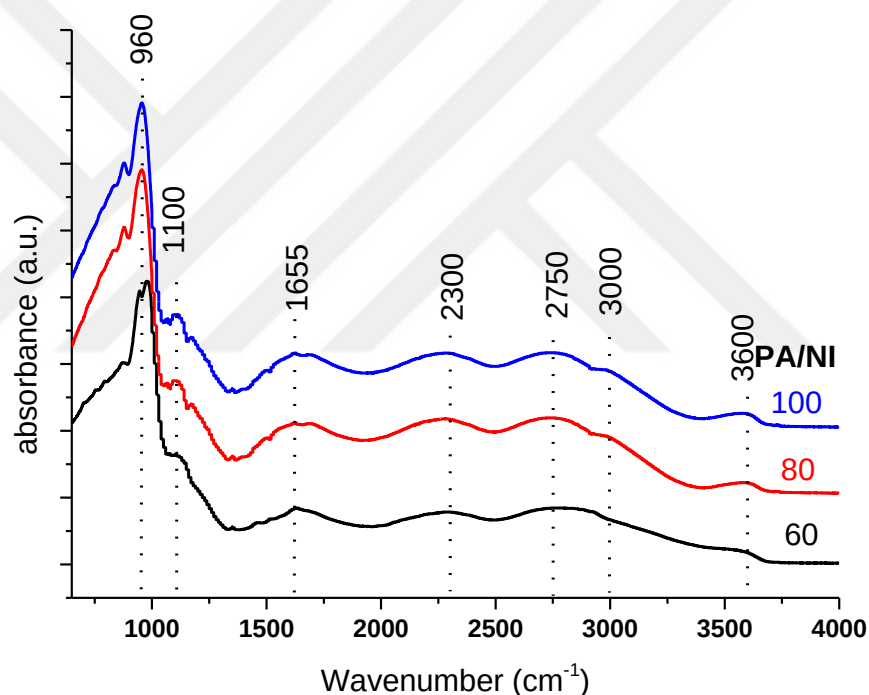


Figure 2.4: FTIR spectra of PA-NI60, PA-NI80, and PA-NI100

The PA-NI60, PA-NI80, and PA-NI100 samples were analyzed by FTIR spectroscopy at room temperature (Figure 2.4). As the PA concentration of the LC gels was very high, the overall spectra resembled the PA spectrum. The peaks at approximately 960 and 1100 cm^{-1} were due to the PA bending and stretching modes, respectively.[52], [56] The broad peak at ~ 1655 cm^{-1} was caused by the H_2O bending mode, and it was broadened most likely because of the protonation of water throughout the mesophase network.

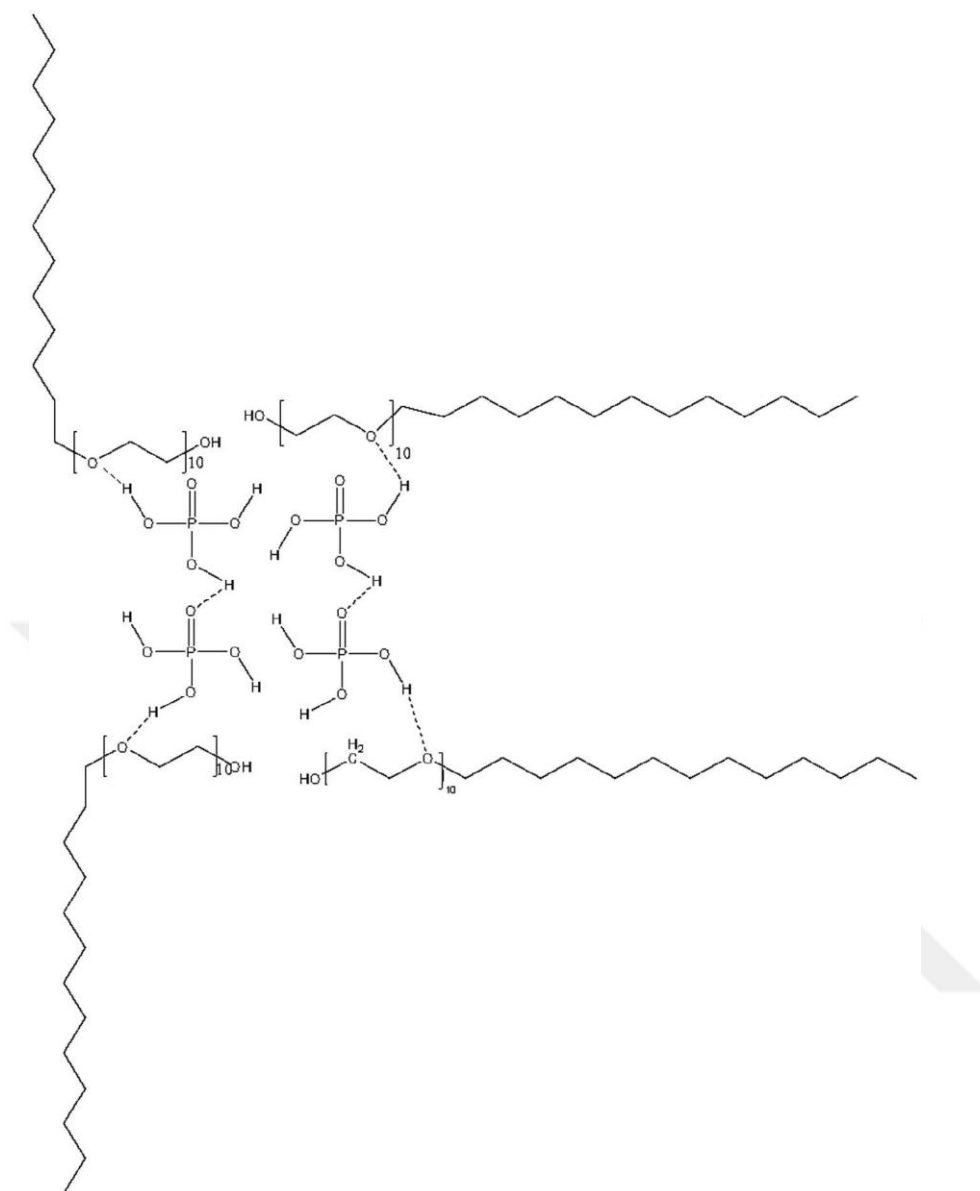


Figure 2.5: Hydrogen-bonding network

Hydrogen bonding probably occurred between the PA and oxygen of the ethoxy groups of NI, and also between the PA molecules (see Figure 2.5), which causes broadening of the FTIR peaks. The peaks at 2300, 2750, 3000, and 3600 cm^{-1} originated from the several stretching modes of PA, with the H_2O S stretching vibrations spanning entire PA- H_2O network [52], [56] . The peak at 2750 cm^{-1} originated from the CH and CH_2 stretching modes of NI.



Figure 2.6: LC gel electrolyte split cell

The fabrication process of the supercapacitor described in the previous section is illustrated in Figure 2.6. The electrodes, electrolyte, and separator layers were simply pressed together in the split cell to form the supercapacitor. The LC PA:NI mole ratio was adjusted by carrying out numerous electrochemical analyses using rGO-coated graphite foam electrodes in two-electrode cells. Here, we chose to use two-electrode-cell configurations because they provide more realistic results than the three-electrode measurement systems.

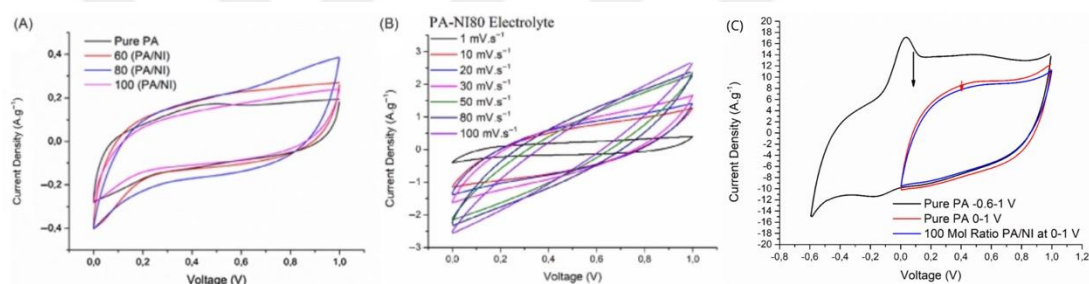


Figure 2.7: (a) Cyclic voltammograms of the LCs and pure PA in different molar ratios at a scan rate of 1 mV s⁻¹. (b) Electrochemical performance of LC gel prepared with the 80:1 PA:NI mole ratio measured at various scan rates (c) Cyclic voltammograms obtained in a three-electrode measurement configuration

Electrochemical performance of rGO-coated graphite electrodes was examined using either the LC gel or pure PA electrolyte. In concentrated H₃PO₄ ($\approx$ 85 wt %), auto-dissociation generates two functionally distinct ion streams. The highly mobile protons, H⁺, shuttle along the acid's extended hydrogen-bond network via the Grotthuss mechanism and accumulate at the negatively polarized rGO surface, imparting the gel with its outstanding ionic conductivity and virtually negligible iR-drop. The accompanying, bulkier phosphate anions—predominantly H₂PO₄⁻ with minor HPO₄²⁻ and polyphosphate species—migrate more slowly toward the positive electrode, where they uphold electroneutrality, locally buffer pH, and assemble a compact Helmholtz layer that suppresses parasitic gas evolution. The complementary roles of these cation–anion fluxes enable rapid charge

compensation, extend the safe operating window, and ultimately underpin the unusually high specific capacitance observed in the PA-based bicontinuous-cubic gel cells. As shown in Figure 2.7, PA exhibited a pseudocapacitive effect of around 0.45 V. However, when PA was mixed with lauryl ether, the peak at 0.45 V disappeared. This indicates that the liquid crystal agent suppresses the pseudocapacitive reaction. This effect was also observed in the three-electrode measuring system. Moreover, the formation of LCs did not result in any notable alterations in the voltammogram characteristics. It is clear that with the addition of LC, the operating voltage range did not shift, and an additional peak was not observed. This indicates that the LC is inert within the predicted super- capacitor operating voltage range and does not undergo a further electrochemical reaction. Moreover, CV measurements indicated that the LC gel electrolyte provides one significant contribution, that is, capacitive improvement; this is typical for electric double-layer capacitors (EDLCs), and is related to the non-Faradaic charges between the porous electrode and electrolyte. The main reason for this is that the LC gel located at the electrode- electrolyte interface allows the ions to move in a more controlled manner thereby suppressing parasitic Faradaic side-reactions, damping local pH fluctuations, and preventing proton-induced surface etching that would otherwise accelerate electrode degradation. In neat PA, the unrestricted proton flux facilitates rapid redox micro-cycling at defect sites, progressively roughening the graphene surface and shortening device lifetime. Embedding the acid within the bicontinuous LC matrix imposes nanoscale tortuosity on the transport pathways, acting as a quasi-solid-electrolyte interphase that equalises charge-compensation kinetics, stabilises the electric double layer, and preserves capacitive performance over extended cycling. The $C_{s(CV)}$ data for the different electrolytes were calculated using cyclic voltammetry. The $C_{s(CV)}$ of the electrolyte containing no LCs was 942 F g^{-1} , while PA-NI60, PA-NI80, and PA- NI100 exhibited $C_{s(CV)}$ values of 1138, 1263, and 854 F g^{-1} , respectively.

CV window was confined to 0–1 V because, in aqueous proton-conducting electrolytes such as the PA–NI gel, water splitting becomes appreciable as the cell potential nears the thermodynamic stability limit of water ($\sim 1.23 \text{ V}$). Practical work on acidic aqueous supercapacitors therefore limits operation to $\approx 1.0 \text{ V}$ to suppress gas evolution, avert pH shifts, and preserve coulombic efficiency and

electrode integrity; even strongly acidic systems fail rapidly above 1.0–1.3V. Restricting the sweep to 0–1V keeps each rGO electrode within the electrochemically inert potential range of graphene, maintains the high proton mobility of the phosphoric-acid/Ni bicontinuous cubic network, and ensures purely capacitive, rectangular CV traces. Extending the window to 1.2–1.3 V would contribute negligible extra capacitance yet would trigger oxygen evolution, increase the ohmic (iR) drop, accelerate surfactant degradation, and markedly shorten cycle life. Accordingly, 0–1 V represents the optimal balance between energy density and long-term electrochemical stability for the PA–Ni electrolyte.

PA-Ni80 exhibited the largest CV curve area, indicative of the highest $C_{s(CV)}$. As observed from the CV curve area in Figure 2.7a, the capacity decreased both above and below this optimum amount. Cyclic-voltammetry demonstrates that incorporating the non-ionic surfactant at a 100 : 1 PA : Ni mole ratio preserves the ideal rectangular 0–1 V window of neat phosphoric acid while eliminating the small pseudocapacitive peak that appears at ≈ 0.45 V in pure PA (Figure 2.7c). The optimised bicontinuous-cubic PA-Ni80 gel, interposed between high-surface-area rGO electrodes, maintains this rectangular profile across scan rates of 1–100 mV s^{-1} (Figure 2.7b), with peak current scaling almost linearly with sweep rate—clear evidence of dominant double-layer charging. Three rate-dependent regimes emerge: at 1 mV s^{-1} protons fully percolate the 3.9 nm channels, yielding a gravimetric capacitance of 1263 F g^{-1} (1128 F g^{-1} at 0.1 A g^{-1}) and an energy density of ~ 39 Wh kg^{-1} ; between 5 and 30 mV s^{-1} the voltammogram remains rectangular but the integrated charge plateaus, signalling the onset of mild diffusion control; and above 50 mV s^{-1} the curves contract into a spindle yet remain free of new Faradaic features, providing rapid sub-second charge–discharge at a modest loss in capacitance. Electrochemical-impedance analysis of the PA-Ni80 cell ($R_s \approx 36 \Omega$, $R_{ct} \approx 4 \Omega$) confirms that charge-transfer resistance stays low while series resistance remains acceptable, underscoring that scan rates $\leq 10 \text{ mV s}^{-1}$ maximise energy whereas $\geq 50 \text{ mV s}^{-1}$ prioritise power without compromising chemical stability.

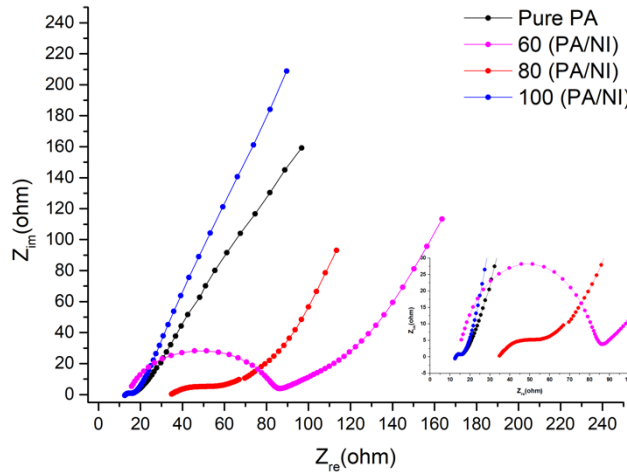


Figure 2.8: Electrochemical impedance spectra of LCs and pure PA at different molar ratios in the frequency range of 100 000 to 0.01 Hz and the elements in the equivalent electrical circuit model for the supercapacitor

The CV results were verified using EIS tests (Figure 2.8). The Nyquist plots indicate that the combination of the rGO on the working electrode and the gel electrolyte can affect the equivalent series of resistance (R_s and R_{ct}), and hence, the electrochemical performance of the corresponding supercapacitor system. A semicircle appeared on the EIS spectra in the high frequency region, while a straight line appeared in the low frequency region. Moreover, the plots showed a smaller semicircular diameter, a smaller ohmic resistance, and rapid charge transfer in the high-frequency field. The line in the high resistance region indicates a proper capacitance action with rapid ion transfer in the electrolyte. This confirmed the supercapacitor cell's capacitive nature, arising from the diffusion of ions through the active materials. The equivalent circuit was used to fit the obtained EIS spectra. Due to the incomplete and slightly elongated semicircle, double-layer capacitance (C_{dl}) is connected in parallel with the charge transfer resistance (R_{ct}) in the equivalent circuit. The capacitor with R_s was placed in series to model the series intercalation capacitance C_p . [57], [58] Therefore, in order to detect the diffusion process of ions into the electrode, a Warburg element W was placed in the equivalent circuit. The electrochemical impedance data of the rGO | PA-NI lyotropic-gel supercapacitor were fitted with the extended Randles circuit $R_s - (C_{dl} || R_{ct}) - W - C$. This five-element scheme is the simplest that still recreates—and physically explains—every feature of the Nyquist plot. The high-frequency intercept is set by the uncompensated ohmic resistance of the gel

electrolyte, porous electrodes, current collectors, and leads, and is therefore represented by the series resistor R_s . The slightly depressed semicircle that follows stems from simultaneous double-layer charging on accessible rGO surfaces and a residual, kinetically limited pseudocapacitive redox reaction; this composite response is captured by the parallel pair $Cdl||R_{ct}$. At mid-frequencies the spectrum tilts into an $\approx 45^\circ$ line, signalling proton diffusion through the 5–15 nm mesopores of rGO and the 3.9 nm bicontinuous nano-channels of the cubic gel phase; the frequency-dependent impedance of this transport process necessitates inclusion of the finite Warburg element W . Finally, in the low-frequency limit the curve rises almost vertically, indicating that all charge-storage sites have equilibrated and the cell behaves as an ideal capacitor; the series capacitor C was added to ensure the model reflects the fully capacitive behavior seen at very low frequencies. Simpler circuits (e.g., R_s-C or $R_s-Cdl||R_{ct}$) fail to represent the full shape of the Nyquist plot because they cannot capture the gradual capacitive buildup at low frequencies. The additional capacitor C was specifically introduced to model this slow, long-timescale charge storage process, which becomes significant only after ion diffusion and double-layer formation are complete. On the other hand, more complex circuits add too many parts without making the results clearer or more accurate. Consequently, the chosen five-element circuit is both parsimonious and physically meaningful, yielding parameters (R_s , R_{ct} , W , Cdl , C) that quantitatively track the compositional optimisation and underpin the electrochemical analysis presented herein. Additionally, correlating these fitted parameters with complementary CV and GCD diagnostics affords a predictive framework for assessing rate capability and long-term cycling stability across the optimised formulations. The extracted R_s and R_{ct} values are summarised in Table 2.1.

Table 2.1: Ohmic and charge transfer resistance of supercapacitor cells

Mole ratio of PA–NI gel	R_s (Ω)	R_{ct} (Ω)
Non-gelled electrolyte (pure PA)	12.94	2.901
60	16.65	58.45
80	36.21	4
100	13.41	2.5

The ionic conductivity of the electrolyte is an imperative parameter for the efficient operation of a super-capacitor cell. However, the absence of an NI at the solid-liquid interface increases self-discharge, resulting in a low discharge capacity, which can cause the electrodes to deteriorate quickly.

The LC is active at the electrode- electrolyte interface, providing a more controlled penetration of the ions on the electrode surface. However, the use of NI in quantities above the optimal amount degrades the interaction between the electrode and electrolyte and results in a decrease in system performance. The results of CV, EIS, and GCD analyses confirmed this. There was an initial increase in $R_s + R_{ct}$ (40.21 Ω) with increasing mole ratio due to the formation of the necessary limitation at the electrode-electrolyte interface. In this manner, the CV curves of the cell containing PA- NI80 electrolyte showed the highest capacity. Similarly, an increase in the equivalent series resistance was observed as a voltage drop in the discharge curves; however, there was a significant increase in the discharge capacity. [59]

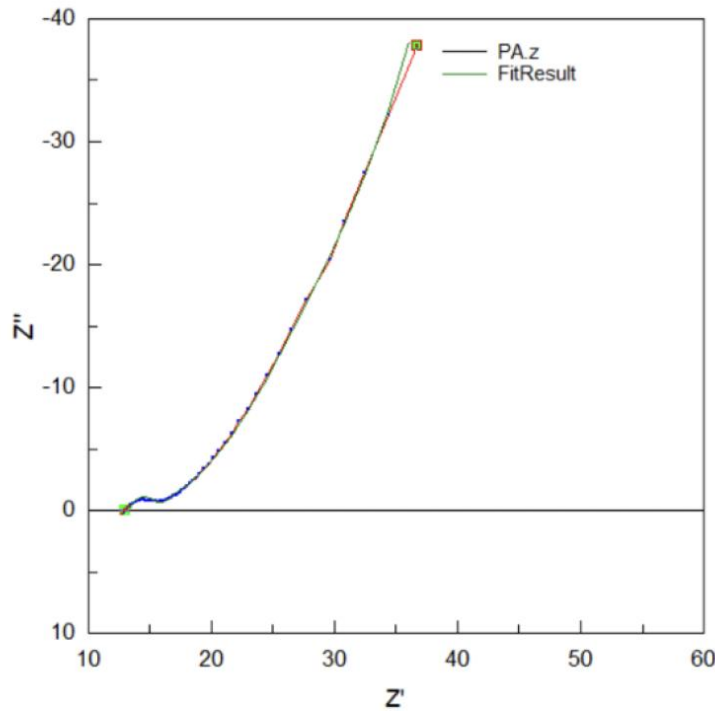


Figure 2.9: Nyquist plot of the rGO | 85 wt % H_3PO_4 | rGO cell with extended-Randles fit; $R_s-(Cdl||(R_{ct}+W_s))-C$ accurately captures charge transfer and proton diffusion.

EIS measurements performed for supercapacitor cells allowed us to interpret the ionic conductivity of LCs with different mole ratios. As expected, the highest total

resistance ($R_s + R_{ct}$) was obtained in the system containing the highest percentage of NI, whereas the lowest value was determined for the pure PA system. The $R_s + R_{ct}$ value of the PA-NI100 was very close to that of pure PA.

The high ionic conductivity values are most likely due to the strong hydrogen bonding between PA and the ethoxy groups of NI and among the PA molecules. Thus, it was deduced that the PA-NI80 LC prepared had excellent ionic conductivity. Proton conduction through the LC gel electrolyte most likely occurs by the hopping mechanism of hydrogen ions via hydrogen bonds (Grotthuss mechanism). [60] Figure 2.9: confirms that the extended-Randles circuit $R_s - (Cdl \parallel (R_{ct} + W_s)) - C$ reproduces the measured Nyquist plot almost perfectly, accurately capturing both charge-transfer kinetics and semi-infinite proton diffusion in the neat H_3PO_4 -filled rGO||rGO cell.

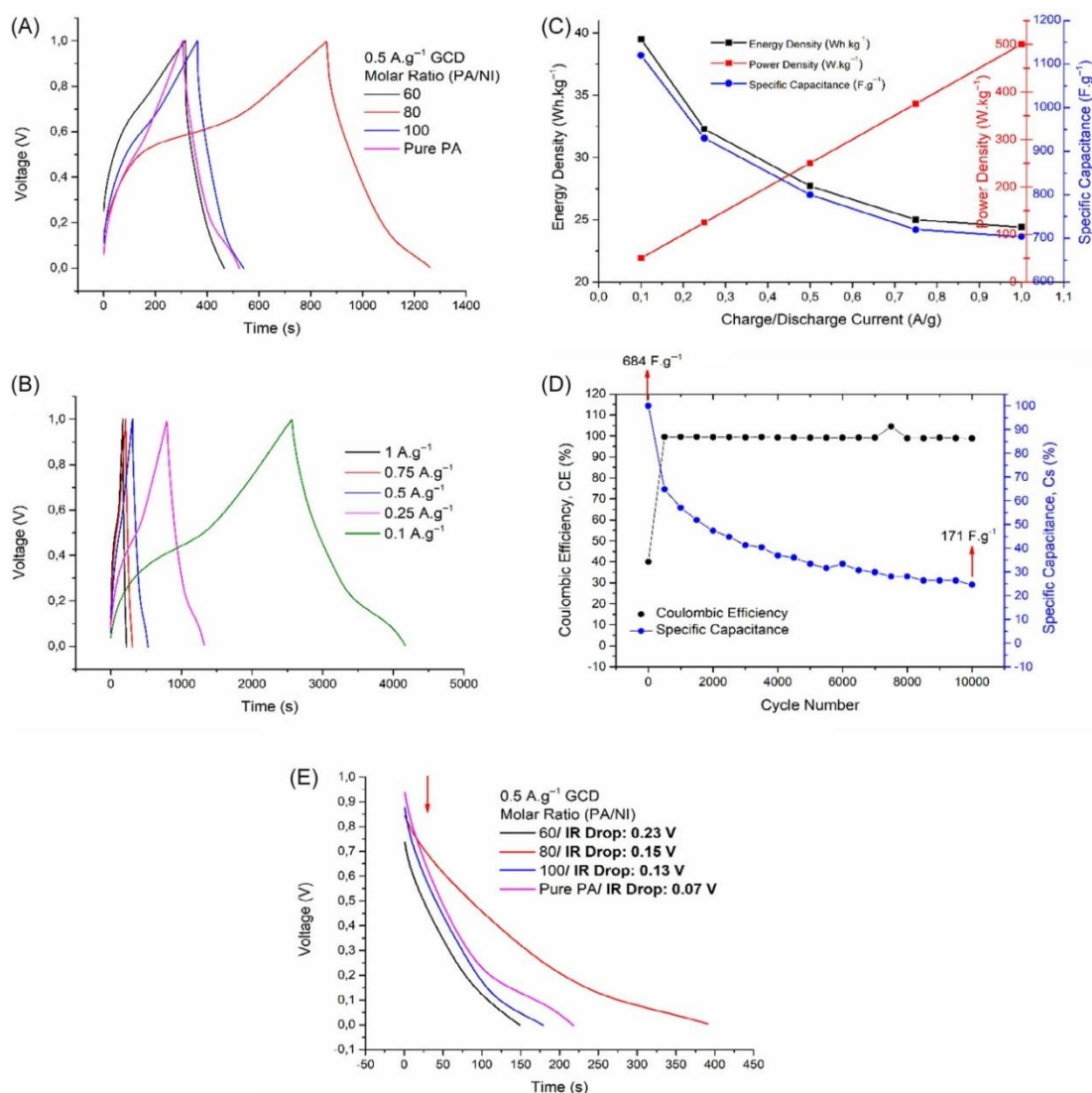


Figure 2.10: (a) GCD profiles of supercapacitor cells containing pure PA, PA-NI60, PA-NI80, and PA-NI100. (b) GCD profile of PA-NI80 measured at various current densities. (c) Energy density, power density, and specific capacitance obtained at different current densities from the system with PA-NI80 electrolyte. (d) Cycling stability of supercapacitor cell prepared with PA-NI80 electrolyte. (e) Discharge curves and voltage drop for supercapacitor cells containing pure PA, PA-NI60, PA-NI80, and PA-NI100.

Figure 2.10a shows the GCD profiles of gel electrolytes containing PA and LCs at different ratios at 0.5 A g⁻¹. The GCD curves had an approximately symmetrical triangular shape, indicating fast, sequential reversible pseudocapacitive reactions on the electrodes. This indicates that there are pseudocapacitive effects originating from the PA electrolyte. The use of non-ionic surfactants for the preparation of electrolytes did not change their working potential. This is because PA acts as an active ion source. For this reason, measurements in all CV and GCD tests were performed in the 0 to 1 V range. Thus, all electrolytes were tested at the same

operating voltage ranges. As a result of the GCD tests performed at 0.1 A g^{-1} , the electrolyte that contained only pure PA exhibited a C_s of 644 F g^{-1} . The C_s of PA-NI60, PA-NI80, and PA-NI100 were 760, 1128, and 700 F g^{-1} , respectively. Specific capacitance values calculated by GCD tests confirm the specific capacitance data calculated by cyclic voltammograms. Because PA-NI80 showed the best performance in all electrochemical tests, it was considered the optimal composition, and further analysis was performed using this electrolyte.

The C_s of the supercapacitor using the PA-NI80 electrolyte was larger than those using pure PA and gel electrolytes with other mole ratios; the larger C_s value can be attributed to the optimal wettability and the more controlled diffusion of PA-NI80. PA-NI80 also exhibits higher ohmic resistance than pure PA. It is clear that the highest charge-discharge capacities were obtained with PA-NI80, confirming the CV results. In addition, the R_s and R_{ct} values determined by EIS for PA-NI80 were considered optimal for this system. In this manner, the high-mole-ratio gel structures (PA-NI100) lead to an increase in the ionic conductivity, which results in corrosion and degradation of the electrodes. A very high specific capacitance was observed while using the pure PA electrolyte. However, since the ionic conductivity of PA is very high, and the ions in the electrolyte can easily penetrate the electrode surface, we assumed that confining the electrolyte in a gel structure could increase the specific capacitance; however, a large amount of NI may be required. The use of more than the required amount of NI increases the internal resistance provided by the electrolyte. Consequently, limiting the ion mobility leads to specific capacitance loss. Thus, the expected increase in specific capacitance was not observed with the use of PA-NI60. When the molar ratio of PA to NI dropped below 60:1, the high viscosity of the LC gel electrolyte made it impossible to assemble a supercapacitor cell. Therefore, GCD tests at different current densities were performed using PA-NI80, as shown in Figure 2.10. The curves showed approximately nonlinear supercapacitor behavior as a result of the pseudocapacitance of the charge-storage process.

Furthermore, the E and P values of a supercapacitor with the PA-NI LC gel electrolyte and rGO electrodes were calculated using Equations (2.2) and (2.3) as 24.4 Wh kg^{-1} and 499.9 W kg^{-1} , respectively, at 1 A g^{-1} current density. In comparison with lithium-ion batteries, supercapacitors usually have high P ;

however, their E values are almost 10 times lower than those of batteries.[61] Here, the E of the supercapacitor is relatively high compared with that of common symmetric EDLC supercapacitors. To further increase the E of the LC gel supercapacitor, it can be combined with asymmetrical electrodes in a pseudocapacitor, which is known to have higher E values than symmetrical supercapacitors. The E and P plots of the supercapacitor cell with the highest performance are shown in Figure 2.10. The C_s , E , and P attained at 0.1 A g^{-1} were 1128, 39.1, and 50 W kg^{-1} , respectively. As expected, E decreased, and P increased with growing current density. In the GCD tests performed at the highest current densities, P reached approximately 0.5 kW kg^{-1} , while E was 39.1 Wh kg^{-1} measured at the lowest current density. The results obtained for the supercapacitor cell with the best performance demonstrated that E of the system was similar to those of battery systems. After 10 000 GCD tests at 0.5 A g^{-1} , the cell through PA-NI80 showed decent cycling stability. It offered a specific capacitance, C_s of 684 F g^{-1} in the first cycle. The assembly of the electrodes remains undamaged despite of minor capacitance losses over 10 000 cycles. The C_s of the 10 000th cycle is 171 F g^{-1} . This shows that the electrolyte offers very high performance even after 10 000 cycles of use. On the other hand, coulombic efficiency (CE) was 40% at the beginning, but after reaching the 500th cycle, it increased above 99% and continued at this level until 10 000 cycles.

The $\approx 75 \%$ capacitance decline measured after the 10 000 cycles is attributable chiefly to degradation of the PVDF binder in the thick rGO/carbon electrodes. First, PVDF's hydrophobic, electrically insulating chains partially obstruct the 3.9 nm phosphoric-acid nano-channels, leaving 'dead' surface regions within the high-mass-loading electrode and increasing internal resistance. Second, prolonged exposure to concentrated H_3PO_4 causes the binder to swell, soften and eventually lose adhesion, which raises contact resistance and electrically isolates rGO flakes. This binder instability is especially detrimental at mass loadings at higher mass loadings, where limited electrolyte penetration further impedes ion transport and accelerates performance fade. Finally, gradual dehydration-shrinkage of the PA-NI gel and cyclic mechanical stress within the composite layer promote micro-crack formation that interrupts both electronic and ionic pathways. Together, these coupled mechanisms progressively reduce the accessibility of

charge-storage sites, leading to a substantial decline in effective capacitance over long-term cycling. Galvanostatic cycling of the optimised PA–NI80 cell starkly illustrates the cumulative impact: specific capacitance falls from 684 F g⁻¹ in the first cycle to just 171 F g⁻¹ after 10 000 cycles at 0.5 A g⁻¹, amounting to a ~75 % loss of active charge-storage capacity.

Capacitance declines rapidly with extended cycling durations. Impedance spectroscopy registers escalating resistance as intra-electrode conductive pathways progressively fracture over time. This increased resistance amplifies the iR-drop during discharge, diminishing deliverable power and energy density significantly. Accordingly, reinforcing electrode–binder adhesion remains paramount for durable, long-lasting device operation and reliability.

Table 2.2: Performance comparison of different carbon-based electrodes

Electrode	Electrolyte	Specific Capacitance (F·g ⁻¹)	Test Configuration	Current density (A·g ⁻¹)	Ref
Carbon from cornhusk (agricultural waste)	Seawater	130	Two electrodes	0.5	[62]
Green needle coke-derived porous carbon	1 M Na ₂ SO ₄	274.9	Two electrodes	1	[63]
N-doped carbon	0.5 M H ₂ SO ₄	202	Two electrodes	3	[64]
Graphitic carbon nitride graphene hybrids	1 M H ₂ SO ₄	265.6	Three electrodes	1	[58]
Gelatin-derived nitrogen-doped porous carbon	6 M KOH	248.1	Three electrodes	1	[23]
Porous electro-reduced graphene oxide on Cu wire (pErGO)	PVA/H ₃ PO ₄ gel (solid-state)	81 ± 3	Symmetric two-electrode (wire-shaped)	0.5 A g ⁻¹	[65]

Table 2.2 (continued): Performance comparison of different carbon-based electrodes

Electrode	Electrolyte	Specific Capacitance (F·g ⁻¹)	Test Configuration	Current density (A·g ⁻¹)	Ref
rGO/H _x PO _y hybrid film (acid-intercalated graphene)	1 M H ₃ PO ₄ (aq)	104.4	Symmetric two-electrode (film)	0.25 A g ⁻¹	[66]
Graphite carbon paper	PVA/H ₃ PO ₄ gel	312.4	Symmetric two-electrode (planar)	0.5 mA cm ⁻²	[67]
rGO	80:1 mole ratio PA-NI	1128	Two electrodes	0.1	This study

To sum up, with the LC gel electrolyte developed in this study, superior electrochemical test results were obtained as compared with the supercapacitors in the literature shown in Table 2.2. Capacitance declines rapidly with extended cycling durations. Impedance spectroscopy registers escalating resistance as intra-electrode conductive pathways progressively fracture over time. This increased resistance amplifies the iR-drop during discharge, diminishing deliverable power and energy density significantly. Accordingly, reinforcing electrode–binder adhesion remains paramount for durable, extended-life device operation and reliability. Figure 2.10e shows the discharge curves obtained using different electrolyte compositions and the resulting voltage drops. The highest voltage drop was obtained with the electrolyte system containing the highest amount of LC (60:1 mol ratio of PA/NI). The lowest voltage drop was obtained with the electrolyte containing only PA. These findings align closely with equivalent circuit resistance records gained from EIS. In the symmetric rGO || rGO cell incorporating the bicontinuous-cubic PA–NI₈₀ gel, cyclic-voltammetry delineates three scan-rate regimes. Up to $\approx 30 \text{ mV s}^{-1}$ the CV loops remain virtually rectangular, showing that protons fully traverse the 3.9 nm bicontinuous channels; the specific

capacitance exceeds $1.2 \times 10^3 \text{ F g}^{-1}$ and ohmic distortion is negligible. Between ≈ 30 and 50 mV s^{-1} the voltammetric area plateaus, the rectangles contract and tilt, and a 45° tail emerges—classical evidence of diffusion-limited charging—while the summed series + charge-transfer resistance rises toward $\sim 40 \Omega$. At 100 mV s^{-1} ion transport stands largely confined to the outer rGO shallow, the capacitance falls significantly from its low-rate value (exact retention not quantified) value, and a pronounced iR-drop appears in galvanostatic traces. These high-rate losses occur because the ions cannot move fast enough through the gel to keep up with the rapid voltage changes, rather than due to any unwanted chemical reactions.

2.3 Conclusions

This study showed that the high ionic conductivity of PA- NI LC mesophase gels make them suitable electrolytes for advanced supercapacitors. Stable LC mesophase gel electrolytes were developed using PA and NI at mole ratios ranging from 60 to 100:1, which facilitated the formation of the LC gel mesophase. A bicontinuous LC mesophase was formed at all mole ratios with a lattice distance of 3.9 nm, as determined by XRD and polarized optical microscopy. This new type of gel electrolyte showed superior electrochemical supercapacitor performance at the PA:NI mole ratio of 80:1 with a high C_s of 1128 F g^{-1} . The C_s was 684 F g^{-1} in the initial cycle and decreased to 171 F g^{-1} after 10 000 cycle at 0.5 A g^{-1} . The formation of an LC gel mesophase is the reason for the high electrolyte performance. The high ionic conduction for the LC electrolyte is thought to originate from the hydrogen bonds formed throughout the electrolyte via the Grotthuss mechanism (hydrogen hopping). The highest energy density measured for the LC gel electrolyte supercapacitor with rGO electrodes was $\sim 39.1 \text{ Wh kg}^{-1}$.



3. UNDERSTANDING THE ROLE OF WATER IN THE LYOTROPIC LIQUID CRYSTALLINE MESOPHASE OF HIGH-PERFORMANCE FLEXIBLE SUPERCAPACITOR ELECTROLYTES USING A RHEOLOGICAL APPROACH²

Water's influence on the structural framework, properties, and overall adaptability of C₁₂E₂₃-LiCl-H₂O gel electrolytes were examined. Structural probes like XRD and POM, combined with dynamic tests, were employed to evaluate the rheological attributes of the LLC mesophase under a range of hydration conditions. The studies yielded quantitative insights into how water proportion and LiCl level influence gel robustness, gelling threshold, and overall structural rebound. The gel's 3-D network traps Li⁺ and Cl⁻ ions within its hydrophilic regions, demonstrating considerable potential for use in supercapacitors. The increase in storage modulus observed as the water content diminishes is associated caused by changes in both junction-point count and mean dimension as the network progressively entangles. The study's results emphasize that an overabundance of water molecules, which disrupt micellar bonds, leads to the gel's weakening. In contrast, when water concentrations are low, the micellar regions become intertwined, exhibiting viscoelastic properties similar to those of a temporary polymer network. Wearable technology, including smartwatches, health trackers, and electronic textiles, has catalyzed the evolution of flexible wearable gadgets. Furthermore, recent breakthroughs in wearable and implantable medical electronics have driven development of power modules that scavenge bodily energy produced through daily respiration, sweat secretion, muscular activity, and physical motions. Supercapacitors are considered ideal for wearable applications owing to their durability, high power output, and adaptability to miniaturization [4]. Supercapacitors

² This chapter was published in “Özkaynak, M. U., Kocaaga, B., Dönmez, K. B., Dağlar, S., Türker, Y., Karatepe, N., Güner, F. S., & Dag, Ö. (2024). Understanding the role of water in the lyotropic liquid crystalline mesophase of high-performance flexible supercapacitor electrolytes using a rheological approach. *Journal of Molecular Liquids*, 394, 123705.”

offer optimal suitability in applications including hybrid electric vehicles plus efficient energy backup systems[5].

The electrochemical performance of supercapacitors may degrade because of their poor mechanical properties, which limit their application in flexible devices [6]. Reliable flexibility, shape adaptability, moldability, and self-healing properties play a critical role in the performance and multifunctionality of flexible electronic devices [20], [24], [25]. The flexibility and self-healing properties endow supercapacitors with a variety of shapes, light weight, and strong deformation abilities and extend their life [16], [17], [18], [21].

An electrolyte is an essential part of a supercapacitor and supplies ionic conduction between the anode and the cathode. The current flows through the electrolyte between the two electrodes, charging or discharging the supercapacitor. Generally, electrolytes are classified according to their ionic conductivity, working-temperature range, stability, operating voltage range, and safety [7]. The development of highly conducting electrolytes is important for optimizing the performance of supercapacitors[8]. However, in recent years, it has been shown that rheological properties have a significant effect on supercapacitor performance[9], [22], [68].

Various acids, bases, and salts have been used as ion sources for electrolytes. H_3PO_4 , KCl , KOH , and H_2SO_4 have been widely used as ion sources for aqueous electrolytes. Tertiary butyl-ammonium salts are commonly used as the organic electrolytes[69]. Aqueous and non-aqueous electrolytes of LiCl , LiClO_4 , LiOH , Li_2SO_4 , and LiPF_6 salts have excellent compatibility with various porous electrodes owing to the small size of Li ions, expanding their application in capacitors and batteries [70]. Yet, fluid electrolytes present drawbacks when constructing bendable supercapacitor devices effectively. Since solid electrolyte conductivity remains inadequate, and liquid variants suffer leakage or evaporation issues, gel-based options become preferable choices for flexible devices. Many liquid electrolytes are hazardous and corrosive, demonstrate poor durability, and demand costly enclosures when producing flexible electrochemical capacitors for industry. Thus, solid-state electrolytes are vital here due to their superior ionic conductivity, broad voltage tolerance, robust mechanical strength, and outstanding cycle life under operation. [69].

Various lithium salts and acids have been previously shown to form lyotropic liquid crystalline (LLC) mesophases (gels)[71], [72], [73], [74] with oligo(ethylene oxide)-type nonionic surfactants and have already been employed in different energy-storage systems with good performance [30], [73], [74], [75]. An LLC mesophase comprises two main components: an amphiphile (surfactant) and solvent (water and aqueous salt solutions). LLC mesophases of aqueous alkali metal salts have superior physical properties such as good thermal stability, high ionic conductivity, and nonvolatility [73], [75], [76]. Moreover, oligo (ethylene oxide)-type surfactants have self-healing properties because they exhibit shear-thinning properties owing to the dynamic nature of hydrogen bonds, which allows the network to provide viscous flow and autonomously revert to solid-like behavior when the stress is removed [77].

Rheological tests effectively explore gelation behavior in thorough detail. Viscosity and dynamic modulus relate directly to the physical and mechanical traits of the gel during manufacturing and operational processes in practice.

Dag et al. demonstrated that LiCl salts could form highly ordered mesostructured liquid crystalline gels [71], [72]. According to these studies, overconcentrated aqueous LiCl solutions can form highly ordered mesostructured liquid crystalline gels with nonionic surfactants. The aqueous solution acts as a solvent in the assembly of 10-lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{10}OH$, abbreviated as $C_{12}E_{10}$), in which a highly concentrated electrolyte solution can be considered as a molten salt. A strong ion-dipole interaction exists between the salt species and water molecules, in addition to a network of hydrogen bonds in the mesophase; the salt-water couple collaboratively acts as a solvent to form LLC mesophases [74], [75], [76], [77]. The liquid crystalline mesophase of the LiCl- $C_{12}E_{10}$ -H₂O mixture and any other salt-surfactant mesophase have not yet been implemented in an energy storage system.

Most researchers have focused on using inorganic and/or organic additives to improve the performance of gelated electrolytes. In this study, 23-lauryl ether ($C_{12}E_{23}$, $C_{12}H_{25}(OCH_2CH_2)_{23}OH$), LiCl, and H₂O were combined to prepare novel gel structures to overcome the disadvantages of conventional gel structures, thereby improving the physical and electrochemical properties and optimizing the overall performance of the gel electrolytes. Rheological measurements of the gel-electrolyte formulations containing different proportions of water were performed to optimize the mechanical properties. In this context, strain, frequency sweep, temperature sweep,

and creep recovery analyses were conducted. In addition, the shear thinning and self-healing properties were examined. The electrochemical performance of the gel electrolyte prepared by combining 23-lauryl ether, LiCl, and H₂O was evaluated by electrochemical and rheological characterization.

3.1 Experimental Part

3.1.1 Materials

LiCl, N-methyl-2-pyrrolidone (NMP), polyvinylidene fluoride (PVDF), carbon black, and used in this work were Sigma-Aldrich grade, and C₁₂E₂₃ (23-lauryl ether, C₁₂H₂₅(OCH₂CH₂)₂₃OH) was provided by JK Scientific and used as received with purities of 99% and above.

Olive waste was converted into activated carbon via controlled pyrolysis followed by chemical activation, wherein the precursor was heated under an inert atmosphere before treatment with activating agents. The resulting carbon functioned as a high-performance supercapacitor electrode, displaying excellent electrochemical behaviour and strong promise for energy-storage devices. Detailed electrode fabrication procedures are outlined in the Electrochemical Characterization section for reader reference therein.

3.1.2 Preparation of electrolytes

LiCl (0.106 g) was dissolved in different amounts (0.875, 1.000, 1.125, and 1.250 mL) of deionized (Milli-Q) water and stirred for 5 min to achieve homogeneity. Then, 0.5g C₁₂E₂₃ was added to each solution. Finally, the mixture was maintained at 80°C for 1 h. The gel samples were denoted as LC_x(H₂O), where x is the amount of water (Table 3.1).

Table 3.1: Formulation of gel structures.

Sample	LiCl (g)	LE (g)	H ₂ O (mL)
LC _{0.875} (H ₂ O)	0.106	0.5	0.875
LC _{1.000} (H ₂ O)	0.106	0.5	1.000
LC _{1.125} (H ₂ O)	0.106	0.5	1.125
LC _{1.250} (H ₂ O)	0.106	0.5	1.250

3.1.3 Structural characterization

A Rigaku Miniflex diffractometer equipped with a powerful Cu K α source, operating at 30 kV/15 mA, was employed to obtain X-ray diffraction (XRD) patterns. Room-temperature measurements were performed by spreading the samples on glass slides. The polarizing optical microscope (POM) images were captured using a ZEISS Axio Scope A1 POM in transmittance mode.

3.1.4 Rheological characterization

The rheological properties of the samples were investigated using an Anton Paar MCR rheometer with a 25 mm diameter plate and plate (PP) or cone and plate (CP) geometry and a Peltier temperature hood (H-PTD 200; $\pm 0.1^\circ\text{C}$). Viscotherm VT2 controls the temperature of the sample. The gap between the probe and samples was recorded at 1.3 mm distance in all measurements. The samples were heated to 80°C and allowed to melt completely for 5 min before being placed on a rheometer plate. During all the measurements, the samples were tightly sealed. All the experimental parameters are listed in Table 3.2.

Table 3.2: Experimental setup for rheological characterization.

Experiment	Measured parameters	Temperature ($^\circ\text{C}$)	Stress (Pa)	Strain (%)	Frequency (rad.s^{-1})	Time (min)
Strain sweep	G' , G'' , $\tan \delta$, LVE, gel point	25	-	0.1-1000	1	-
Frequency sweep	G' , G'' , $\tan \delta$, complex viscosity	25	1	1	1-100	-
Time sweep	G' , G'' , $\tan \delta$	25	1	1	1	30
Temperature sweep	G' , G'' , $\tan \delta$, gel point	-10 - +60		1	1	-
Thixotropy	G' , G'' , $\tan \delta$	25	-	1, 1000	1	12
Creep-recovery	Strain	25	10, 25	-	-	15
Stress relaxation	G/G_0 , relaxation time (τ)	-10, 25, 45, 60	-	1	-	16.6

3.1.5 Dynamic oscillatory measurements

Strain sweep tests were performed to determine the following: (i) linear viscoelastic range (LVE) or critical strain (γ_L), (ii) G' LVE, (iii) flow point, which is the strain (stress) caused by internal structure failure to the point, where the material flows (γ_f) ($G'=G''$), and (iv) the cross point of the elastic and viscous moduli (G_f).

Frequency sweep tests were performed to determine in the frequency range the slopes of the complex viscosity, elastic modulus (G'), viscous modulus (G''), and damping factor ($\tan \delta$) of the samples within the LVE region.

3.1.6 Time and temperature dependence

The effects of time and temperature on the elastic and loss moduli were determined within the range of the LVE. The heating/cooling rate for temperature sweep analysis was $1^\circ\text{C}\cdot\text{min}^{-1}$. During the temperature sweep analysis, the cryostat was filled with an antifreeze solution to avoid freezing Peltier pipes.

3.1.7 Thixotropic oscillation strain test

The thixotropic oscillation strain test was performed at a temperature of 25°C and frequency of $1\text{ rad}\cdot\text{s}^{-1}$ to evaluate the capacity of the sample for rapid self-healing. A low strain (1%) step was maintained for one minute at the beginning of the six-cycle test, followed by a high strain (1000%) step at the end of each cycle.

3.1.8 Creep-recovery analysis

Standard techniques for examining the transient viscoelastic characteristics of numerous materials include creep recovery and stress relaxation tests. These methodologies are employed to investigate time-dependent rheological behavior within the linear viscoelastic domain, with both approaches utilizing mechanical models in their respective analyses.(e.g., Kelvin–Voigt) for creep behavior.

For creep recovery assays, two constant shear stresses (25 Pa or 10 Pa) were applied for 300 s and then released. The strain was allowed to recover for 600 s and measured as a function of time during the creep and recovery phases. Dynamic rheological testing revealed that the applied shear stress (either 25 Pa or 10 Pa) was within the linear viscoelastic limit.

The stress relaxation modulus was recorded over time of the samples $LC_{1.000(H_2O)}$, $LC_{1.125(H_2O)}$ and $LC_{1.250(H_2O)}$ at -10, 25, 45, and 60°C. The specimens were maintained at the designated temperature for 15 minutes, subjected to a 1% strain, and subsequently, the stress relaxation patterns were recorded[16].

3.1.9 Electrochemical characterization

Electrochemical analyses were carried out utilizing a PARSTAT MC 1000 electrochemical workstation. A typical split cell (two-electrode measurement system) comprising an $LC_{1.25(H_2O)}$ electrolyte and two identical active carbon-coated current collectors as the working and counter electrodes was used to determine the electrochemical properties of the electrolyte at room temperature.

In a typical experiment, 35 mg of activated carbon, 5 mg of Polyvinylidene fluoride (PVDF), and 5 mg of carbon black were slowly dispersed in 1.5 mL of N-methyl-2 pyrrolidone (NMP) by ultrasonic treatment and maintained until the solution was completely dispersed. The dispersion was then dropped onto carbon foam and left at 70°C overnight to remove excess NMP on the electrode. A 1.2 cm diameter cellulose acetate filter membrane was soaked in the gel for 30 s, and the filter membrane was immediately assembled between identical electrodes to ensure no water loss. An asymmetrical supercapacitor cell was prepared from two 1.1-cm-diameter active-carbon-coated carbon foam electrodes.

Following cell sealing, the electrolyte underwent activation through a 50-cycle cyclic-voltammetry (CV) sweep. The procedure spanned -1 to +1 V at a scan speed of 25 mV s⁻¹. Once the cell attained zero open-circuit potential (OCV), potentiostatic electrochemical-impedance spectroscopy (EIS) was recorded using a 10 mV perturbation across 0.1 Hz–100 kHz. Subsequent CV and galvanostatic charge–discharge (GCD) experiments were implemented within a 0–0.5 V window to evaluate internal resistance, capacitance retention, and overall electrochemical stability under the chosen conditions throughout testing.

3.2 Results and Discussion

By combining 23-lauryl ether ($C_{12}E_{23}$), LiCl, and H_2O , novel gel structures were created to overcome the limitations of conventional gels and to improve the physical

and electrochemical properties of gel electrolytes. The mechanical properties of the gel-electrolyte formulations were optimized through rheological measurements, allowing adjustment of the water proportions. As a result, the novel gel electrolyte exhibited remarkable enhancements in physical and electrochemical performance, surpassing the capabilities of traditional gel structures. Electrochemical tests demonstrated the superior electrochemical performance of the gel electrolyte composed of 23-lauryl ether, LiCl, and H₂O. Furthermore, the gel exhibits intriguing shear-thinning and self-healing properties, indicating its potential for various applications in advanced electrochemical systems.

3.2.1 Structural characterization

XRD patterns of the liquid crystalline phase containing a 5.63 mol ratio of LiCl:C₁₂E₂₃ are shown in Figure 3.1a. The sequence of the XRD patterns of the liquid crystalline gel was recorded to demonstrate that no structural changes occurred during the water evaporation; a mesophase, prepared using 1.125 g water, lost water from ca. 25.1 down to 4-5 H₂O/LiCl for several hours under ambient XRD conditions. The fresh sample may have approximately 25 water molecules per LiCl and display weaker and relatively broader diffraction lines; however, with aging and water loss, the diffraction lines become sharper and well-resolved and can be indexed to a cubic system. There may be some shift in the diffraction lines with water evaporation, but this is minimal between the 10- and 30-min samples, with almost no change in the diffraction angles. The lines are observed at 0.93°, 1.49°, 1.89°, 2.00°, 2.25°, and 3.00°, 2 θ , and are indexed to the (110), (210), (220), (300), (311), and (420) planes of the cubic structure with a unit cell parameter of 13.2 nm. It was difficult to determine the water content during the XRD measurements; however, it was kept constant in all rheological measurements by sealing the samples. The LiCl/C₁₂E₂₃ molar ratio (5.63) was considered low for the salt-surfactant mesophase of such a large surfactant. For instance, LiCl-C₁₂E₁₀-H₂O (C₁₂E₁₀ is C₁₂H₂₅(OCH₂CH₂)₁₀OH) mesophases are 2D/3D hexagonal, even at much higher salt concentrations[71], [72], and a bicontinuous cubic phase is usually observed at high surfactant concentrations in liquid-crystalline mesophases. [78], [79]. However, C₁₂E₂₃ has a much longer polar (23 ethylene oxide units) head group than the short nonpolar alkyl chain (only 12 C, C₁₂H₂₅ units), making it more hydrophilic and forming spherical micellar domains that pack into cubic micellar mesophases. POM images also confirmed the formation of a cubic mesophase

at all water contents; they all appeared dark between the crossed polarizers (Figure 3.1b).

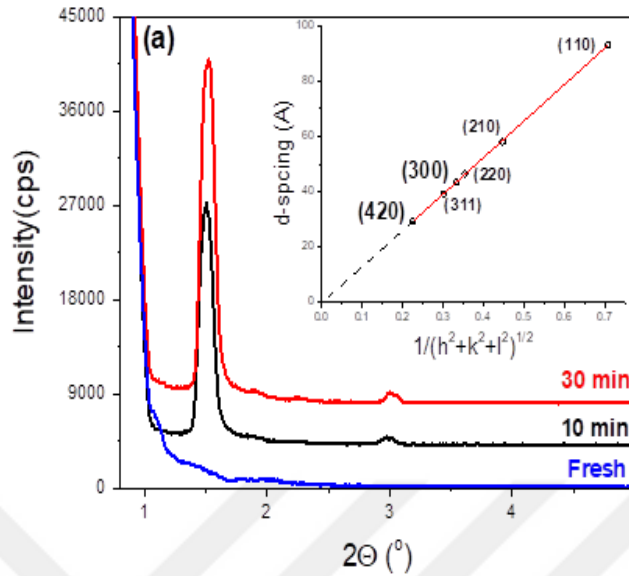


Figure 3.1: 5.63 LiCl:C12E23:1.125 g H₂O sample: aging-time-dependent XRD patterns (inset: plot of d-spacing versus hkl relation for cubic phase)

3.2.2 Rheological characterization

Oscillatory rheology measurements are widely used to investigate the viscoelastic behavior of systems. It is widely recognized that the frequency dependence of the storage and loss moduli of a system can differentiate between solids and liquids. Dynamic rheological tests within the linear viscoelastic range yielded three parameters: G' and G'' and the loss factor ($\tan \delta = G''/G'$). The G' value quantifies the elastic behavior of a sample by determining the deformation energy absorbed during shear. On the other hand, G'' measures the deformation energy consumed and subsequently lost by the sample during shear. Numerous variables, including concentration, temperature, degree of dispersion, dissolution, and electrical and ionic charges, affect the rheological characteristics of the structures[80], [81], [82].

The performance of these newly fabricated supercapacitors strongly relies on the device architecture precisely assembled from the mixture of 23-lauryl ether, LiCl salt, and water together. Excellent mechanical flexibility, shape adaptability, moldability, and self-healing properties play critical roles and high ionic conductivity in the performance and multifunctionality of flexible supercapacitors[17], [25]. The construction of flexible and robust electrolyte-electrode interfaces with excellent

mechanical properties and charge stability for robust electrolytes is vital. Therefore, detailed rheological analysis was performed to understand the relationship between the structure, mechanical properties, and flexibility of the gel structures. Although there is no chemical reaction between the gelling agent and the ion source, viscosity and elasticity changes can occur owing to electrostatic and hydrogen-bonding interactions. Molecular interactions (intermolecular or intramolecular) among gel species affect the dynamic properties of the final structure.

3.2.3 Strain sweep analysis

Strain-sweep testing routinely distinguishes a linear viscoelastic domain—where G' and G'' remain essentially constant under minor deformation—from nonlinear zones, where G' and G'' progressively fall while strain rises during large, dramatic shear-induced deformation events.

The results showed γ_f was significantly higher for $LC_{0.875H_2O}$ (3.18%), indicating greater stability under strain (Table 3.3). Whereas the flow points of $LC_{1.125H_2O}$ and $LC_{1.250H_2O}$ (1.22%) were smaller, $LC_{2.000H_2O}$ had the lowest flow point (0.289%), reflecting a very weak structure.

Table 3.3: γ_f , G' LVE and G'_f , damping factor ($\tan \delta$), temperature-induced gel point, and recovery (RS) of the elastic modulus after high strain of the gels.

Code	γ_f (%)	G'_{LVE} (Pa)	G'_f (Pa)	$G'_{0(f)} /$ $G''_{0(f)}$	$\tan \delta$	Gel point (°C)	RS%
$LC_{0.875(H_2O)}$	3.18	113.00	54.400	2.58	0.237	54.22	50.76
$LC_{1.000(H_2O)}$	1.97	100.00	45.500	1.18	0.394	52.73	100
$LC_{1.125(H_2O)}$	1.22	97.80	37.700	1.17	0.424	50.10	100
$LC_{1.250(H_2O)}$	1.22	82.00	28.700	0.71	0.518	47.77	100
$LC_{1.500(H_2O)}$	1.22	4.17	4.231	-	-	-	-
$LC_{2.000(H_2O)}$	0.289	160.00	22.000	-	-	-	-

The strength of gel-electrolyte formulations can be evaluated by measuring their G'LVE Gf as well as their G' values at the crossover point. When the water content decreased, the observed increase in the storage modulus suggested strong interactions between the molecules, resulting in a more rigid network structure[83], [84], [85], [86]. The LC_{0.875(H₂O)} formulation exhibited the highest G'LVE (113.00 Pa) and Gf (54.400 Pa) values, indicating a high degree of intermolecular interactions and entanglement. However, as the water content increased, both G'LVE and Gf decreased, leading to weaker gel-electrolyte structures.

An effective supercapacitor should have high power density, quick charge/discharge rate, extended service life, and a wide variety of temperature applications. To resist various mechanical deformations, such as stretching, bending, and compression, supercapacitor gel-electrolytes must have a significant deformation capacity[87]. Therefore, because the G'_f values of the LC_{1.5(H₂O)} and LC_{2.0(H₂O)} formulations were 4,231 Pa and 22 Pa (Table 3.3), respectively, indicating a weaker structure, these formulations were not considered for further investigation.

3.2.4 Frequency sweep analysis

The results of the frequency sweep analysis can be used to categorize gel solutions as dilute, concentrated (entanglement network systems), weak, or strong[88]. According to the results, with an increase in salt concentration from LC_{1.250(H₂O)} to LC_{0.875(H₂O)}, the storage modulus, G' becomes higher, while the dependency of frequency decreased. Because G' and G'' are slightly frequency-dependent, and G' is more elevated than G'' without any crossover for the LC_{0.875(H₂O)}, LC_{1.000(H₂O)}, and LC_{1.250(H₂O)} formulations, the gels have interconnected gel-like network structures with a typical solid-like and predominantly elastic behavior. This is consistent with the suggested cubic structure. However, with increasing water content (LC_{1.250(H₂O)} formulation), the gel exhibited liquid-like behavior (G' < G'') in low oscillatory frequency region (ω) and solid-like behavior (G' > G'') in the high- ω region (Figure 3.2a). For the lowest water concentration (LC_{0.875 (H₂O)} formulation), G'₀ (storage modulus at 0.1 rad.s⁻¹) is 2.58 orders of magnitude higher than G''₀ (the loss modulus at 0.1 rad.s⁻¹). However, in the presence of more water, the ratio (G'₀/G''₀) decreased to 0.71 (Table 3.3).

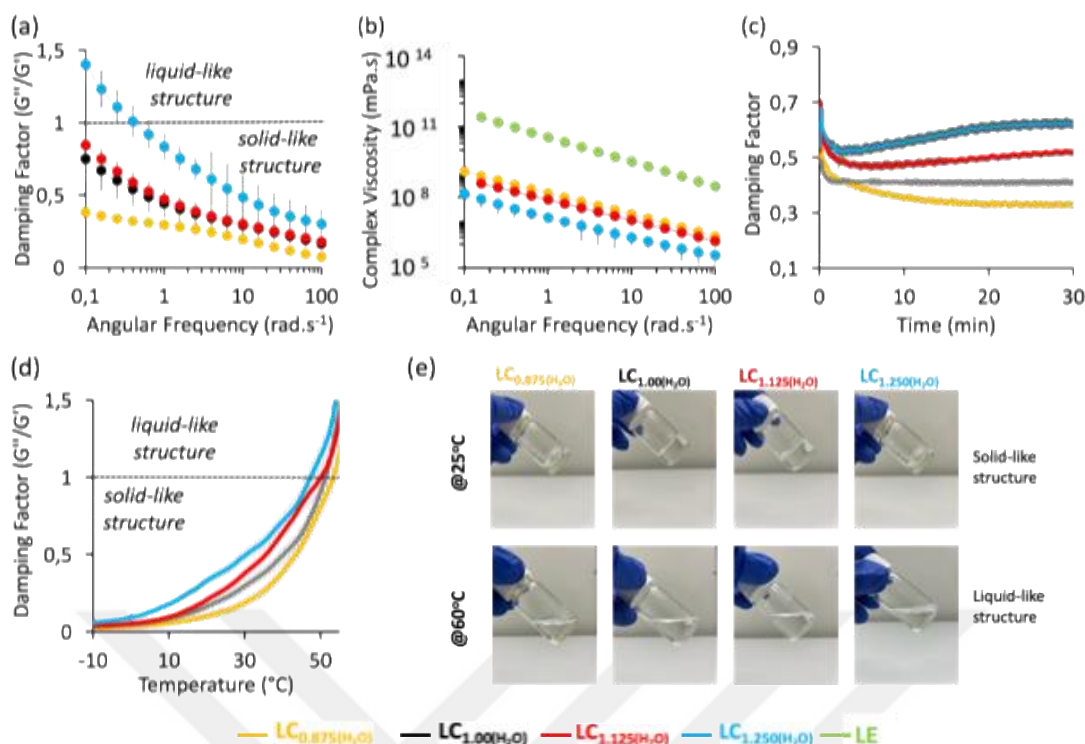


Figure 3.2: Oscillatory analysis of structures. **(a)**damping factor at various angular frequencies, **(b)**complex viscosity analysis, and **(c)**damping factor analysis related to the time sweep. **(d)**Damping factor analysis related to temperature sweep. **(e)**Visual observations further support temperature-induced gelation; at 25°C, they were able to hold their weight in the inverted vial at a particular angle, and at 60°C, all the samples exhibited flowable characteristics.

The frequency dependence of G' was described using the power law [89], [90]. Figure 3.2a shows the changes in the damping factor (G''/G') of the samples depending on their water content. Rheological measurements showed that $\tan \delta$ decreased significantly when the water concentration was reduced to 0.875 g, resulting in a stronger structure (Figure 3.2a)[91]. This phenomenon also suggests that hydrogen bonding among the gel species is essential for the development of gel structures. In aqueous salt solutions, water molecules solvate ions and form significantly stronger interactions than water molecules in media[92]. At high salt concentrations (low water content), micelles hold each other more tightly than at high water content, producing a typical viscoelastic behavior similar to that of transient polymer networks,[93], [94], [95] which appears to involve physical interactions (particularly hydrogen bonding) rather than chemical bonding. The system could move slowly, even under a small shear force, and glide along one another while displaying partial or complete disentanglement. This is because the water molecules enter the mesostructure. The

increase in stiffness with decreasing water content can be explained by the entanglement of micelles and aggregation established in the mesophase.

3.2.5 Shear thinning property

The shear thinning properties of the formulations were examined by frequency sweep tests in the oscillatory mode using complex viscosity curves (Figure 3.2b). All gels displayed a typical unique shear-thinning behavior, which imparted self-healing and remolding properties to the gels, as the complex viscosity decreased with increasing shear rate [94], [96]. The shear-thinning behavior of the samples can be attributed to the alignment of the micellar domains with flow [94], [97]. Viscosity peaked progressively as water content declined. At minimal hydration, viscosity rose sharply, signifying a shift from a dilute system to a semi-dilute regime once the self-assembled micelles extended enough in length to interlock and entangle with one another within the network. [98].

3.2.6 Time sweep

Time-sweep analyses were conducted at 1% strain and 1 rad.s^{-1} at 25°C for 30 min, and the storage (G') and loss (G'') moduli were monitored for all formulations. It is readily apparent from the damping factor ($\tan \delta$) curves as a function of time that all formulations were almost stable for 30 min (Figure 3.2c). A slight increase in $\tan \delta$ of the $\text{LC}_{1.250}(\text{H}_2\text{O})$ and $\text{LC}_{1.125}(\text{H}_2\text{O})$ formulations indicated a small amount of structural weakening.

3.2.7 Temperature sweep

To conduct environmental monitoring associated with temperature changes, temperature sweep assessments were carried out over a wide temperature range from -10 to $+60^\circ\text{C}$. It is known that a supercapacitor structure can lose its ionic conductivity if it is prone to freezing when exposed to temperatures below zero, limiting its use in extremely cold climates[99]. At low temperatures, the storage modulus (G') of all gels was much greater than the loss modulus (G''). The formulations maintained their gel-like behavior up to approximately 50°C . (Figure 3.2 d,e and Table 3.3). Although G' tended to decrease with increasing temperature, G'' began to increase. This can be explained by the significantly reduced association strength of hydrogen bonding at high temperatures, which resulted in the formulation having a liquid-like

character[72]. However, at low temperatures, the association strength of the hydrogen bonding was significant. The lifetime is such that the interactions among the gel species behave like weak crosslinks between the chains[100]. As shown in Table 3.3, the temperature-induced gelation point (crossover point of G' and G'' ; gel point, °C) decreased with increasing water content of the formulations, similar to strain-induced gelation (γ_f) (Figure 3.2). This can be explained by the production of more ion-dipole (salt-water) and hydrogen bonding interactions in highly concentrated electrolyte solutions. Furthermore, with increasing salt concentration, the jammed or more compact packing of the micelles in the mesophase provides outstanding resistance to large strains owing to the multiple hydrogen bonds that form in the coronal chains, as confirmed by strain sweep tests. It can be speculated that in the case of high salt concentrations ($LC_{0.875(H_2O)}$ and $LC_{1.000(H_2O)}$) at high temperatures, intermicelle bridges through coronal hydrogen bonds remained, hindering the progression of the liquid character of the structure.

Recently, antifreezing techniques involving the incorporation of LiBr or LiCl have been utilized in wearable applications. However, very high salt concentrations or post-procedural methods have been employed to prepare them [68], [101], [102]. The introduction of water and salt species in a confined space also reduces the freezing point of the aqueous salt solutions and salts. This phenomenon is known as confinement effect (CE). CE stabilizes salt-surfactant mesophases at very low temperatures [79], [103].

3.2.8 Self-Healing property

In the past decade, rapid advances in biologically inspired self-healing materials have made the integration of autonomous repair into devices a compelling strategy to greatly improve their operational lifetime, reliability, and functional performance. This self-repair arises from the reversible dynamics of weak linkages, encompassing both covalent and non-covalent chemical bonds [104]. A self-healing supercapacitor can mend cracks, fractures, or other mechanical damage as they arise, thereby restoring its original performance or at least limiting any loss of properties. This autonomous repair stems from the material's shear-thinning nature, which enables it to flow under applied shear stress and then resolidify once the stress is removed, recovering its structure. [105].

A six-cycle oscillation strain test, also referred to as a thixotropic test, was conducted at 25°C and 1 rad.s⁻¹ to assess the mesostructures' ability for quick self-healing. Under conditions of low strain, all formulations demonstrated a storage modulus (G') that was greater than the loss modulus (G'').(Figure 3.3). This implies that the mesostructural network remains intact under a small oscillatory strain. Subsequently, when the formulations were subjected to a considerable amplitude of shear strain, G' decreased drastically by approximately 5000 times, and the structures started to behave as viscous-like structures (G''>G'), indicating rupture of the system. Subsequently, the mesostructures were subjected to small-amplitude strain in the following cycle.

The recovery rate of the structures after the 6th cycle was measured using Equation 3.1,

$$RS (\%) = 100 - \left[\frac{G'_{11}}{G'_1} \times 100 \right] \quad (3.1)$$

where RS (%) represents the storage modulus ratio before and after the cycling. G'₁₁ and G'₁ are the average storage moduli at the 11th and 1st steps, respectively, and according to the results, the gel-like character (G'>G'') was instantaneously recovered for all water concentrations. The G' and G'' values recovered to their initial values for the LC_{1.000(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)} samples (Figure 3.3; RS% values in Table 3.3). The LC_{0.875(H₂O)} sample recovered 50.76% of the starting G'. All the results indicate an excellent healing capacity for the LC_{1.000(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)} supercapacitor structures, which is a benefit of the dynamic reversible hydrogen bonding in the structures (Figure 3.3 b, c and d). Hydrogen bonding between the ethylene oxide group and water molecules provides the structures with excellent self-healing properties [106], [107]. The LC_{0.875(H₂O)} sample, which showed the weakest self-healing properties, was eliminated, and further rheological tests were performed for formulations LC_{1.000(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)}, which exhibited excellent electrical conductivity.

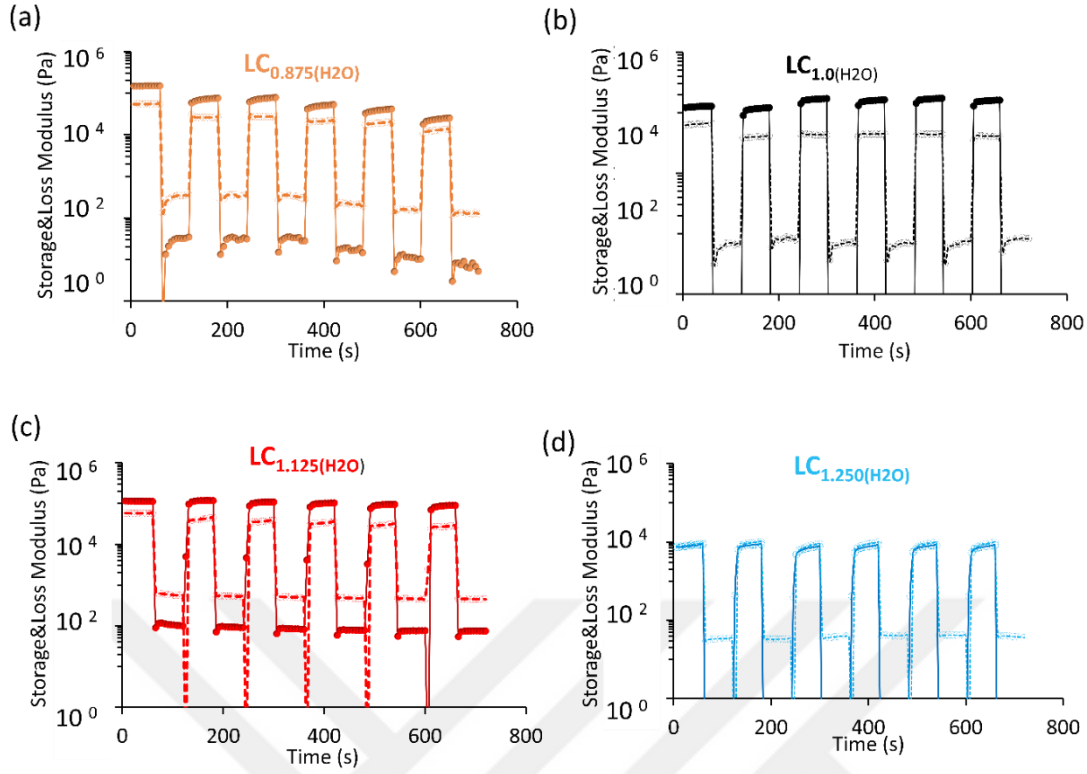


Figure 3.3: Rapid self-healing determination of (a) $LC_{0.875}(H_2O)$ (b) $LC_{1.000}(H_2O)$, (c) $LC_{1.125}(H_2O)$, and (d) $LC_{1.250}(H_2O)$ formulations by oscillation strain steps

3.2.9 Creep recovery

Creep, a time and temperature-dependent phenomenon. Creep-recovery tests were performed to determine the long-term durability and reliability of the materials.[108], [109], [110], [111], [112] The system is exposed to two different constant shear stresses (creep) (25 Pa or 10 Pa) for 300 s, and time-dependent deformation of the mesostructures is evaluated. Then after the stress is released, the deformation recovery is recorded for an additional 600 s[113].

The creep curves contained (i) instantaneous elastic deformation, (ii) delayed elastic deformation, and (iii) viscous Newtonian flow components within the strain [113]. Following the release of the shear stress, the instantaneous part was first recovered, followed by the retardation element, and finally the viscous strain[113], [114]. Creep-recovery results (recorded response) are reported as creep compliance, ($J(t)$), defined as the ratio of measured strain to applied shear stress on the specimen, as given in Equation 3.2: [108], [115].

$$J(t) = \gamma(t) / \sigma \quad (3.2)$$

where $\gamma(t)$ denotes shear deformation (strain) and σ represents the applied constant shear stress. Creep–recovery experiments were analysed with the four-parameter Burgers model, comprising a Maxwell element in series with a Kelvin–Voigt element, arranged to describe viscoelastic response [116][108]. The Maxwell element introduces instant compliance (springlike) plus zero shear viscosity, regulating overall permanent deformation [117], [118], [119]. The final recovery percentage of the entire system ($RC\%$) is calculated from J_{max} and J_{min} , according to the following equation, which was proposed by Dolz, Hernandez, and Delegido (Equation 3.3) [94], [120], [121], [122].

$$RC(\%) = \frac{J_{max} - J_{min}}{J_{max}} \times 100 \quad (3.3)$$

In this context, J_{max} denotes the peak deformation associated with compliance after stress release, whereas J_{min} represents the compliance measured over the longest duration period. Figure 3.4a illustrates how varying salt concentration influences the creep (0–300 s) and recovery (300–900 s) profiles in these gel matrices over time. Greater compliance ($J(t)$) implies that smaller $J(t)$ denotes a sturdier material framework in practice [121], [123].

As shown in Figure 3.4a, we observed slow changes in creep compliance over very long periods, indicating that the secondary interactions of the mesostructures can break or reorganize during deformation [62]. During the creep phase of all formulations, we initially observed first an elastic response (Maxwell spring), then a strain buildup (Kelvin–Voigt element) approaching an asymptotic limit over time. During the recovery phase ($300 < t < 900$ s), after removing the applied shear stress, we recorded the maximum deformation (J_{max}), followed by a severe reduction in creep compliance owing to the permanent deformation behavior. Furthermore, reducing the shear stress value from 25 Pa to 10 Pa resulted in reduced compliance and strain (Table 3.4). The data indicate that the $LC_{1.000(H_2O)}$ formulation has the highest creep recovery ($RC\%$) values, indicating greater elasticity than the other formulations, which is consistent with the G' data from the frequency sweep analysis. Additionally, decreasing the water concentration increased the robustness and flexibility of the formation, as suggested by the data. The creep curves also suggest that the formulation with the highest water content ($LC_{1.250(H_2O)}$) displays more extensive permanent viscous deformation as the

viscoelastic response increases. This formulation had the lowest RC% (6.6% at 25 Pa and 9.1% at 10 Pa) (Table 3.4). Our findings indicate that reducing the water concentration, strain, and creep compliance leads to improved stiffness of the material, which is consistent with the results of oscillatory frequency sweep and stress relaxation tests.

Table 3.4: Maximum deformation corresponding to the compliance value $J_{max,25}$ at 25 Pa, Creep recovery percentage at 25 (RC_{25} %) and 10 (RC_{10} %) Pa, Zero shear viscosities at 25 and 10 Pa, and Activation Energies of the formulations.

Code	$J_{max,25}$ (1/Pa)	RC_{25} %	RC_{10} %	η_0 (at 25 Pa) (Pa.s)	η_0 (at 10 Pa) (Pa.s)	E_a (Kj.mol ⁻¹)
LC _{1.000} (H ₂ O)	0.00115	79.3	-	85.854	-	63.82
LC _{1.125} (H ₂ O)	0.000162	14.09	27.78	18.745	34.381	47.37
LC _{1.250} (H ₂ O)	0.0000423	6.60	9.09	2.635	5.682	41.40

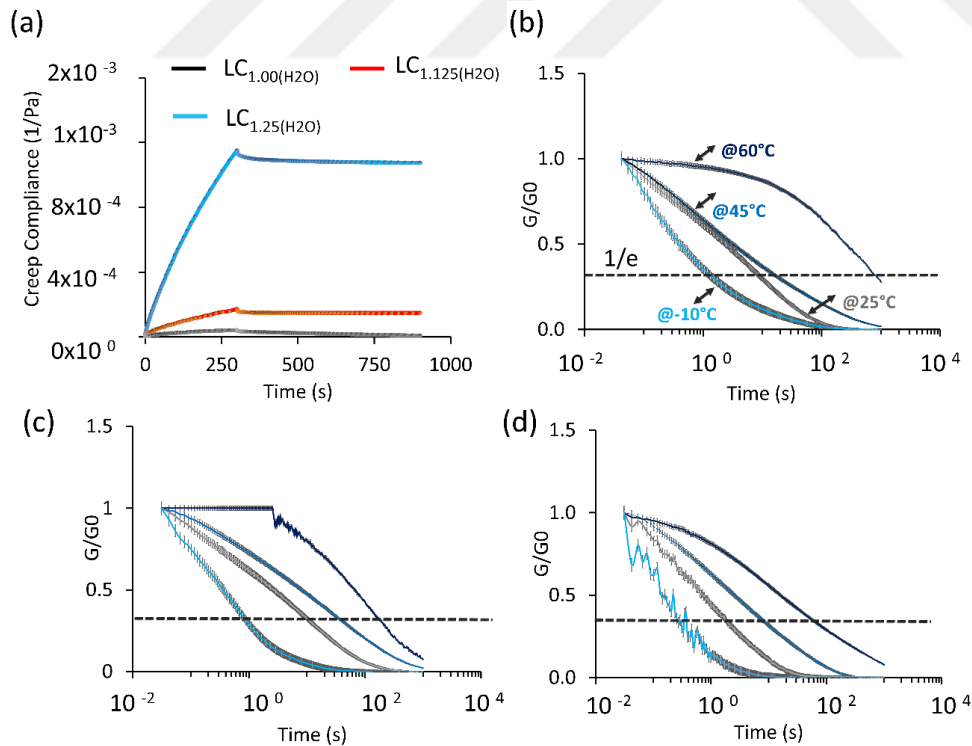


Figure 3.4: (a) Creep curves of LC_{1.000}(H₂O), LC_{1.125}(H₂O), and LC_{1.250}(H₂O). Stress relaxation test of (b) LC_{1.000}(H₂O), (c) LC_{1.125}(H₂O), (d) LC_{1.250}(H₂O) formulations.

3.2.10 Zero-shear viscosity

Creep-recovery tests are crucial for obtaining zero-shear viscosity and describing material behavior and internal structure systems [117], [124], [125]. Therefore, zero-shear viscosity (viscosity of a material when it is effective at rest, η_0) was determined at the end of the creep phase (Equation 3.4).

$$\eta_0 = \frac{\tau_k}{\tan\beta} \quad (3.4)$$

where τ_k is the shear stress, and $\tan\beta$ is the slope of the creep curve. The shear strain-time curve showed a constant slope that depended only on τ_k . The results showed that the zero-shear viscosity decreased with increasing applied shear stress (Table 3.4).

3.2.11 Stress relaxation

Stress relaxation experiments were performed to provide insight into the extent of secondary bond exchange and propensity for creep [126]. The characteristic relaxation times (τ) of the samples, namely LC_{1.000(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)}. (Figure 3.4 b,c, and d).

The stress relaxation curves for all temperatures exhibited a straightforward relaxation process for the modulus values (Figure 3.4b,c,d). This suggests that because of the reversible hydrogen bonding and superior self-healing ability of the LC_{1.000(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)} formulations, all samples were likely to restructure their mesostructure through dynamic hydrogen bonds and electrostatic forces. The temperature dependence of the relaxation behavior varied for the sample with the highest water content (LC_{1.250(H₂O)}), which showed a much shorter relaxation time than the other formulations at all temperatures, indicating a better dynamic exchange (Figure 3.4c). In contrast, the formulation with the lowest water content (LC_{1.000(H₂O)}) showed a significant decrease in network mobility when the temperature was lowered to -10 °C. Interestingly, all formulations exhibited faster relaxation at higher temperatures, with significant stress release observed at 45 °C and 60 °C, as the structures could flow around these temperatures (Figure 3.4d). The relaxation process is mainly controlled by thermo-dissociated hydrogen bonding in the mesophase, as described in the temperature sweep section. The sample with the highest water content (LC_{1.250(H₂O)}) showed rapid stress relaxation to zero within a few seconds at 45 and 60

°C because of its gel point of 47 °C. At temperatures above the gel point, the characteristic relaxation times (τ) of all formulations become equal, indicating no temperature dependence on the stress relaxation behavior. This can be attributed to the low energy barrier above the gel point and the heating to this temperature, facilitating rapid bond exchange. It is proposed that the observed relaxation time of 1 s is determined by the interval network dynamics.

Due to the associative exchange mechanism of hydrogen bonding, the relationship between τ and temperature for the LC_{1.000(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)} samples can be described by Maxwell relation (Equation 3.5), and Arrhenius relationship (Equation 3.6).

$$\eta = G \cdot \tau \quad (3.5)$$

$$\ln(\tau) = \ln(\tau_0) + \frac{E_a}{RT} \quad (3.6)$$

Based on this formulation, the activation energy (E_a) of the formulations can be obtained according to the linear correlation of $\ln(\tau)$ with $1/T$. The E_a value of LC_{1.250(H₂O)} is equal to 41,40 KJ.mol⁻¹, which is smaller than those of LC_{1.000(H₂O)} (63.82 KJ.mol⁻¹) and LC_{1.125(H₂O)} (47.37 KJ.mol⁻¹) samples, indicating a dynamic bond exchange in the mesostructure. The high stability of LC_{1.000(H₂O)} can be associated with a low water concentration and has a much higher E_a among the formulations[127].

The diffusion-limiting topology at high salt concentrations may explain why E_a increased with increasing salt concentration. Electrochemical experiments have shown that a more densely packed structure has a greater tendency to restrict the mobility of molecules and diffusion of ions than low-viscosity systems. This, in turn, prevents bond exchange and leads to an increase in activation energy [27].

The findings of this study offer a promising approach for developing self-healing, anti-freezing, and shear-thinning supercapacitors over a broad temperature range in which they can operate with excellent flexibility.

3.2.12 Electrochemical performance

The gel electrolytes prepared in this study were formulated with varying molar ratios (LC_{0.875(H₂O)}, LC_{1.00(H₂O)}, LC_{1.125(H₂O)}, and LC_{1.250(H₂O)}) to investigate their suitability for

application in supercapacitors. Initial observations revealed distinct differences in viscosity and gel-like structure formation among different molar ratios. The $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolyte exhibited the lowest viscosity, resembling that of a nongelled electrolyte. This finding suggests that at higher molar ratios, the electrolyte becomes more fluid-like, hindering the formation of a stable gel network. In contrast, the $\text{LC}_{0.875}(\text{H}_2\text{O})$ electrolyte exhibited the highest viscosity, which resembled that of a solid-like material. The higher viscosity could be attributed to the increased concentration of gel-forming agents within the electrolyte. The high viscosity of the $\text{LC}_{0.875}(\text{H}_2\text{O})$ electrolyte may impede ion diffusion and hinder overall ionic conductivity, thereby limiting its potential as a gel electrolyte for supercapacitor applications. Considering these results, further investigations focused on the supercapacitor performance of gel electrolytes with $\text{LC}_{1.00}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$. The chosen molar ratios were intended to assess how the gel-like structure and ionic conductivity affect the supercapacitor's electrochemical characteristics.

All the electrochemical tests were performed at room temperature. A standardized procedure was employed to mitigate the critical issue of water loss in the gel electrolyte during supercapacitor testing. Specifically, the gel electrolyte was promptly sandwiched between the positive and negative electrodes and placed in a split cell configuration. This split-cell design, equipped with o-rings, provided a hermetically sealed environment for the gel electrolyte. By creating a closed-pack system, the split cell effectively prevented gaseous species from entering or escaping the cell. Consequently, the loss of water from the gel electrolyte owing to evaporation was effectively minimized. The careful process of assembling and sealing cells is essential for preserving the gel electrolyte's quality and durability during supercapacitor experiments, thus guaranteeing accurate and reproducible outcomes.

To further confirm the roles of water content $\text{LC}_{1.00}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolytes were investigated using a two-electrode split cell (Figure 3.5). The CV curves of the $\text{LC}_{1.00}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolytes at a scan rate of 50 mV.s^{-1} were measured between symmetrical active carbon electrodes. Although each electrolyte formulation exhibited well-shaped, balanced, and rectangular CV curves, the highest specific capacitance was obtained for the $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolyte. This can be explained by the fact that $\text{LC}_{1.250}(\text{H}_2\text{O})$ has a relatively higher water content with

more free ions (Li^+ and Cl^-), and its mobility. The capacitance is enhanced due to the absence of limitations imposed by surfactant domains that accumulate through electrostatic forces. The CV curves were compatible with the rheological behavior of the materials. Rheological behavior reveals how dominant the aggregation becomes with decreasing water content (aggregation slows down and/or limits the free ion mobility). A 0 – 0.5 V window was deliberately chosen because it lies well inside the thermodynamic stability limits of both water and chloride in this highly concentrated $\text{LiCl}/\text{C}_{12}\text{E}_{23}/\text{H}_2\text{O}$ bicontinuous-cubic gel. At ± 0.25 V per carbon electrode the system remains ≥ 0.6 V away from H_2 , O_2 or Cl_2 evolution, ensuring that the electrolyte operates strictly as an electrical-double-layer medium. Staying below this threshold also avoids the local field strengths that would disrupt the 13 nm cubic channels whose viscoelastic integrity—and hence ionic conductivity—are central to our rheology-centred study. Empirically, CV loops in this window remain perfectly rectangular and GCD traces are isosceles triangles with ~ 100 % coulombic efficiency, while Nyquist spectra show only a small high-frequency semicircle followed by a near-vertical tail—signatures of ideal capacitive behaviour with negligible charge-transfer resistance. Extending the sweep toward 1 V immediately introduces Faradaic features and gas nucleation that both distort the mesophase and confound rheological correlations. Accordingly, confining electrochemical testing to 0 – 0.5 V guarantees chemical quiescence, preserves the gel's mechanical framework, and allows a clean linkage between storage modulus, loss modulus and the purely capacitive charge-storage response. The specified scan rates, the CV curves for each electrolyte formulation reveal a balanced rectangular shape, signifying optimal capacitive performance.

EIS measurements were also performed over a frequency range of 100.000 Hz to 0.1 Hz with a 10 mV amplitude to characterize the response of electrolyte systems to alternative currents. All Nyquist plots, a semicircle is observed in the high-frequency domain, which then shifts to a linear pattern as the frequency lowers. Among the $\text{LC}_{1.000}(\text{H}_2\text{O})$, $\text{LC}_{1.125}(\text{H}_2\text{O})$, and $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolytes, the Nyquist plot of the $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolyte shows a smaller ohmic resistance, exhibiting a lower solution resistance in the high-frequency region than the other electrolytes, which directly indicates an increase in ion mobility. Compared with the $\text{LC}_{1.000}(\text{H}_2\text{O})$ and $\text{LC}_{1.125}(\text{H}_2\text{O})$ electrolytes, the $\text{LC}_{1.250}(\text{H}_2\text{O})$ electrolyte showed a lower Warburg impedance, corresponding to faster diffusion of ions into the electrode. Gel electrolytes prepared

with varying molar ratios exhibit distinct viscosities and gel-like structures. The $LC_{1.250}(H_2O)$ electrolyte exhibited the highest ionic conductivity but lacked normal gel-like properties. Thus, the $LC_{1.125}(H_2O)$ electrolyte was chosen for galvanostatic charge and discharge tests. This molar ratio represents the lowest concentration of the gelling agent while still providing sufficient material to form a stable three-dimensional gel structure with high ionic conductivity.

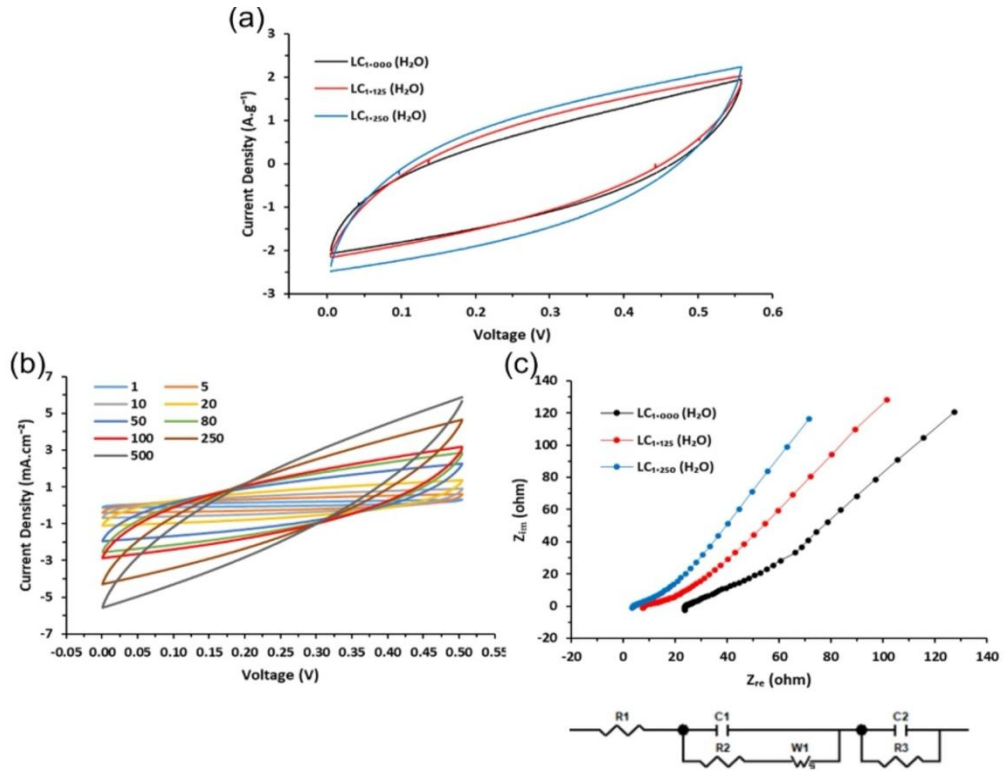


Figure 3.5: Cyclic voltammograms of (a) $LC_{1.000}(H_2O)$, $LC_{1.125}(H_2O)$, and $LC_{1.250}(H_2O)$ electrolytes, (b) $LC_{1.250}(H_2O)$ electrolyte at different scan rates in the voltage window of 0-0.5 V, and (c) electrochemical impedance spectra of the $LC_{1.000}(H_2O)$, $LC_{1.125}(H_2O)$, and $LC_{1.250}(H_2O)$ electrolytes in the frequency range of 0.1 Hz to 100.000 Hz.

To evaluate the performance of the $LC_{1.125}(H_2O)$ electrolyte further, GCD measurements were performed at different current densities. Figure 3.6a shows the GCD curves of the $LC_{1.125}(H_2O)$ electrolyte in a symmetric supercapacitor cell.

The GCD curves revealed a nearly isoscale-triangular shape with a small ohmic drop, which illustrates that the $LC_{1.125}(H_2O)$ electrolyte has ideal capacitive performance and good charge reversibility, which is consistent with the CV curves. Moreover, a linear discharge potential on-time behavior was observed, suggesting that no central Faradaic process occurred. The specific capacitances, derived from the charge-discharge

profiles based on the GCD curves at different current densities, are also depicted in Figure 3.6a. As expected, at 0.25 A.g⁻¹ current density, the cell exhibits the highest specific capacitance, 316 F.g⁻¹. Even at a high current density of up to 1 A g⁻¹, the specific capacitance of the electrode covered with LC_{1.125}(H₂O) was approximately 80%. Figure 3.6b shows the cycling stability of the LC_{1.125} (H₂O) electrolyte in the two-electrode system at 0.5 A.g⁻¹ for 1500 cycles. The specific capacity remained almost constant during testing. The electrolyte was stable for the remaining 500 cycles, although a small drop occurred in capacitance after 1000 cycles. The corresponding coulombic efficiency was approximately 80% after almost 1000 cycles, which was attributed to its excellent stability and high conductivity. The LC_{1.125}(H₂O) gel structure exhibits good cycling stability and coulombic efficiency. The impedance spectrum of the symmetric activated-carbon | LC_{1.125}(H₂O) lyotropic-gel | activated-carbon cell is reproduced by the minimal equivalent circuit $R_1 - (R_2 \parallel C_1) - W_s - (R_3 \parallel C_2)$, where (i) R_1 quantifies the uncompensated ohmic resistance of the gel electrolyte, current collectors and leads; (ii) the high-frequency branch $R_2 \parallel C_1$ models the depressed semicircle arising from interfacial contact resistance (R_2) and the rough-surface double-layer/pseudocapacitive capacitance (C_1) at the working electrode; (iii) the finite-length Warburg element W_s captures mid-frequency Li⁺/Cl⁻ diffusion through the bicontinuous nano-channels of both gel and porous carbon, producing the characteristic 45° tail that flattens when the diffusion length matches the electrode thickness; and (iv) the low-frequency branch $R_3 \parallel C_2$ represents charge-transfer resistance (R_3) and coupled pseudocapacitance (C_2) at the counter electrode. By assigning a distinct, physically meaningful process to each element, this four-element model achieves an excellent simultaneous fit to the magnitude and phase of the experimental impedance across the 100 kHz–0.1 Hz range without introducing superfluous parameters that would obscure interpretation

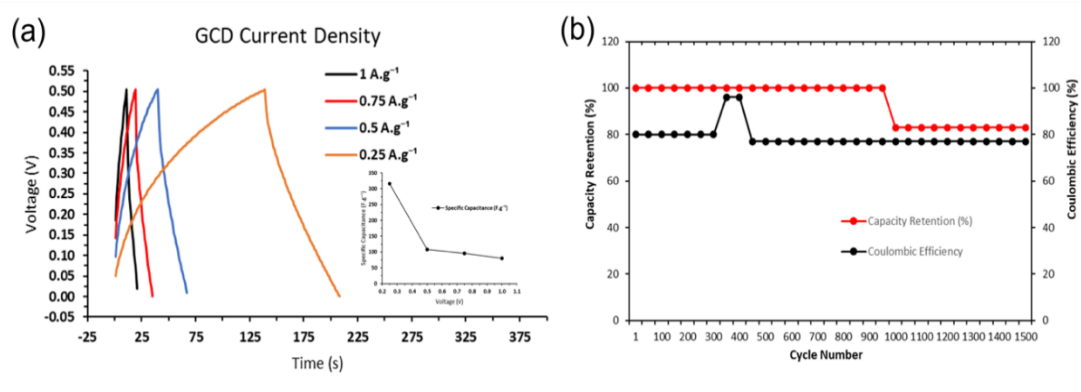


Figure 3.6: (a) Galvanostatic charge-discharge curves of the LC1.125(H₂O) electrolyte at different current densities (inset is specific capacitance versus current density) and **(b)** variation of coulombic efficiency (%) and capacity retention (%) depending on the number of cycles.

Figure 3.7 visualizes the coupled migration of Li⁺ and Cl⁻ ions through the water-filled nanochannels of the C12E23–LiCl–H₂O bicontinuous-cubic gel. Fast vehicular Li⁺ diffusion toward the negative electrode is charge-balanced by slower Cl⁻ drift toward the positive side, while the tortuous geometry restrains convective flow.

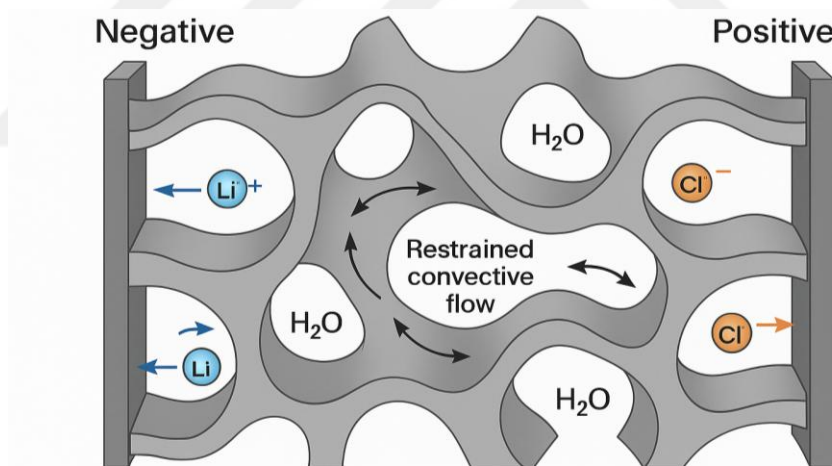


Figure 3.7: Schematic Li⁺/Cl⁻ transport pathways and restrained convective flow within the bicontinuous-cubic C₁₂E₂₃–LiCl–H₂O gel electrolyte.

The XRD patterns displayed diffraction lines originating from a cubic phase with a unit cell parameter a of 13.2 nm for the liquid crystalline mesophase with a LiCl: C₁₂E₂₃ mole ratio of 5.63. The increase in the line intensity over 30 min indicates some water loss and improved orientation within the stable structure. In the strain-sweep analysis, The LC_{0.875}(H₂O) formulation exhibited the highest strain amplitude at the flow point (3.18%), whereas the LC_{1.125}(H₂O), LC_{1.250}(H₂O), and LC_{2.000}(H₂O) formulations

exhibited lower flow points (1.22% and 0.289%, respectively), indicating weaker structures. The LC_{0.875(H₂O)} formulation had the highest storage modulus at the critical point (G'_{LVE}) of 113.00 Pa and a flow point (G_f) of 54.400 Pa, suggesting extensive intermolecular interactions and a stiffer network structure. In the frequency sweep analysis, the LC_{0.875(H₂O)}, LC_{1.000(H₂O)}, and LC_{1.250(H₂O)} formulations displayed solid-like behavior, with a storage modulus (G') higher than the loss modulus (G''). The LC_{1.250(H₂O)} formulation exhibited liquid-like behavior at low frequencies and solid-like behavior at high frequencies. The storage modulus ratio at 0.1 rad.s⁻¹ (G'₀) to loss modulus at 0.1 rad.s⁻¹ (G''₀) decreased with increasing water content. In the shear-thinning analysis, the gel formulations exhibited decreased complex viscosity with increasing shear rate, indicating a shear-thinning behavior. The LC_{0.875(H₂O)}, LC_{1.000(H₂O)}, and LC_{1.250(H₂O)} formulations showed maximum viscosity values at lower water content, indicating a transition from a dilute to a semi-dilute regime. During self-healing evaluation, the LC_{0.875(H₂O)}, LC_{1.000(H₂O)}, and LC_{1.250(H₂O)} formulations demonstrated the ability to recover 100% of their initial storage moduli after rupture. The LC_{1.000(H₂O)} formulation exhibited a slightly lower recovery rate of 50.76%. The zero-shear viscosity decreased with increasing applied shear stress, as observed in the creep recovery tests. In the stress relaxation analysis, the LC_{1.250(H₂O)} formulation exhibited shorter relaxation times, indicating better dynamic exchange among other systems. The activation energy (E_a) values were smaller for the LC_{1.250(H₂O)} formulation (41.40 KJ.mol⁻¹) compared to the LC_{1.000(H₂O)} (63.82 KJ.mol⁻¹) and LC_{1.125(H₂O)} (47.37 KJ.mol⁻¹) formulations, indicating a dynamic bond exchange in the mesostructures. The LC_{1.250(H₂O)} formulation exhibits the highest specific capacitance, whereas the LC_{1.000(H₂O)} formulation display a high specific capacitance of 316 F.g⁻¹ at 0.25 A.g⁻¹. The LC_{1.250(H₂O)} electrolyte demonstrated good cycling stability, maintaining an almost constant specific capacity over 1500 cycles with a coulombic efficiency of approximately 80%.

3.3 Conclusions

Different gel formulations with a constant LiCl to C₁₂E₂₃ mole ratio (5.63:1) and different water concentrations were studied from mechanical and electrochemical

points of view for flexible supercapacitor applications. Although the liquid crystalline mesophase loses water as soon as thin films are prepared, it exhibits a strong diffraction line over time at all water concentrations. Both XRD and POM data confirmed the formation of a cubic mesophase at all water concentrations. Rheological measurements yielded precise insights into how gel strength and gelation kinetics varied with water content, LiCl concentration, as well as temperature. In addition, the present work systematically illustrates the reorganizing behavior (self-healing) of a gel structure prepared for the first time by combining water/23-lauryl ether with LiCl salt. The designed gel structure encapsulates Li^+ and Cl^- ions by forming a three-dimensional network in the hydrophilic domains and exhibits significant performance in supercapacitor applications.





4. MOLTEN SALT ASSISTED ASSEMBLY (MASA) OF NOVEL MESOPOROUS $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ FOR HIGH-PERFORMANCE ASYMMETRIC SUPERCAPACITORS³

Mesoporous transition metal oxides (TMO) are immensely investigated as electrode materials in supercapacitors. The molten salt assisted self-assembly (MASA) process enables a facile route for the synthesis of the mesoporous TMO. In this study, mesoporous nickel manganese cobaltite ($\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$) is synthesized for the first time using a MASA process and is evaluated as a novel electrode-active material for asymmetric supercapacitors. The objective of this work is to quantitatively measure the performance improvement in the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode based on its composition and reveal the improvement mechanism through electrochemical methods. The electrochemical performance of the NiCo_2O_4 and MnCo_2O_4 prepared by MASA is also investigated, in order to understand the synergistic effect of Ni and Mn elements in the same cobaltite structure. In line with the data obtained from half cells, a full asymmetric cell is prepared by assembling the appropriate amount of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ and activated carbon through the charge balance theory. The test results show that the specific capacitance (C_s) values are 2.62 F/cm^2 (92.1 F/g) for mesoporous NiCo_2O_4 , 0.26 F/cm^2 (9.8 F/g) for mesoporous MnCo_2O_4 , and 9.53 F/cm^2 (338.5 F/g) for mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ under the test conditions of 5 mA/cm^2 . The asymmetric supercapacitor assembled with $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ and activated carbon demonstrates a superior energy density of 79.52 Wh.kg^{-1} at 1 mA/cm^2 . The findings of the study highlight the importance of substituting the electrode with $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ to enhance the C_s by achieving proper surface properties and electrochemical activity.

In recent years, there has been a heightened emphasis on developing energy storage devices that are both cost-efficient and possess high energy density, while also being environmentally sustainable, with a particular focus on their application in electric

³ This chapter was published in “Özkaynak, M.U., Türker, Y., Bahadır Dönmez, K., Dağlar, S., Çobandede, Z., Metin Çelenk, M., Karatepe, N., Seniha Güner, F., & Dag, Ö. (2024). Molten Salt Assisted Assembly (MASA) of novel mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ for high-performance asymmetric supercapacitors. *Electrochemistry Communications*, 168, 107811.”

vehicles.[128]. Among these devices, electrochemical capacitors, also called supercapacitors, stand out as promising options due to their ability to meet the rapid energy demands of electric vehicles and high-power electronic devices [30], [129], [130].

Supercapacitors are governed by two fundamental principles: EDLCs capture energy through the adsorption of ions, while pseudocapacitors, also known as asymmetric supercapacitors, depend on rapid redox reactions at the surface where the electrode meets the electrolyte.[1], [131], [132]. Pseudocapacitive materials offer higher energy and power densities than symmetrical EDLCs [133], [134]. As the field of supercapacitors evolves, there is a growing recognition of the pivotal role that electrolyte formulation and electrode materials play in enhancing device performance, including improved energy density, power density, and cycle life, necessitating ongoing advancements in these areas. [129].

Among various metal oxides, mesoporous spinel structures has recently drawn great interest owing to its stability, high theoretical capacitance, low cost, easy synthesis, environmental friendliness, good electrical conductivity, and low toxicity [130], [135], [136], [137]. Its mesoporous structure offers increased ion-accessible surface areas, maximizing the redox activity and specific capacitance [138], [139], [138], [139]. The efficiency of redox reactions, provided by the electroactive surface area of the electrode material and the wettability of the electrode in the electrolyte, enhancing the surface area where the electrode and electrolyte meet leads to better performance. This enhanced surface area facilitates efficient redox reactions, crucial for improved electrochemical performance during charge-discharge cycles. This feature accelerates the Faradaic reactions on the electrode surface, where the valence states of $\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{M}^{2+}/\text{M}^{3+}$ ($\text{M} = \text{Ni}$ or Mn) are involved, ultimately improving the electrochemical performance [140], [141], [142]. Increasing the specific surface area of transition metal oxides (TMOs) improves the performance of supercapacitors and increases the number of ion diffusion nodes in the active area [138], [143], [144].

Dag et al. introduced a straightforward one-step synthesis method for mesoporous spinel NiCo_2O_4 and MnCo_2O_4 in 2021 [145]. This synthesis method involved using metal nitrate hexahydrate precursors assembled with non-ionic and ionic surfactants in their lyotropic liquid crystalline phase, followed by high temperature calcinations [146], [147], [148], [149]. The authors investigated mesoporous spinel metal cobaltite

as an electrocatalyst for the oxygen evolution reaction (OER) in alkaline solutions [145].

In contrast, the molten salt assisted self-assembly (MASA) method represents a cutting-edge technique for producing complex materials that are challenging to create using conventional methods. This method combines two solvents and two surfactants to induce self-assembly. The first solvent, volatile in nature, uniformly mixes all ingredients, whereas the second solvent, a molten salt variant, arranges the mixture into a Lyotropic Liquid Crystal (LLC) mesophase once the first solvent evaporates. Additionally, the MASA method employs both a non-ionic surfactant, typically of the oligo(ethylene oxide) type, to aid in forming the LLC phases of the salt and surfactants, and an ionic surfactant to enhance the salt content in the salt-surfactant LLC mesophases. In practice, a clear solution containing all the ingredients is spread over a substrate to form an ordered thin LLC film, which is then converted to a mesoporous thin film through high temperature calcination [145], [150], [151], [152].

Although the MASA method has been previously utilized to produce metal oxides and binary metal oxide structures[153], [154], its application in synthesizing ternary metal oxide structures has remained unexplored [30], [31]. This study introduces the first synthesis of mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, achieved through the MASA method, showcasing its exceptional surface area and enhanced redox behavior, resulting in remarkable energy storage performance. The electrochemical properties of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ were systematically investigated to uncover its inherent energy storage capabilities given its unique combination of three TMOs. Our investigation aims to reveal the synergistic effects and potential enhancements in energy storage performance resulting from this novel compositional interplay. $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ not only offers a substantial surface area for electrode/electrolyte interaction but also introduces additional oxidation reduction step(s) originating from the manganese sites within the structure. These added redox phases contribute to the improved electrochemical behavior of the electrode, enhancing its overall energy storage capabilities.

4.1 Experimental Part

4.1.1 Synthesis of mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , MnCo_2O_4

To prepare $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, 0.232 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.192 mmol Ni), 0.203 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.798 mmol Mn), 0.929 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.798 mmol Co), and 0.291 g of $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$ (0.798 mmol $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$) were dissolved in 5 mL of ethyl alcohol and stirred at room temperature. After 15 minutes, 0.5 g (0.798 mmol $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, $\text{C}_{12}\text{E}_{10}$) a non-ionic surfactant, dodecyl ethylene glycol monododecyl ether ($\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, $\text{C}_{12}\text{E}_{10}$) were added to the solution, and the mixture was mixed for 30 min. The homogeneous and clear solution obtained was poured into a petri dish and evaporated overnight at 60 °C. The Petri dish was placed in an oven heated to 400 °C at a rate of one degree per min and maintained at this temperature for 180 min. The synthetic route is illustrated in Figure 4.1.

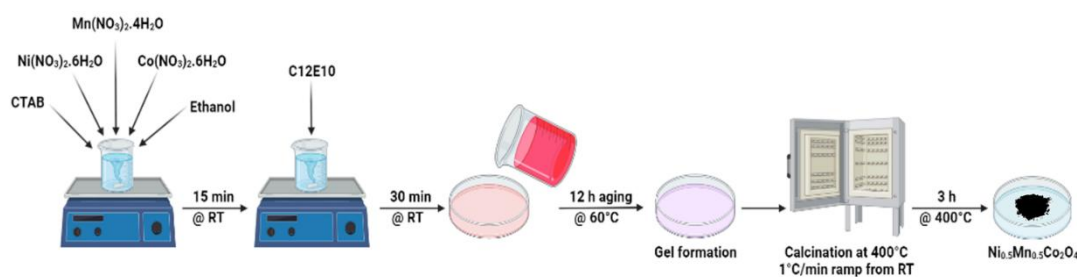


Figure 4.1: Schematic illustration of the fabrication routes of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$

4.1.2 Synthesis of activated carbon

In this study, activated carbon was used as the negative active material during the preparation of an asymmetric device.

4.1.3 Preparation of active carbon coated carbon foam

In a typical experiment, 35 mg of active carbon (AC), 3 mg of polyvinylidene fluoride (PVDF), and 3 mg of carbon black were mixed in N-methyl-2-pyrrolidone (NMP) using a mortar and maintained until the solution was completely dispersed. The required amount was then plastered onto the carbon foam surface. Subsequently, the dispersion was dropped onto carbon foam and left overnight in an oven at 70 °C to remove excess NMP from the electrode. The drop-drying process was repeated when necessary to increase the coating thickness on the surface. The porosity properties of activated carbon hold significance, as many of its properties are shaped by or closely linked to this attribute.

4.1.4 Preparation of active mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ coated Nickel Foam

$\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ (35 mg), PVDF (5 mg), and carbon black (3 mg) were mixed. After the mixture was homogeneously mixed in a mortar, an appropriate amount of NMP was added, and the slurry-like solution was dropped onto the current collector surface. The nickel foam was left in an oven at 70 °C overnight to remove excess NMP from the electrode. The drop-drying process was repeated when necessary to increase the amount of active material in the current collector.

4.1.5 Characterization of materials

The gel phases were observed using a ZEISS Axio Scope A1 polarizing optical microscope, and their X-ray diffraction (XRD) patterns were obtained using a Rigaku Miniflex diffractometer. This diffractometer features a Cu $K\alpha$ X-ray source ($\lambda = 1.54056 \text{ \AA}$) and operates at 30 kV/15 mA. Nitrogen adsorption-desorption isotherms were measured with a Micromeritics Tristar 3000, ranging from 0.01-0.99 P/Po. Before these measurements, around 150 mg of the sample underwent dehydration at 35-40 mTorr and 200 °C for 2 hours. The saturated pressure was checked every 120 minutes over 6 to 10 hours. Scanning electron microscopy (SEM) images were taken using a FEI Quanta 200 F microscope on aluminum holders. X-ray photoelectron spectroscopy (XPS) spectra were gathered using a Thermo Scientific K- α spectrometer with an Al $K\alpha$ micro-focused monochromatic source (1486.68 eV, 400 μm spot size), complemented by a flood gun for charge balancing. Fourier transform infrared (FTIR) spectroscopy was conducted on a Thermo Scientific Nicolet IS10 device, and Raman spectroscopy was performed using a Renishaw in via microscope spectrometer, equipped with a 532 nm laser source.

4.1.6 Electrochemical measurements

All measurements were performed at room temperature. In this study, a saturated calomel reference electrode (SCE), a Pt wire auxiliary electrode, and metal oxide-coated Ni foam working electrodes were used in the three-electrode measurement configuration. Cyclic voltammetry (CV) measurements were performed from -0.5 to 0.8 V for three cycles. The exposed area of the working electrode is 0.48 cm^2 . The CV plots of the NiCo_2O_4 , MnCo_2O_4 , and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrodes were recorded at various scan rates (1, 5, 10, 20, 50, 100, 250, and 500 mV.s^{-1}) in a potential range of -0.5 to 0.8 V. The third voltammogram was obtained for each specimen.

Electrochemical impedance spectroscopy (EIS) measurements were performed in the 100.000 Hz to 0.1 Hz frequency range with a 10-mV amplitude. GCD measurements were also carried out for each electrode material in the 0 -0.45 V range at various current densities (5, 10, 15, 20, 25, 50 mA.cm⁻²). For each current density, 10 cycles were performed, and the 5th cycle was used to calculate the areal C_s .

4.1.7 Assembly of asymmetric supercapacitor

Mesoporous metal oxide-coated Ni foam electrodes were used as positive electrodes, whereas active carbon-coated carbon foam electrodes were used as negative electrodes. Prior to each analysis, the filter paper was immersed in a 6 M KOH solution for 60 s and subsequently used as a separator. Full-cell supercapacitor tests were performed on the MTI-split cells. CV measurements were studied between -1.5 to 1.5 V and 0 to 1.5 V. The EIS measurements of the two-electrode system were conducted between 100,000 Hz to 0.1 Hz 10 mV. In the last step, 10,000 cycles of GCD tests were performed for full cells with current densities of 1, 2, 4, 8, 20 mA.cm⁻².

4.1.8 Calculation methods

The areal specific capacitance (C_s , F.cm⁻²) of the supercapacitor was calculated from the GCD curves using the following equation [155]:

$$C_A = \frac{I\Delta t}{A\Delta V} \quad (4.1)$$

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (4.2)$$

Where I (A) is the GCD current density, Δt (s) is the discharge time, A (cm²) is the active surface area of the working electrode in contact with the electrolyte, m (g) is the mass of the active material coated onto the current collector, and ΔV (V) is the discharge voltage within Δt . In Equation 4.2, C_A is the areal-specific capacitance of a single electrode in a three-electrode configuration and V (V) is the operating voltage during the GCD measurement. Equation 4.1 where C_s is the specific capacitance (F/g), I is the discharge current (A), Δt is the time for full discharge(s), and ΔV is the potential window.

Before assembling the full cell, the specific capacitances of the negative and positive electrodes were calculated using Equation 4.2, and the mass ratio between the positive

and negative active materials was calculated based on mass balance theory. (3) represents the specific capacitance obtained from the cyclic voltammogram, C (F/g) is the specific capacitance, m (g) is the mass of the active material loaded in the working electrode, v (V/s) is the scan rate, I (A) is the instantaneous current in the CV curve, and V is the potential window. A and B limit the voltage range of the half cells in which the positive and negative active materials operate, and the exact values are mentioned in the Results and Discussion section[156]. Utilizing the obtained specific capacity results, researchers applied the charge balance theory (Equation 4.4) to establish the proper mass balance between the electrodes. [157]. Consequently, by examining the capacitance values and their respective potential windows for both electrodes, the proportion of masses between the positive and negative electrodes was set to (m_+/m_-) 0.54.

$$C_{cv} = \frac{1}{2mv\Delta V} \int_A^B IdV \quad (4.3)$$

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (4.4)$$

Utilizing the GCD curves obtained from the asymmetrical device, calculations were performed to determine the energy density (E , Wh·kg⁻¹) and power density (P , kW·kg⁻¹) of the full cells. These computations employed the subsequent Equations [158].

$$E = \frac{1}{2} C_s \Delta V^2 \quad (4.5)$$

$$P = \frac{E}{\Delta t} \quad (4.6)$$

4.2 Results and Discussion

Three clear and homogeneous solutions were prepared with a 6:1 molar ratio of the total metal nitrate salts (Ni (II), Mn (II), and Co (II)) to the surfactant (C12E10), where for every 6 moles of total metal nitrate salts, 1 mole of surfactant was used. These solutions were prepared in 5.0 mL of ethanol. The solutions were drop-cast onto glass slides, and ethanol evaporation and gelation (mesophase formation) were monitored using a polarized optical microscope (POM) and small-angle XRD measurements to identify the structure of the mesophase. Figure 4.2g, h, and I show the LLC gels with

POM images, displaying characteristic textures that indicate anisotropic LLC mesophases. The fresh samples display diffraction lines at small angles (Figure 4.2a-c) due to the ordered structure in the mesophase where the molten salt species resides in the hydrophilic domains. However, the LLC mesophase loses its order at 60 °C, as can be seen from the XRD results. Before calcination at 400 °C, the samples were aged at 60 °C overnight to remove excess ethanol in the media. After calcining the samples at 400 °C, sharp diffraction lines were observed in the high-angle XRD patterns, indicating the formation of NiCo_2O_4 (Figure 2(d)), MnCo_2O_4 (Figure 4.2e), and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ (Figure 4.2f) with the formation of a small amount of NiO and are disordered in mesoscale. The XRD patterns of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ displayed lines at 18.79° , 30.9° , 36.3° , and 44° , which were indexed to the (111), (220), (311), and (400) planes, respectively, of the face-centered cubic (fcc) structure of MnCo_2O_4 (JCPDS no. 23-1237). NiCo_2O_4 has an inverse spinel structure, characterized by the positioning of all Ni ions at the octahedral sites, whereas Co ions are evenly distributed between both the tetrahedral and octahedral sites within the structure (JCPDS card No. 20-0781). The calcination process was controlled using FTIR spectroscopy.

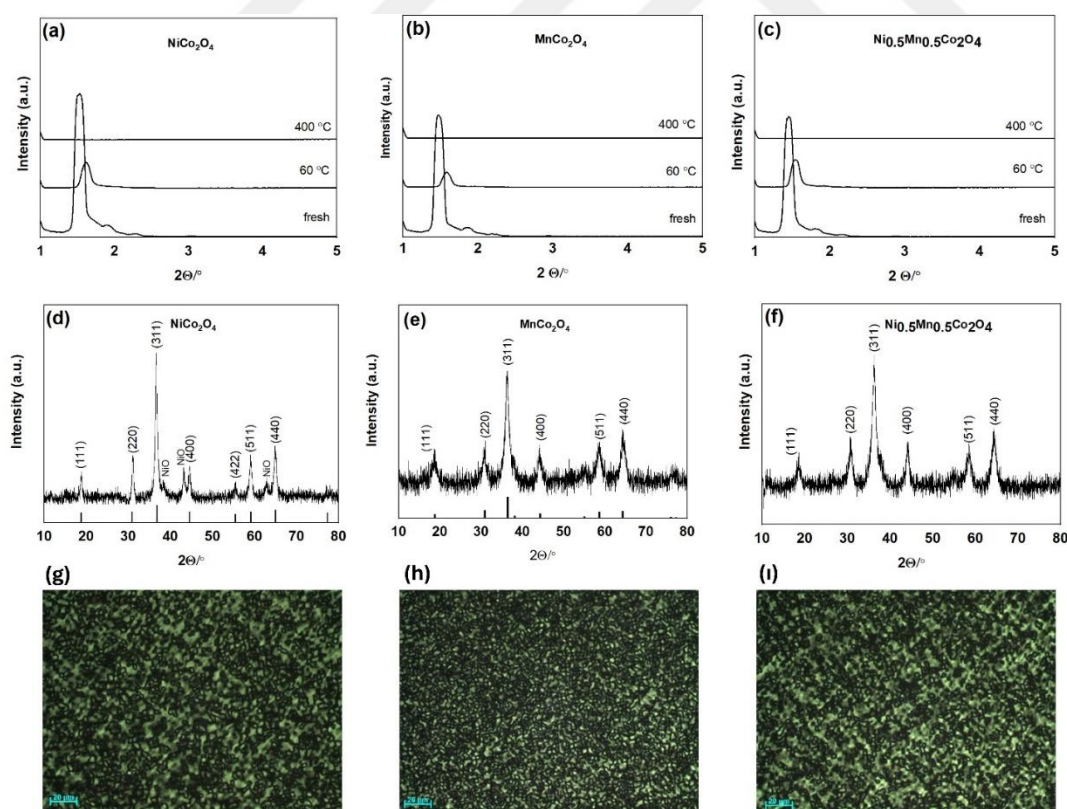


Figure 4.2: XRD patterns of (a) NiCo_2O_4 fresh samples, (b) MnCo_2O_4 fresh samples (c) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ fresh samples; high angle XRD pattern after calcination at 400 °C; (d) NiCo_2O_4 (e) MnCo_2O_4 (f) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, POM images for (g) NiCo_2O_4 (h) MnCo_2O_4 (i) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$

We also obtained XPS spectra of the O 1s, Co 2p, Ni 2p, and Mn 2p regions, to evaluate the chemical nature and composition of the as-synthesized mesoporous cobaltite. Full-scan survey XPS spectra confirmed the formation of NiCo_2O_4 , MnCo_2O_4 , and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$. Upon examining the EDS mapping images, it can be seen that the Ni, Mn, and Co elements exhibit nearly the same distribution. This indicates that no pure oxide forms of the individual metals are present in the environment, demonstrating the success of the synthesis. Raman spectroscopy was performed to further understand the composition of these structures. For the sample of MnCo_2O_4 , the Mn–O and Co–O vibrational Raman modes at low wavenumber region can be seen between 400 and 700 cm^{-1} . In the case of NiCo_2O_4 , the split peak between 410 and 590 cm^{-1} is attributed to the excitation of Co–O and Ni–O stretching modes. The peaks for the M–O stretching modes are observed at around 520 and, 650 cm^{-1} corresponding to Mn–O Ni–O and Co–O stretching in the mixed spinel $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ [159].

The calcined samples were also used to collect N_2 adsorption/desorption isotherms of calcined samples, see Figure 4.3.

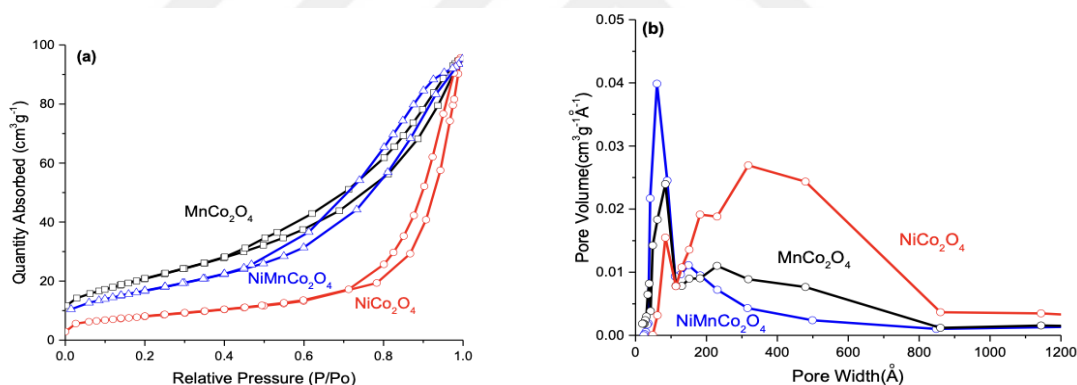


Figure 4.3: (77 K) N_2 adsorption–desorption isotherms, (a) and pore-size distribution plots, (b) of (I) NiCo_2O_4 , (II) MnCo_2O_4 and (III) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$

According to the adsorption-desorption isotherms in Figure 4.3a, the isotherms are typical, type IV, and characteristic of mesoporous materials. This means that all three metal cobaltite samples have a mesoporous structure. BET surface areas of mesoporous NiCo_2O_4 , MnCo_2O_4 , and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ were 29, 76, and 61 m^2/g , respectively. MnCo_2O_4 and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ display a double pore system with a relatively narrow pore size distribution, one at around 5.5 nm and the other at around 15 nm. It is likely that small pores are formed by burning the surfactant domains of the mesophase. With further heating and crystallization of the pore walls, the pores expand to larger pores. The expanded pores are around 35 nm in the case of NiCo_2O_4 , see

Figure 4.3(b). This is also consistent with the XRD data, where the diffraction lines of the NiCo_2O_4 sample are much narrower than those of the MnCo_2O_4 and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ samples.

SEM and TEM characterizations were performed to obtain morphological information about the samples, as illustrated in Figure 4.4. According to the SEM analysis, the NiCo_2O_4 (Figure 4.4a), MnCo_2O_4 (Figure 4.4b), and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ (Figure 4.4c) samples are made up of homogeneous, small, and spherical particles that occasionally coalesce to form larger particles. The low magnification TEM images of the as-synthesized NiCo_2O_4 (Figure 4.4d), MnCo_2O_4 (Figure 4.4e), and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ (Figure 4.4f) showed that the NiCo_2O_4 particles are much larger (20-30 nm) and their pores are more disordered as evidenced from the pore-size distribution plots, but the MnCo_2O_4 and more importantly the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ particles are relatively smaller (less than 10 nm) and more uniform.

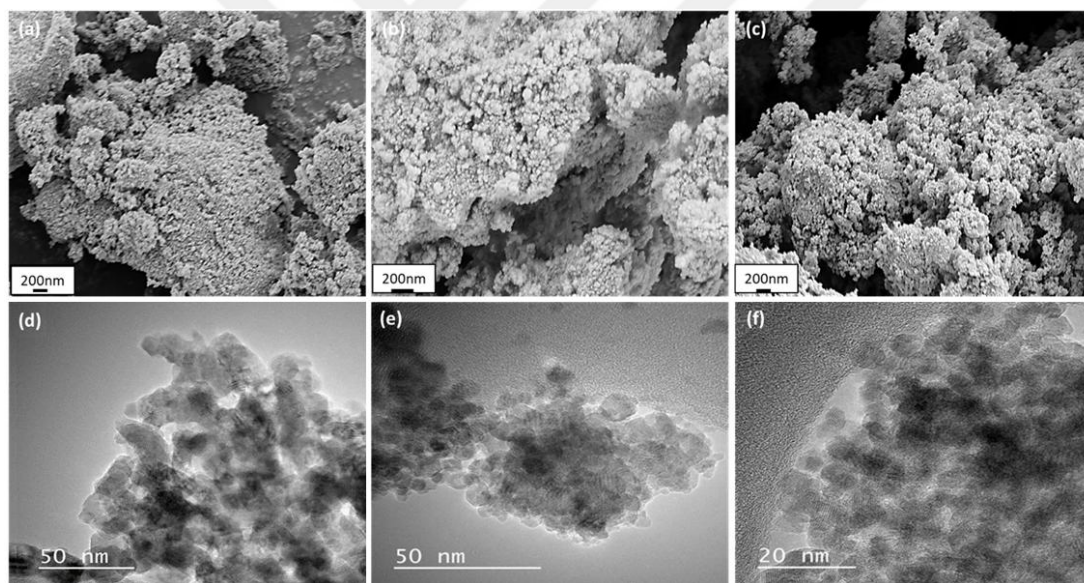
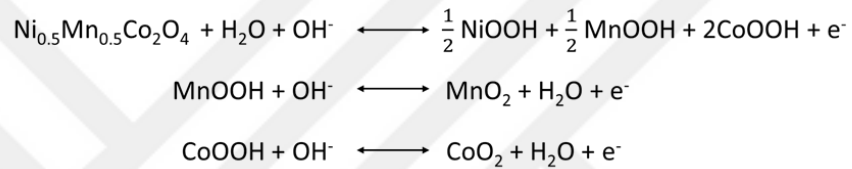


Figure 4.4: SEM images of (a) NiCo_2O_4 , (b) MnCo_2O_4 and, (c) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, and TEM images of (d) NiCo_2O_4 , (e) MnCo_2O_4 , (f) $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$

The electrochemical performances of NiCo_2O_4 , $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, and MnCo_2O_4 electrodes were first tested in a three-electrode configuration in a 6 M KOH solution. Figure 4.5(a) shows the cyclic voltammograms obtained for NiCo_2O_4 , $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, and MnCo_2O_4 electrodes between -0.5 and 0.8 V. All voltammograms display a pair of redox peaks derived from the Faradaic reaction of reversible $\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ conversion triggered by OH^- ions. Mesoporous

$\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ has a large surface area and numerous electroactive sites for pseudocapacitive reactions. In the CVs curves of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ and MnCo_2O_4 electrodes, there was a peak due to $\text{MnOOH}/\text{MnO}_2$ oxidation. In addition, the open spaces of the mesoporous structures serve as reservoirs for OH^- species and enhance the penetration of electrolytes into the surface of the active material. The active material and current-collector interface are essential for the electrode to provide fast electron transfer. The direct contact of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, with its good intrinsic electrical conductivity and robust adhesion on a bare Ni substrate, supports the fast transport of electrons. This indicated that fast redox reactions provided an electron transfer mechanism in the supercapacitor cell. The Faradaic reactions that occur in the electrochemical cell are as follows [147].



The reactions occurring in multiple steps allow the electrode's active material to offer a higher specific capacitance. During these fast-redox reactions, OH^- ions migrate and diffuse to the electrode surface during the charging process, leading to the conversion of Ni^{2+} , Mn^{2+} , and Co^{3+} species to their XOOH forms. During this process, electron transfer occurs due to the oxidation of Mn^{2+} and Ni^{2+} . This represents the first step of the charging reaction, although a complete conversion of the electrode has not yet been achieved. Excess OH^- ions in the environment undergo oxidation reactions to active material forms such as MnOOH and CoOOH , creating oxide forms, and along with these reactions, electron transfer occurs again. These reactions are reversible, and during discharge, previously formed compounds, such as Mn_xO_y and Co_xO_y , are reduced back to their hydroxyl forms. In the second step of discharge, NiOOH , MnOOH , and CoOOH undergo another reduction reaction, reforming the stable $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ structure.

Figure 4.5a shows the CV curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams. An oxidation peak around 0.45 V and a reduction peak around 0.2 V are observed in the NiCo_2O_4 coated sample. In the sample containing $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, the oxidation peak shifted to a slightly more positive potential, and the reduction peak shifted to a slightly more negative potential. In addition, another reduction peak was

observed at around -0.2 V. This was probably due to the reduction in Mn^{2+} . As shown in the voltammograms, the area under the peaks was the highest for the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode. In addition, the lowest OER occurred over this electrode. This also indicates that the slow OER and both the electrode and electrolyte can be protected for a longer time at the electrode/electrolyte interface. The area under the curve of the cyclic voltammograms indicates the specific capacitance.

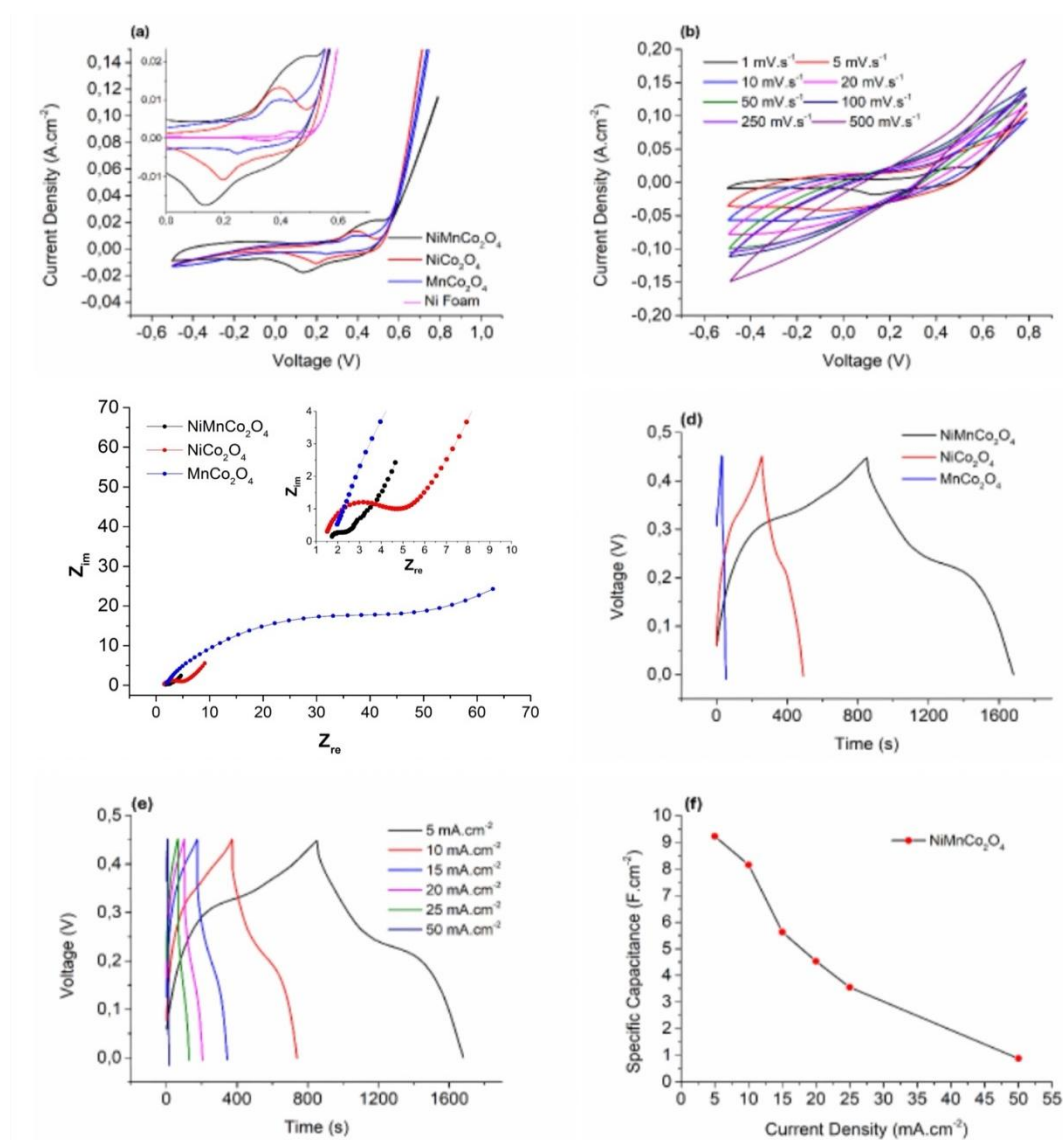


Figure 4.5: (a) CV curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams in 6 M KOH (Reference Electrode: SCE), (b) CV curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ coated Ni foam at a scan rate of 1, 5, 10, 20, 50, 100, 250, and 500 $\text{mV}\cdot\text{s}^{-1}$ (Electrolyte: 6 M KOH, Reference Electrode: SCE), (c) Nyquist plots of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams in 6 M KOH (Reference Electrode: SCE), (d) GCD curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 coated Ni foams in 6 M KOH (Reference Electrode: SCE, Current Density at 5 $\text{mA}\cdot\text{cm}^{-2}$), (e) GCD curves of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ at a current density of 5, 10, 15, 20, 25, and 50 $\text{mA}\cdot\text{cm}^{-2}$ (Electrolyte: 6 M KOH, Reference Electrode: SCE), (f) Areal specific capacitance at various current densities

Table 4.1: Specific capacitance data calculated by GCD and CV

Sample	Specific Capacitance (F.g ⁻¹)(*)	Specific Capacitance (F.cm ⁻²)(*)	Specific Capacitance (F.cm ⁻²)(**)
Ni _{0.5} Mn _{0.5} Co ₂ O ₄	338.5	9.53	11.51
NiCo ₂ O ₄	92.1	2.62	6.36
MnCo ₂ O ₄	9.8	0.26	4.65

(*)Specific capacitance values calculated from galvanostatic charge and discharge curves obtained with a current density of 5 mA.cm⁻² (0.18 A.g⁻¹)

(**)Specific capacitance values calculated from cyclic voltammograms obtained with a scanning rate of 1 mV.s⁻¹

The C_s of Ni_{0.5}Mn_{0.5}Co₂O₄, NiCo₂O₄, and MnCo₂O₄ were calculated to be 11.51, 6.36 and 4.65 F.cm⁻², respectively. On the other hand, the potential for capacitive contribution of Ni foam without any coating was investigated by conducting measurements within the same voltage window. In this context, the CV obtained at a scan rate of 1 mV.s⁻¹ is shown in the inset of Figure 4.5a. The C_s was calculated by integrating the area between 0.2 V and 0.52 V in this voltammogram, and it was found to be less than 0.005 F.cm⁻². This indicates that the capacitive contribution of Ni foam is negligible compared to Ni_{0.5}Mn_{0.5}Co₂O₄. Additionally, the active material film on the electrode surface will hinder the electrolyte from reaching the current collector, resulting in an even lower capacitive contribution. Figure 4.5b shows the CV curves of the Ni_{0.5}Mn_{0.5}Co₂O₄ electrode at scan rates ranging from 1 to 500 mV.s⁻¹. At low scan rates (1, 5, and 10 mV. s⁻¹), oxidation and reduction peaks with fast redox transitions were observed in the CVs curves. A pair of redox peaks were found at 0.0-0.25 V and 0.3-0.45 V at a scan rate of 1 mV.s⁻¹, however, the redox peaks gradually become inconspicuous at higher scan rates. Spindle-shaped voltammograms were obtained at increasing scan rates at low scan rates (1, 5, and 10 mV.s⁻¹), and the ions in the electrolyte and active electrode material (Ni_{0.5}Mn_{0.5}Co₂O₄) had sufficient time to interact with each other. This indicates that the Ni_{0.5}Mn_{0.5}Co₂O₄ electrode had a high energy density. Ni_{0.5}Mn_{0.5}Co₂O₄ gives the highest charge storage of the three spinels studied. At 1 mV s⁻¹ CV (or 5 mA cm⁻² GCD) it delivers 338 F g⁻¹, equal to 11.5 F cm⁻², with redox peaks at 0.48 V and 0.18 V vs SCE. This behavior is attributed to its mesoporous structure (5–15 nm) and low charge-transfer resistance (~1.2 Ω), which together support efficient ion and electron transport across a wide range of scan

rates. When the rate reaches $100\text{--}500\text{ mV s}^{-1}$ the CVs shrink into leaf-like loops, yet the redox peaks remain and no oxygen evolution appears in 6 M KOH, showing that Mn–Co synergy delays OER. For a $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ ||activated-carbon device this means scan rates up to 20 mV s^{-1} give almost full capacity, while higher rates still provide useful capacitance with minimal iR drop due to the spinel's robust lattice and low resistance.

Nyquist plots were used to compare the impedance behavior of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 active materials, as shown in Figure 4.5c. The intercept of the X-axis represents the total ohmic resistance (R_s), and the diameter of the arc represents the charge-transfer resistance (R_{ct}), which is affected by the active sites of the electrode and the electrochemical activity of the active material. Because all three electrodes were measured in a 6 M KOH electrolyte, the ohmic resistances were almost the same. However, as expected, the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode exhibited the lowest charge transfer resistance, whereas the MnCo_2O_4 active material exhibited the highest charge transfer resistance. The R_{ct} values of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ and NiCo_2O_4 electrodes were 1.2 and $3.4\ \Omega$, respectively. The highest charge transfer resistance is indeed obtained by MnCo_2O_4 , as expected. Both R_{ct} values obtained from the Nyquist plots were compatible with the C_s calculated from the CV curves. As expected, the more vertical line in the low-frequency range is related to the increased diffusion ability of OH^- ions into the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode active sites. This shows that the Mn-Co synergy not only improves the electrochemical activity of the electrode but also facilitates electron transfer by enhanced diffusion in alkaline media.

GCD tests were performed to determine the service properties of the different active materials as electrodes. As shown in Figure 4.5d, $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ exhibited the highest charge and discharge capacities. As expected, the lowest discharge capacity was obtained from the MnCo_2O_4 material. The C_s of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 were calculated to be 9.53 F.cm^{-2} (338.5 F.g^{-1}), 2.62 F.cm^{-2} (92.1 F.g^{-1}), and 0.26 m.cm^{-2} (9.87 F.g^{-1}) respectively. Therefore, we used an electrode containing $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ as the positive electrode to prepare a full cell. Thus, the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode was subjected to in-depth electrochemical characterization. The strains in the charge curves between 0.25–0.40 V are due to electrochemical reactions originating from the oxidation of metallic species (Ni, Mn, Co) in alkali media. The charge-transfer mechanism that occurs with the use of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$

electrode is illustrated in Figure 4.6. Reversed reactions are obtained in the discharge curve between 0.1 to 0.3 V and represent the reduction of the oxidized species in previous step. This mechanism is discussed later in this study. These results correlate with the oxidation and reduction responses obtained from the cyclic voltammograms. GCD measurements of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode at different current densities are shown in Figure 4.5e. In this study, the C_s response of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrodes at different current densities was investigated. In this context, GCD tests were performed at current densities of 5, 10, 15, 20, 25, and 50 $\text{mA}\cdot\text{cm}^{-2}$. As expected, C_s decreased with an increase in the current density. Nevertheless, even at a high current density of 50 $\text{mA}\cdot\text{cm}^{-2}$, a C_s of approximately 1 $\text{F}\cdot\text{cm}^{-2}$ was obtained.

The maximum performance of an energy storage device can only be achieved by closing the device pack with an appropriate mass ratio between the positive and negative active materials. Therefore, determining the appropriate mass ratio between the negative and positive electrodes is crucial before assembling an asymmetrical device. In this context, the most practical method is to perform CV measurements with 3-electrode configuration systems prepared separately using negative and positive electrodes and to calculate the mass ratio in line with the C_s obtained [160], [161]. The mass ratio between the anode and cathode of the asymmetrical device was calculated using Eq. (4). Cyclic voltammograms at a scan rate of 1 $\text{mV}\cdot\text{s}^{-1}$ were used to determine the C_s of the activated carbon-coated carbon foam and $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ coated Ni foam electrodes (Figure 4.7(a)). The C_s s were calculated using the areas under the voltammograms (Equation 4.3). A range of -1 to -0.1 V was used to calculate the C_s of activated carbon (9 mg), while the range of -0.2 to 0.55 V was used for the calculation of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ (13 mg) coated Ni foam electrode. In this regard, the m^+/m^- ratio was determined to be 0.54. Thus, the asymmetric device was prepared with a mass ratio of 0.54 between the negative and positive electrodes.

Half-cell cyclic voltammetry in 6 M KOH (Figure 4.5b) shows that the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ cathode undergoes its complete $\text{M}^{2+}/\text{M}^{3+}/\text{M}^{4+}$ redox sequence between -0.20 V and +0.55 V vs SCE, while the activated-carbon anode remains purely double-layer capacitive from -1.00 V to -0.10 V vs SCE. Adding these non-overlapping limits yields a theoretical window of ~1.55 V; limiting the full cell to a round 1.50 V therefore ensures safe margins from the water-splitting thresholds. Staying within this 0–1.5 V range exploits the full pseudocapacitive charge of the

spinel without triggering unwanted side reactions in either electrode. Consistently, galvanostatic tests (Figure 4.5a–d) deliver an energy density of 79.5 Wh kg^{-1} at 1 mA cm^{-2} and maintain $\sim 72 \%$ of the initial capacitance after 4 000 cycles confirming 0–1.5 V as the optimal compromise between high energy output and long-term electrochemical stability for the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ AC device.

An asymmetric device (ASC) was fabricated to further examine the real-world performance of the engineered composite electrode materials. This ASC utilized the newly created Ni Foam/ $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ composite as the positive electrode, while employing AC/carbon foam as the negative electrode. The structure of this assembled device was depicted in a schematic representation in Figure 4.6. This figure also schematizes the events that occur on the positive electrode surface of the asymmetric supercapacitor during charging. With the formation of the potential difference, ion migration occurs, and the mesoporous reservoirs of the TMO structure are filled with water and excess OH^- ions in the positive active material. Faradaic reactions triggered by OH^- ions occur, and electron transfer takes place. In this reaction, MnOOH and CoOOH species were formed on the electrode. Further Faradaic oxidation reactions occur at a more positive potential by OH^- ion triggering, and MnO_2 and CoO_2 structures are formed.

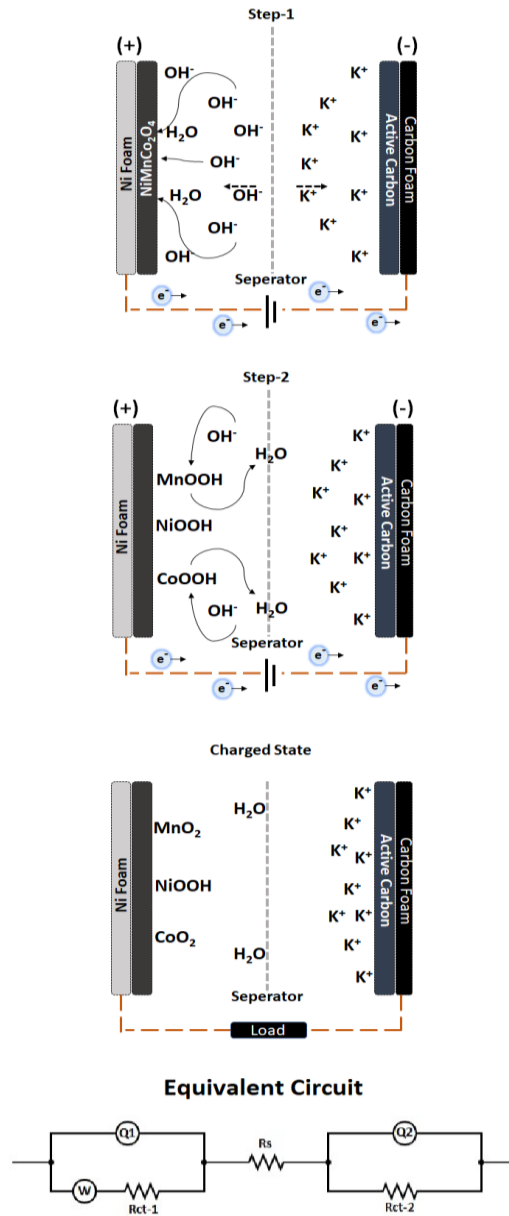


Figure 4.6: Charge transfer mechanism of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode in $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4// \text{KOH//active carbon}$ asymmetrical device (charging mechanism of asymmetric device)

The electrochemical performance of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{AC}$ asymmetric supercapacitor is systematically investigated. Figure 4.7 shows the Nyquist plot of the asymmetrical device in the frequency region of 0.01 Hz to 100000 Hz and Figure 4.7 shows the equivalent circuit used to calculate the variables. According to the fitting results of the EIS spectra, the ohmic resistance of the electrolyte and the charge transfer resistance of the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{KOH//active carbon}$ asymmetric device were 2.348 and 0.672 Ω , respectively. This indicates that the series internal resistance of the asymmetric system was relatively low, and charge storage/ion transport could be easily provided. Figure 4.7a,d show the GCD curves at current densities of 1, 2, 4, 8, and 20

mA.cm⁻² and the capacitance values obtained from these curves, respectively. Table 4.2 summarizes the fitted element values, confirming that each parameter is well-defined within acceptable error margins for reliable electrochemical interpretation.

Table 4.2: Equivalent-circuit parameters extracted from fitting the EIS data

Element	Value*	Error	Error (%)
R1	2.348	0.009 826 1	0.418 49
C1	$1.377\ 7 \times 10^{-4}$	$5.829\ 1 \times 10^{-6}$	4.231
R2	0.678 34	0.021 321	3.143 1
W1-R	31.71	0.842 81	2.657 9
W1-T	73.15	2.937 4	4.015 6
W1-P	0.551 28	0.002 384 1	0.432 47
C2	0.003 033	0.000 450 67	14.859
R3	0.361 65	0.022 336	6.176 1

The ASC exhibited a maximum energy density of 79.52 Wh.kg⁻¹ at 1 mA.cm⁻² current density, while showing 585 W.kg⁻¹ power density at 20 mA.cm⁻². To determine the long-term cycling stability of the asymmetric device, a charge-discharge test was conducted for 4000 cycles at a current density of 25 mA.cm⁻². The changes in capacity retention (%)

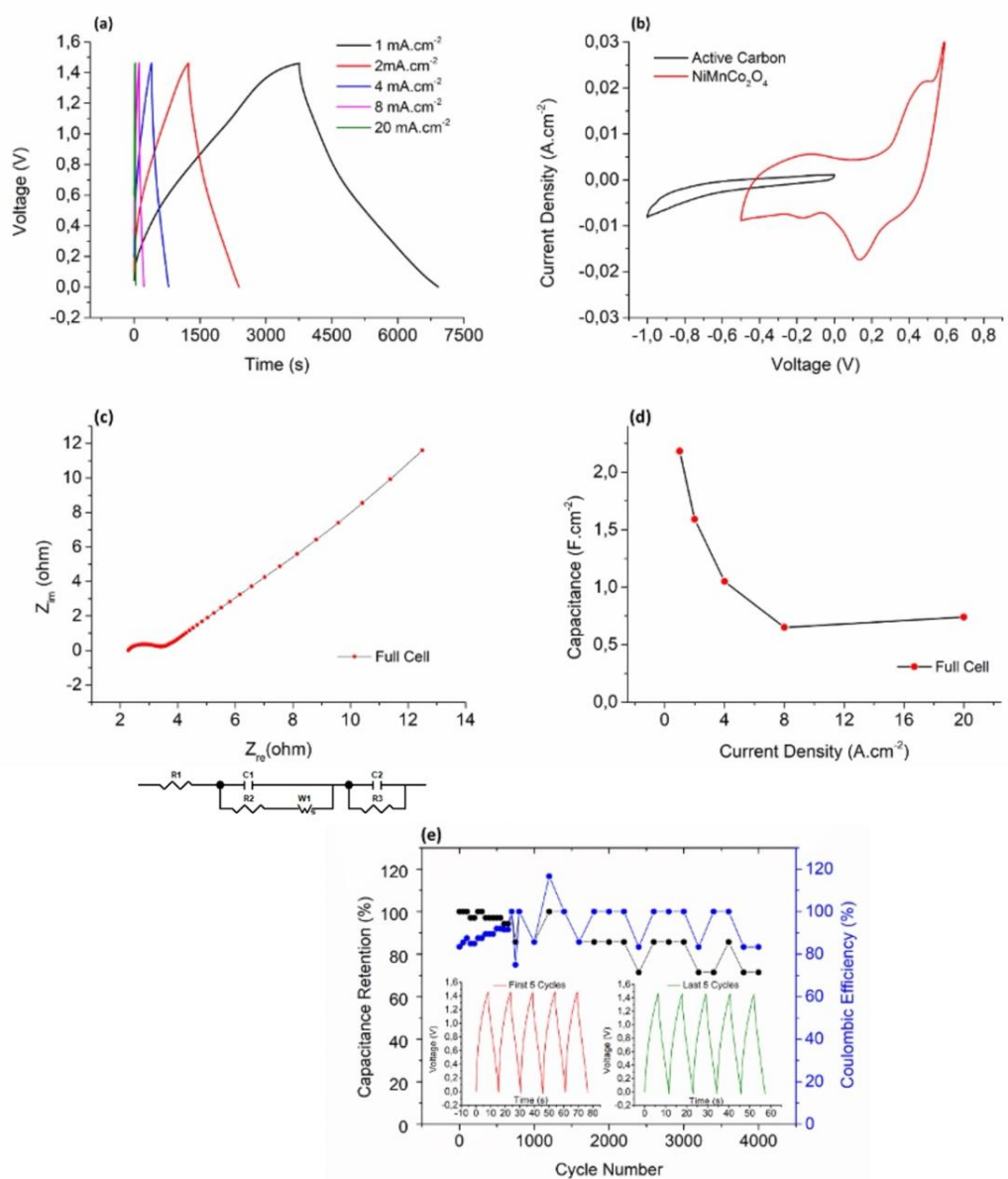


Figure 4.7: (a) GCD curves of the device at different current densities (b) CV measurements performed with separate half-cells of the anode and cathode (Red/electrolyte 6 M KOH, scan rate: 1 mV.s⁻¹, Black/ electrolyte:6 M KOH, scan rate 1 mV.s⁻¹), (c) Nyquist plot of the Ni_{0.5}Mn_{0.5}Co₂O₄//Active Carbon device, (d) Areal capacitance at various current densities (e) Long term cycling stability of the asymmetrical device

and coulombic efficiency with cycle numbers, as well as the first 5 and last 5 charge-discharge curves, are shown in Figure 4.7e As seen from the charge-discharge curves for the first and last 5 cycles, no change in the shape of the curves has been observed. This indicates that the Ni_{0.5}Mn_{0.5}Co₂O₄ electrode has maintained its properties. It is observed that there are slight decreases in the specific capacity with increasing cycle numbers. The Coulombic efficiency slightly decreased at the cycle numbers where

capacity losses occurred. These capacity losses are considered to result from the reduced reversibility of the charge and discharge reactions during those cycles. The cyclic voltammograms obtained from half-cell measurements of the active material at high scan rates (250 mV.s^{-1} and 500 mV.s^{-1}) confirm this situation, and it is clear that the oxidation and reduction reactions of this material, which offers superior energy density, will be more reversible at lower scan rates (1 mV.s^{-1} and 5 mV.s^{-1}). Nevertheless, after the test conducted with a considerably high current density for 4000 cycles, the cell exhibited approximately 72 % capacity retention. On the other hand, the initial coulombic efficiency is approximately 83%. As the cell is used, the coulombic efficiency increases. After approximately 600 cycles, the coulombic efficiency exceeds 95 %. Table 4.3 compares the performance characteristics of the asymmetric device prepared with the synthesized $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ positive electrode in this study with some similar structures in the literature. These results underscore the particularly high energy density of the material. To assess the changes in the morphological structure of the electrode after the long cycling cycle, SEM analyses were conducted for a thorough comparison before and after GCD cycling. The analysis revealed that the electrode maintained its structural integrity, showing no significant morphological changes on the surface even after extensive cycling. These results highlight the robustness and stability of the electrode material under prolonged operating conditions. summarizes the fitted element values, confirming that each parameter is well-defined within acceptable error margins for reliable electrochemical interpretation.

Table 4.3: Comparison of the electrochemical performance of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{AC}$ and similar devices.

Asymmetrical Device	Energy Density Wh.kg^{-1}	Power Density W.kg^{-1}	Retention %	Ref.
$\text{NiCo}_2\text{O}_4/\text{NiCoSe}_2//\text{AC}$	54.5	2045	80 %	[162]
$\text{NiCo}_2\text{O}_4@\text{MnO}_2//\text{AC}$	70.1	2400	97.3 %	[161]
$\text{NiCo}_2\text{O}_4 // \text{AC}$	25.7	7969	82.9 %	[163]
$\text{rGO}/\text{NiCo}_2\text{O}_4@\text{ZnCo}_2\text{O}_4/$ $//\text{AC}$	71	6040	71.6 %	[164]
$\text{NiCo}_2\text{O}_4 // \text{Graphite}$	45.8	5689	80.7%	[165]

Table 4.3 (continued): Comparison of the electrochemical performance of $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{AC}$ and similar devices.

Asymmetrical Device	Energy Density Wh.kg^{-1}	Power Density W.kg^{-1}	Retention %	Ref.
$\text{MnCo}_2\text{O}_4/\text{NiCo}_2\text{O}_4//\text{AC}$	68	540	96.4%	[166]
$\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{AC}$	20.2	≈ 6000	82%	[167]
$\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4//\text{AC}$	79.52	585	72%	This Study

4.3 Conclusions

MASA process was employed for the first-time synthesis of mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, which was subsequently evaluated as a novel electrode-active material for asymmetric supercapacitors, highlighting its promise within the realm of energy storage. MASA method ensures the synthesis of mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, NiCo_2O_4 , and MnCo_2O_4 with a relatively high surface area by simply changing the salt type and composition in the initial clear solutions used to prepare the LLC mesophases and by calcination of the electrodes. The results of the half-cell measurements showed that the mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode had the highest C_s among the three materials, with a value of 11.51 F.cm^{-2} . Moreover, the $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode exhibited the lowest charge transfer resistance and highest electrochemical activity compared to NiCo_2O_4 and MnCo_2O_4 . The asymmetric device was prepared using $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, as it exhibited the best performance in half-cell measurements. The mass ratio between the negative and positive electrodes in the asymmetric device was determined, and the device was prepared accordingly. Then, an asymmetrical supercapacitor device was assembled, and the device showed a low ohmic resistance of 2.348Ω , charge transfer resistance of 0.672Ω , and high capacitance even at high current densities. These results demonstrate that $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ is a promising material intended for deployment as a positive electrode in asymmetric supercapacitors. The $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrode exhibited high C_s and desirable energy density. This excellent performance makes $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$, synthesized by the MASA approach, a promising electrode for asymmetrical energy storage devices.



5. CONCLUSION

Within the framework of this thesis, we focused on developing novel electrolyte formulations and electrode materials to enhance the performance of supercapacitors. Our research primarily addressed two critical aspects of supercapacitor technology: the creation of advanced gel electrolytes and the synthesis of top-tier electrode materials.

In the first part of our study, we successfully developed a novel liquid crystal (LC) gel electrolyte by combining phosphoric acid (PA) and a non-ionic surfactant (NI) at an optimized mole ratio of 80:1 (PA-NI80). This formulation yielded stable LC-mesophase gel electrolytes whose viscosity falls within an optimum window under a moderate shear rate, providing ideal conditions for supercapacitor use. Our PA-NI80 LC gel achieved a remarkable specific capacitance of 1128 F g^{-1} at 0.1 A g^{-1} using reduced graphene oxide (rGO) symmetric electrodes.

In the second part of this thesis, we systematically investigated the role of water in shaping the lyotropic liquid crystalline (LLC) mesophase properties of C12E23-LiCl-H₂O gel electrolytes, with a focus on their mechanical and electrochemical performance in flexible supercapacitors. Rheological analysis provided quantitative information on how gel strength, gelation point, and structural recovery changed with water content and LiCl concentration. The reduction in water content corresponded to an increase in storage modulus, a phenomenon linked to alterations in the quantity and mean size of junction points arising from system entanglement. Findings indicated that surplus water molecules compromise micellar connections, resulting in gel weakening. Alternatively, micellar domains intertwine at low water levels, demonstrating viscoelastic characteristics akin to those observed in transient polymer networks. The gel structures exhibited self-healing properties, attributed to their shear-thinning behavior. This property allows the gels to flow under shear stress and self-recover once the stress is removed. By varying water content while maintaining a 5.63:1 LiCl-to-C12E23 molar ratio, we observed that reduced water content significantly enhanced gel rigidity, as evidenced by an increase in storage modulus (G') from 82 Pa for

LC_{1.125}(H₂O) to 113 Pa for LC_{0.875}(H₂O). Structural analyses using XRD revealed cubic mesophases with a unit cell parameter of 13.2 nm across all formulations. Rheological measurements highlighted the gels shear-thinning behavior and self-healing capability, with LC_{1.125}(H₂O) achieving full recovery after strain-induced rupture. Electrochemical tests further demonstrated that LC_{1.125}(H₂O) displayed a specific capacitance of 316 F·g⁻¹ at 0.25 A·g⁻¹ and retained 80% capacity over 1500 cycles, indicating its suitability for robust energy storage systems.

We also explored the synthesis of novel electrode materials using the Molten Salt Assisted Assembly (MASA) method. For the first time, we successfully synthesized mesoporous Ni_{0.5}Mn_{0.5}Co₂O₄, which exhibited exceptional surface area and enhanced redox behavior. Our Ni_{0.5}Mn_{0.5}Co₂O₄ electrode demonstrated the highest specific capacitance among the tested materials, with a value of 11.51 F cm⁻². We found that this material exhibited the lowest charge transfer resistance and highest electrochemical activity compared to NiCo₂O₄ and MnCo₂O₄.

In order to gauge the functional efficacy of our materials, we fabricated an asymmetric supercapacitor system employing Ni_{0.5}Mn_{0.5}Co₂O₄ as the positive electrode material and activated carbon as the negative electrode component. According to the fitting results of the EIS spectra, the ohmic resistance of the electrolyte and the charge transfer resistance of the Ni_{0.5}Mn_{0.5}Co₂O₄//KOH//active carbon asymmetric device were 2.348 and 0.672 Ω, respectively. This indicates that the series internal resistance of the asymmetric system was relatively low, and charge storage/ion transport could be easily provided. The novel gel electrolytes and electrode materials we developed in this research pave the way for future innovations in sustainable and adaptable energy storage systems. Our findings contribute significantly to the ongoing efforts to optimize the rheological and electrochemical properties of LC gels to meet the demands of next-generation applications. The potential of these novel formulations extends beyond symmetric configurations, suggesting their applicability in asymmetric pseudocapacitors for automotive energy storage and other demanding applications.

In conclusion, our research has made substantial progress in advancing supercapacitor technology through pioneering approaches to electrolyte and electrode materials. Table 5.1 and Table 5.2 jointly present the project's key achievements alongside their

corresponding electrochemical performance metrics. The comprehensive study of the structural, mechanical, and electrochemical properties of these novel materials provides a solid foundation for future research and development in the field of energy storage. The outcomes of our study indicate significant potential for advancing the development and efficiency of adaptable, high-capacity, and resilient supercapacitors. These advancements could have broad applications across multiple industries, encompassing wearable gadgets, mobile electronic devices, and automotive technologies.

Table 5.1: Key achievements

Component	Key Achievements
PA–NI bicontinuous cubic gel electrolyte	Formulated a solvent-free phosphoric-acid/lauryl-ether liquid-crystal gel at PA : NI = 60–100 : 1 that forms a bicontinuous cubic mesophase (lattice ≈ 3.9 nm) with an application-friendly viscosity window of 800–5500 mPa s. Delivered a record gravimetric capacitance of 1128 F g^{-1} at 0.1 A g^{-1} in an rGO // rGO symmetric cell (0–1 V). Provided 39.1 Wh kg^{-1} energy density and about 500 W kg^{-1} power density within the same 1 V window. Maintained 171 F g^{-1} after 10 000 cycles ($\approx 25 \%$ retention) with coulombic efficiency rising above 99 % after 500 cycles. Equivalent-circuit analysis showed total $R_s + R_{ct} \approx 40 \Omega$ and confirmed improved ion transport in the gel.
C₁₂E₂₃–LiCl–H₂O lyotropic cubic gel	Created a LiCl/C ₁₂ E ₂₃ /H ₂ O gel that self-assembles into a cubic mesophase (a ≈ 13.2 nm). Comprehensive rheology revealed shear-thinning, full self-healing and tunable gel strength; the LC1.125(H ₂ O) composition offered the best balance of conductivity and mechanical integrity. Symmetric AC//AC split-cell delivered 316 F g^{-1} at 0.25 A g^{-1} within 0–0.5 V. Retained roughly 80 % capacitance with about 80 % coulombic efficiency over 1,500 cycles. Showed the lowest solution and Warburg impedances among tested water ratios, indicating faster ion diffusion.
Ni_{0.5}Mn_{0.5}Co₂O₄ (MASA) electrode	Achieved the first synthesis of mesoporous Ni _{0.5} Mn _{0.5} Co ₂ O ₄ via molten-salt-assisted self-assembly; the same route also produces NiCo ₂ O ₄ and MnCo ₂ O ₄ spinels by varying the salt. Porous architecture verified by BET/SEM/TEM; delivered an areal capacitance of 11.51 F cm^{-2} and a specific capacitance of 338.5 F g^{-1} at 5 mA cm^{-2} , with the lowest charge-transfer resistance among the three spinels. Asymmetric device (Ni _{0.5} Mn _{0.5} Co ₂ O ₄ + // activated-carbon – , 0–1.6 V) offered 79.5 Wh kg^{-1} energy density and 585 W kg^{-1} power density; $R_s = 2.35 \Omega$, $R_{ct} = 0.67 \Omega$. • Demonstrated robust durability with about 72 % capacitance retention after 4 000 cycles at 25 mA cm^{-2} and coulombic efficiency above 95 % after 600 cycles. Proved the MASA approach is versatile for producing other high-surface-area spinel oxides, highlighting its value for next-generation asymmetric supercapacitors.

Table 5.2: Electrochemical performance metrics

Active material	Cell configuration	ΔV	Cs (F g ⁻¹)	E Wh kg ⁻¹	P W kg ⁻¹	Rs / Rct /Cdl /Zw (Ω)	%Cs
PA–NI bicontinuous cubic gel electrolyte	rGO // rGO symmetric split 2-electrode cell	0 – 1	1128 @ 0.1 A g ⁻¹	39.1	500	36.2 / 4.0 / 8.6 × 10 ⁻⁶ /185	25 % after 10 000 cycles @ 0.5 A g ⁻¹
C ₁₂ E ₂₃ –LiCl–H ₂ O lyotropic cubic gel	AC //AC symmetric split 2-electrode	0 – 0.5	316 @ 0.25 A g ⁻¹	11	560	8.5 / 0.6 / 9.2 x 10 ⁻⁶ /434 CDL2-0.2	≈ 80 % after 1 500 cycles
Ni _{0.5} Mn _{0.5} Co ₂ O ₄ MASA electrode	Ni _{0.5} Mn _{0.5} Co ₂ O ₄ (+) // AC (-) Asymmetric 2-electrode	0 – 1.5	9.53 F cm ⁻² (338.5 F g ⁻¹) @ 5 mA cm ⁻² .	79.52	585	2.4 / 0.7 / 1.3x10 ⁻⁴ /31 .7 CDL2 3 x 10 ⁻³	≈ 72 % after 4 000 cycles @ 25 mA cm ⁻²

Overall, the thesis establishes a clear performance hierarchy among the three architectures. The PA–NI bicontinuous gel exhibits a record-high specific capacitance of 1128 F g⁻¹ and strong energy–power figures within a 1 V window. However, its long-term retention drops to 25% after 10,000 cycles. In contrast, the LiCl/C₁₂E₂₃/H₂O cubic gel sacrifices capacitance (316 F g⁻¹, 0–0.5 V) for outstanding mechanical resilience and ~80% stability over 1,500 cycles, making it the most durable electrolyte in aqueous systems. Meanwhile, the MASA-derived Ni_{0.5}Mn_{0.5}Co₂O₄ spinel combines high areal capacitance (11.5 F cm⁻²), low internal resistances (Rs ≈ 2.3 Ω, Rct ≈ 0.7 Ω), and the best energy–power balance (79.5 Wh kg⁻¹ at 1 mA cm⁻²; 585 W kg⁻¹ at 20 mA cm⁻²), retaining ~72% of its capacity after 4,000 cycles. Collectively, these findings highlight the distinct advantages of each system: bicontinuous LC gels maximize charge storage, lyotropic gels offer exceptional mechanical self-repair, and MASA spinels enable high-energy asymmetric devices—each providing a complementary pathway toward next-generation supercapacitors.

These results define a versatile energy-storage platform with clear potential for high-impact applications. The PA–NI bicontinuous gel, delivering ~1128 F g⁻¹ and 39 Wh kg⁻¹ at 1 V, positions symmetric supercapacitors to operate in the hybrid regime, making them ideal as lightweight buffers for regenerative braking, start-stop systems,

and torque assist in electric vehicles. The lyotropic electrolyte, which remains solid up to $\sim 70^\circ\text{C}$, shear-thins under stress, and self-heals rapidly, is suited to leak-free, flexible films for skin-contact wearables, biomedical implants, and bendable IoT tags subjected to frequent flexing. Its ordered 3D nanochannels and solvent-free nature also make it ideal for on-chip micro-supercapacitors and printable power layers in aerospace applications, where solvent volatility and thermal stability are critical. Complementing the gel, mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ electrodes offer $\sim 338\text{ F g}^{-1}$ with low charge-transfer resistance, supporting durable, high-rate operation required for grid-edge buffering in solar and wind systems. Their inherent oxygen-evolution activity also makes them suitable as bifunctional electrodes in integrated Zn–air batteries or water-splitting stacks—merging energy storage and catalysis in a single architecture.



6. FUTURE WORK

Advancing flexible and wearable energy storage technologies is crucial for future research, with potential applications in devices like smartwatches, health trackers, and electronic textiles. Future efforts should focus on optimizing these materials for real-world use by enhancing mechanical properties, improving self-healing capabilities, and ensuring stable performance under various deformation conditions.

Exploring novel material combinations and synthesis techniques is essential to further enhance energy storage capabilities. The success of the Molten Salt Assisted Assembly (MASA) method in synthesizing mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ opens possibilities for creating other complex metal oxide structures with tailored properties. Future research should investigate a broader range of metal combinations and ratios to optimize both electrode and electrolyte materials, potentially leading to new ternary and quaternary metal oxide structures with enhanced electrochemical performance. Scaling up these synthesis methods for industrial production will be essential for practical applications.

Developing integrated energy systems that combine the advantages of supercapacitors with other energy storage and harvesting technologies represents an exciting frontier. Integrating the supercapacitors developed in this study with high-energy-density batteries or renewable energy harvesting systems could enhance their already impressive high-power density and long cycle life. Future research should explore hybrid systems that efficiently capture, store, and deliver energy for a wide range of applications, from portable electronics to electric vehicles. This holistic approach to energy management could lead to significant advancements in sustainable and adaptable energy solutions, addressing the growing demand for efficient energy storage in consumer electronics, automotive, and aerospace markets.



REFERENCE

- [1] **Conway, B. E.** (1999). *Electrochemical Capacitors: Scientific Fundamentals and Technological Applications*. New York, NY: Springer.
- [2] **Lemine, A. S., and Zagho, M. M.** (2018). Altahtamouni, T. M. and Bensalah, N. “Graphene a promising electrode material for supercapacitors—A review,” *Int J Energy Res*, 42(13), 4284–4300. doi:10.1002/er.4170.
- [3] **Dutta, A., Mahanta, J. and Banerjee, T.** (2020) “Supercapacitors in the light of solid waste and energy management: a review,” *Adv Sustain Syst*, 4(1), 2000182. doi: 10.1002/adsu.202000182.
- [4] **R. Jamil and D. S. Silvester** (2022). *Ionic liquid gel polymer electrolytes for flexible supercapacitors: Challenges and prospects*. Hollanda: Elsevier. doi: 10.1016/j.coelec.2022.101046.
- [5] **Mathela, S., Kumar, S., Singh, P. K., Chandra Singh, R., Shukla, P. K., Singh, V., ... et al.** (2022). Ionic liquid dispersed highly conducting polymer electrolyte for supercapacitor application: Current scenario and prospects ‘ICSEM 2021’. *High Perform Polym*, 34(6) 652–672. doi: 10.1177/09540083221099432.
- [6] **Singh, R., Tharion, J., Murugan, S., and Kumar, A.** (2017). ITO-Free Solution-Processed Flexible Electrochromic Devices Based on PEDOT:PSS as Transparent Conducting Electrode. *American Chemical Society*. 9(23), 19427-19435. doi:10.1021/acsami.6b09476.
- [7] **Bhat, T. S., Patil, P. S. and Rakhi, R. B.** (2022). *Recent trends in electrolytes for supercapacitors*. Hollanda: Elsevier. doi:10.1016/j.est.2022.104222.
- [8] **Kaur, G., Sivasubramanian, S. C., and Dalvi, A.** (2022). “Solid-state supercapacitors using ionic liquid dispersed Li⁺-NASICONs as electrolytes. *Electrochim Acta*, 434, 141311, doi:10.1016/j.electacta.2022.141311.
- [9] **Chen, J. Shi, D. Yang, Z. Dong, W. and Chen, M.** (2022). A solvent-exchange strategy to develop stiff and tough hydrogel electrolytes for flexible and stable supercapacitor. *J Power Sources*, 532, 231326. doi: 10.1016/j.jpowsour.2022.231326.
- [10] **Iqbal, M. Zakar, S. and Haider, S. S.** (2020). Role of Aqueous Electrolytes on the Performance of Electrochemical Energy Storage Device. *Journal of Electroanalytical Chemistry*, 858, 113793. doi:10.1016/j.jelechem.2019.113793.
- [11] **Chen, Q., Li, X., Zang, X., Cao, Y., He, Y., Li, P., ... et al.** (2014). Effect of different gel electrolytes on graphene-based solid-state supercapacitors. *RSC advances*, 4(68), 36253-36256. doi: 10.1039/c4ra05553e.

- [12] Ruano Torres, G., Iribarren Laco, J. I., Pérez Madrigal, M. D. M., Torras Costa, J., and Alemán Llansó, C. (2021). Electrical and capacitive response of hydrogel solid-like electrolytes for supercapacitors. *Polymers*, 13(8), 1-14. doi:10.3390/polym13081337.
- [13] Pal, B., Yang, S., Ramesh, S., Thangadurai, V., and Jose, R. (2019). Electrolyte selection for supercapacitive devices: a critical review. *Nanoscale advances*, 1(10), 3807-3835. doi:10.1039/c9na00374f.
- [14] Wang, J., Li, X., Yang, J., Sun, W., Ban, Q., Gai, L., ... et al. (2021). Flame-Retardant, Highly Conductive, and Low-Temperature-Resistant Organic Gel Electrolyte for High-Performance All-Solid Supercapacitors. *ChemSusChem*, 14(9), 2056-2066. doi:10.1002/cssc.202100141.
- [15] Liu, Y., Lu, N., Liu, F., Na, R., Wang, G., Guan, S., and Liu, F. (2020). Highly strong and tough double-crosslinked hydrogel electrolyte for flexible supercapacitors. *ChemElectroChem*, 7(4), 1007-1015. doi:10.1002/celec.201902134.
- [16] Wen, L., Li, F., and Cheng, H. M. (2016). Carbon nanotubes and graphene for flexible electrochemical energy storage: from materials to devices. *Advanced Materials*, 28(22), 4306-4337. doi:10.1002/adma.201504225.
- [17] Lu, C., and Chen, X. (2020). Latest advances in flexible symmetric supercapacitors: from material engineering to wearable applications. *Accounts of Chemical Research*, 53(8), 1468-1477. doi:10.1021/acs.accounts.0c00205.
- [18] Dai, H., Zhang, G., Rawach, D., Fu, C., Wang, C., Liu, X., ... et al. (2021). Polymer gel electrolytes for flexible supercapacitors: Recent progress, challenges, and perspectives. *Energy Storage Materials*, 34, 320-355. doi: 10.1016/j.ensm.2020.09.018.
- [19] Muzaffar, A., Ahamed, M. B., and Deshmukh, K. (2021) *Conducting polymer electrolytes for flexible supercapacitors. Flexible supercapacitor nanoarchitectonics*. Beverly, MA: Scrivener Publishing. doi:10.1002/9781119711469.ch9.
- [20] Zhou, K., Wang, H., Jiu, J., Liu, J., Yan, H., and Suganuma, K. (2018). Polyaniline films with modified nanostructure for bifunctional flexible multicolor electrochromic and supercapacitor applications. *Chemical Engineering Journal*, 345, 290-299. doi:10.1016/j.cej.2018.03.175.
- [21] Zang, L., Liu, Q., Qiu, J., Yang, C., Wei, C., Liu, C., and Lao, L. (2017). Design and fabrication of an all-solid-state polymer supercapacitor with highly mechanical flexibility based on polypyrrole hydrogel. *ACS applied materials & interfaces*, 9(39), 33941-33947. doi:10.1021/acsami.7b10321.
- [22] Handayani, P. L., Kim, T., Song, Y. H., Park, J. S., Yang, S. J., and Choi, U. H. (2023). Tailoring molecular interaction in heteronetwork polymer electrolytes for stretchable, high-voltage fiber supercapacitors. *Chemical Engineering Journal*, 452, 139432. doi:10.1016/j.cej.2022.139432.

- [23] **Chen, X. Y., Chen, C., Zhang, Z. J., and Xie, D. H.** (2013). Gelatin-derived nitrogen-doped porous carbon via a dual-template carbonization method for high performance supercapacitors. *Journal of Materials Chemistry A*, *1*(36), 10903-10911. doi:10.1039/c3ta12328f.
- [24] **Alipoori, S., Mazinani, S., Aboutalebi, S. H., and Sharif, F.** (2020). Review of PVA-based gel polymer electrolytes in flexible solid-state supercapacitors: Opportunities and challenges. *Journal of Energy Storage*, *27*, 101072. doi:10.1016/j.est.2019.101072.
- [25] **Peng, X., Peng, L., Wu, C., and Xie, Y.** (2014). Two dimensional nanomaterials for flexible supercapacitors. *Chemical Society Reviews*, *43*(10), 3303-3323. doi: 10.1039/c3cs60407a.
- [26] **Ghannam, M. T.** (2004). Creep–recovery experimental investigation of crude oil–polymer emulsions. *Journal of applied polymer science*, *92*(1), 226-237. doi:10.1002/app.13645.
- [27] **Chen, Y., Tang, Z., Zhang, X., Liu, Y., Wu, S., and Guo, B.** (2018). Covalently cross-linked elastomers with self-healing and malleable abilities enabled by boronic ester bonds. *ACS applied materials & interfaces*, *10*(28), 24224-24231. doi:10.1021/acsami.8b09863.
- [28] **Wang, Q., Wang, X., Liu, B., Yu, G., Hou, X., Chen, D., and Shen, G.** (2013). NiCo₂O₄ nanowire arrays supported on Ni foam for high-performance flexible all-solid-state supercapacitors. *Journal of Materials Chemistry A*, *1*(7), 2468-2473. doi: 10.1039/c2ta01283a.
- [29] **Li, M., Jia, C., Türker, Y., Özkaynak, M. U., Zhao, L., Zhang, D., ... et al.** (2023). Wide-temperature-range flexible micro-supercapacitors using liquid crystal gel electrolyte. *ACS Applied Energy Materials*, *6*(10), 5230-5238. doi:10.1021/acsaem.3c00144.
- [30] **Özkaynak, M. U., Türker, Y., Dönmez, K. B., Karatepe, N., and Güner, F. S.** (2022). High-performance supercapacitor electrolytes based on high-mole-ratio phosphoric acid/lauryl ether surfactant liquid crystalline gel. *International Journal of Energy Research*, *46*(14), 19980-19991. doi:10.1002/er.8126.
- [31] **Yuan, C., Li, J., Hou, L., Zhang, X., Shen, L., and Lou, X. W.** (2012). Ultrathin mesoporous NiCo₂O₄ nanosheets supported on Ni foam as advanced electrodes for supercapacitors. *Advanced Functional Materials*, *22*(21), 4592-4597. doi:10.1002/adfm.201200994.
- [32] **Simon, P., and Gogotsi, Y.** (2008). Materials for electrochemical capacitors. *Nature materials*, *7*(11), 845-854. doi: 10.1038/nmat2297
- [33] **Selvaraj, K., Arumugam, H., Muthukaruppan, A., Kannaiyan, S. K., Krishnan, S., Peethambaram, P., ... et al.** (2022). Supercapacitor and high k properties of CNT–PbS reinforced quinoxaline amine based polybenzoxazine composites. *Soft Matter*, *18*(46), 8779-8791. doi: 10.1039/d2sm00737a.

- [34] **Goubard-Bretesché, N., Crosnier, O., Favier, F., and Brousse, T.** (2016). Improving the volumetric energy density of supercapacitors. *Electrochimica Acta*, 206, 458-463. doi: 10.1016/j.electacta.2016.01.171.
- [35] **Brezesinski, T., Wang, J., Tolbert, S. H., and Dunn, B.** (2010). Ordered mesoporous α -MoO₃ with iso-oriented nanocrystalline walls for thin-film pseudocapacitors. *Nature materials*, 9(2), 146-151. doi:10.1038/nmat2612.
- [36] **Xu, H., and Shen, M.** (2021). The control of lithium-ion batteries and supercapacitors in hybrid energy storage systems for electric vehicles: A review. *International Journal of Energy Research*, 45(15), 20524-20544. doi: 10.1002/er.7150.
- [37] **Iqbal, M. Z., Faisal, M. M., and Ali, S. R.** (2021). Integration of supercapacitors and batteries towards high-performance hybrid energy storage devices. *International Journal of Energy Research*, 45(2), 1449-1479. doi: 10.1002/er.5954.
- [38] **Kumaravel, V., Bartlett, J., and Pillai, S. C.** (2021). Solid electrolytes for high-temperature stable batteries and supercapacitors. *Advanced Energy Materials*, 11(3), 2002869. doi: 10.1002/aenm.202002869.
- [39] Winter, M., and Brodd, R. J. (2004). What are batteries, fuel cells, and supercapacitors?. *Chemical reviews*, 104(10), 4245-4270. doi: 10.1021/cr020730k.
- [40] Jin, Z. Y., Lu, A. H., Xu, Y. Y., Zhang, J. T., and Li, W. C. (2014). Ionic liquid-assisted synthesis of microporous carbon nanosheets for use in high rate and long cycle life supercapacitors. *Advanced materials*, 26(22), 3700-3705. doi: 10.1002/adma.201306273.
- [41] **Huang, T., Long, M. C., Wu, G., Wang, Y. Z., and Wang, X. L.** (2019). Poly (ionic liquid)-based hybrid hierarchical free-standing electrolytes with enhanced ion transport and fire retardancy towards long-cycle-life and safe lithium batteries. *ChemElectroChem*, 6(14), 3674-3683. doi: 10.1002/celec.201900686.
- [42] **Zhong, C., Deng, Y., Hu, W., Qiao, J., Zhang, L., and Zhang, J.** (2015). A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chemical Society Reviews*, 44(21), 7484-7539. doi: 10.1039/c5cs00303b.
- [43] **Verma, S., Padha, B., Mahajan, P., and Arya, S.** (2022). Effect of electrolyte on the performance of supercapacitors. *ECS Transactions*, 107(1), 10821. doi:10.1149/10701.10821ecst
- [44] **Wang, J., Li, X., Yang, J., Sun, W., Ban, Q., Gai, L., ... et al.** (2021). Flame-Retardant, Highly Conductive, and Low-Temperature-Resistant Organic Gel Electrolyte for High-Performance All-Solid Supercapacitors. *ChemSusChem*, 14(9), 2056-2066. doi:10.1002/cssc.202100141.

- [45] **Chen, Q., Li, X., Zang, X., Cao, Y., He, Y., Li, P., ... et al.** (2014). Effect of different gel electrolytes on graphene-based solid-state supercapacitors. *RSC advances*, 4(68), 36253-36256. doi:10.1039/c4ra05553e.
- [46] **Ruano Torres, G., Iribarren Laco, J. I., Pérez Madrigal, M. D. M., Torras Costa, J., and Alemán Llansó, C.** (2021). Electrical and capacitive response of hydrogel solid-like electrolytes for supercapacitors. *Polymers*, 13(8), 1-14. doi:10.3390/polym13081337.
- [47] **Sung, J. H., Kim, S. J., Jeong, S. H., Kim, E. H., and Lee, K. H.** (2006). Flexible micro-supercapacitors. *Journal of power sources*, 162(2), 1467-1470. doi:10.1016/j.jpowsour.2006.07.073.
- [48] **Kaempgen, M., Chan, C. K., Ma, J., Cui, Y., and Gruner, G.** (2009). Printable thin film supercapacitors using single-walled carbon nanotubes. *Nano letters*, 9(5), 1872-1876. doi: 10.1021/nl8038579.
- [49] **Du, H., Wu, Z., Xu, Y., Liu, S., and Yang, H.** (2020). Poly (3, 4-ethylenedioxythiophene) based solid-state polymer supercapacitor with ionic liquid gel polymer electrolyte. *Polymers*, 12(2), 297. doi:10.3390/polym12020297.
- [50] **Sudhakar, Y. N., Selvakumar, M., and Bhat, D. K.** (2015). Preparation and characterization of phosphoric acid-doped hydroxyethyl cellulose electrolyte for use in supercapacitor. *Materials for Renewable and Sustainable Energy*, 4, 1-9. doi:10.1007/s40243-015-0051-z.
- [51] **Rathod, D., Vijay, M., Islam, N., Kannan, R., Kharul, U., Kurungot, S., and Pillai, V.** (2009). Design of an “all solid-state” supercapacitor based on phosphoric acid doped polybenzimidazole (PBI) electrolyte. *Journal of applied electrochemistry*, 39, 1097-1103. doi:10.1007/s10800-008-9764-3.
- [52] **Tunkara, E., Albayrak, C., Polat, E. O., Kocabas, C., and Dag, O.** (2014). Highly proton conductive phosphoric acid–nonionic surfactant lyotropic liquid crystalline mesophases and application in graphene optical modulators. *Acs Nano*, 8(10), 11007-11012. doi:10.1021/nm505199q.
- [53] **Sasi, R., Sarojam, S., and Devaki, S. J.** (2016). High performing biobased ionic liquid crystal electrolytes for supercapacitors. *ACS Sustainable Chemistry & Engineering*, 4(6), 3535-3543. doi:10.1021/acssuschemeng.6b00585.
- [54] **Xia, M., Nie, J., Zhang, Z., Lu, X., and Wang, Z. L.** (2018). Suppressing self-discharge of supercapacitors via electrorheological effect of liquid crystals. *Nano Energy*, 47, 43-50. doi: 10.1016/j.nanoen.2018.02.022.
- [55] **Cao, X. M., Sun, Z. J., Zhao, S. Y., Wang, B., and Han, Z. B.** (2018). MOF-derived sponge-like hierarchical porous carbon for flexible all-solid-state supercapacitors. *Materials Chemistry Frontiers*, 2(9), 1692-1699. doi:10.1039/c8qm00284c.

- [56] **Fadeeva, Y. A., Safonova, L. P., and Persson, I.** (2010). Physico-chemical and structural characterization of the binary system phosphoric acid–N, N-dimethylformamide. *Physical Chemistry Chemical Physics*, 12(31), 8977-8984. doi: 10.1039/b926140k.
- [57] **Song, Y., Liu, T., Li, M., Yao, B., Kou, T., Feng, D., ... et al.** (2018). Engineering of mesoscale pores in balancing mass loading and rate capability of hematite films for electrochemical capacitors. *Advanced Energy Materials*, 8(26), 1801784. doi: 10.1002/aenm.201801784.
- [58] **Lin, R., Li, Z., Abou El Amaiem, D. I., Zhang, B., Brett, D. J., He, G., and Parkin, I. P.** (2017). A general method for boosting the supercapacitor performance of graphitic carbon nitride/graphene hybrids. *Journal of Materials Chemistry A*, 5(48), 25545-25554. doi:10.1039/c7ta09492b.
- [59] **Uzundal, C. B., Mert Balci, F., Ulgut, B., and Dag, O.** (2017). Lyotropic liquid crystalline mesophase of sulfuric acid–nonionic surfactant stabilizes lead (II) oxide in sulfuric acid concentrations relevant to lead acid batteries. *ACS omega*, 2(7), 3785-3791. doi:10.1021/acsomega.7b00833.
- [60] **Röschenthaler, G. V., and Storzer, W.** (1982). A Stable Tetraalkoxy (hydroxy) phosphorane and Phosphorane Oxide Anion by Hydrolysis of Tetraalkoxy (halogen) phosphoranes. *Angewandte Chemie International Edition in English*, 21(3), 208-208. doi: 10.1002/anie.198202081
- [61] **Tafete, G. A., Abera, M. K., and Thothadri, G.** (2022). Review on nanocellulose-based materials for supercapacitors applications. *Journal of Energy Storage*, 48, 103938. doi:10.1016/j.est.2021.103938.
- [62] **Raj, C. J., Manikandan, R., Rajesh, M., Sivakumar, P., Jung, H., Das, S. J., and Kim, B. C.** (2021). Cornhusk mesoporous activated carbon electrodes and seawater electrolyte: The sustainable sources for assembling retainable supercapacitor module. *Journal of Power Sources*, 490, 229518. doi:10.1016/j.jpowsour.2021.229518.
- [63] **Cheng, J., Lu, Z., Zhao, X., Chen, X., and Liu, Y.** (2021). Green needle coke-derived porous carbon for high-performance symmetric supercapacitor. *Journal of Power Sources*, 494, 229770. doi:10.1016/j.jpowsour.2021.229770.
- [64] **Cheng, M., Meng, Y., Meng, Q., Mao, L., Zhang, M., Amin, K., ... et al.** (2018). A hierarchical porous N-doped carbon electrode with superior rate performance and cycling stability for flexible supercapacitors. *Materials Chemistry Frontiers*, 2(5), 986-992. doi:10.1039/C8QM00023A.
- [65] **Purkait, T., Singh, G., Kumar, D., Singh, M., and Dey, R. S.** (2018). High-performance flexible supercapacitors based on electrochemically tailored three-dimensional reduced graphene oxide networks. *Scientific reports*, 8(1), 640. doi:10.1038/s41598-017-18593-3.

- [66] **Cao, J., He, P., Brent, J. R., Yilmaz, H., Lewis, D. J., Kinloch, I. A., and Derby, B.** (2018). Supercapacitor electrodes from the in situ reaction between two-dimensional sheets of black phosphorus and graphene oxide. *ACS applied materials & interfaces*, 10(12), 10330-10338. doi: 10.1021/acsami.7b18853.
- [67] **Xie, Y., and Wang, J.** (2018). Capacitance performance of carbon paper supercapacitor using redox-mediated gel polymer electrolyte. *Journal of Sol-Gel Science and Technology*, 86, 760-772. doi: 10.1007/s10971-018-4678-y.
- [68] **Taghavikish, M., Subianto, S., Gu, Y., Sun, X., Zhao, X. S., and Choudhury, N. R.** (2018). A poly (ionic liquid) gel electrolyte for efficient all solid electrochemical double-layer capacitor. *Scientific reports*, 8(1), 10918. doi:10.1038/s41598-018-29028-y.
- [69] **Alipoori, S., Mazinani, S., Aboutalebi, S. H., and Sharif, F.** (2020). Review of PVA-based gel polymer electrolytes in flexible solid-state supercapacitors: Opportunities and challenges. *journal of energy storage*, 27, 101072. doi:10.1016/j.est.2019.101072.
- [70] **Amaral, M. M., Venancio, R., Peterlevitz, A. C., and Zanin, H.** (2022). Recent advances on quasi-solid-state electrolytes for supercapacitors. *Journal of Energy Chemistry*, 67, 697-717. doi: 10.1016/j.jechem.2021.11.010.
- [71] **Albayrak, C., Cihaner, A., and Dag, Ö.** (2012). A New, Highly Conductive, Lithium Salt/Nonionic Surfactant, Lyotropic Liquid-Crystalline Mesophase and Its Application. *Chemistry-A European Journal*, 18(14), 4190. doi:10.1002/chem.201103705.
- [72] **Yilmaz Topuzlu, E., Okur, H. I., Ulgut, B., and Dag, O.** (2021). Role of water in the lyotropic liquid crystalline mesophase of lithium salts and non-ionic surfactants. *Langmuir*, 37(49), 14443-14453. doi:10.1021/acs.langmuir.1c02411.
- [73] **Balci, F. M., Balci, S., Kocabas, C., and Dag, O.** (2017). Lyotropic liquid-crystalline mesophase of lithium triflate–nonionic surfactant as gel electrolyte for graphene optical modulator. *The Journal of Physical Chemistry C*, 121(21), 11194-11200. doi: 10.1021/acs.jpcc.7b03622.
- [74] **Tunkara, E., Albayrak, C., Polat, E. O., Kocabas, C., and Dag, O.** (2014). Highly proton conductive phosphoric acid–nonionic surfactant lyotropic liquid crystalline mesophases and application in graphene optical modulators. *Acs Nano*, 8(10), 11007-11012. doi:10.1021/nn505199q.
- [75] **Uzundal, C. B., Mert Balci, F., Ulgut, B., and Dag, O.** (2017). Lyotropic liquid crystalline mesophase of sulfuric acid–nonionic surfactant stabilizes lead (II) oxide in sulfuric acid concentrations relevant to lead acid batteries. *ACS omega*, 2(7), 3785-3791. doi: 10.1021/acsomega.7b00833.

- [76] **Özkaynak, M. U., Türker, Y., Dönmez, K. B., Karatepe, N., and Güner, F. S.** (2022). High-performance supercapacitor electrolytes based on high-mole-ratio phosphoric acid/lauryl ether surfactant liquid crystalline gel. *International Journal of Energy Research*, 46(14), 19980-19991. doi: 10.1002/er.8126.
- [77] **Xu, C., Mandal, T., Larson, R. G., Wang, D., and Wang, H.** (2019). A molecular dynamics simulation of the structure of sodium lauryl ether sulfate and poly (vinyl alcohol) at the air/water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 563, 84-94. doi: 10.1016/j.colsurfa.2018.11.060.
- [78] **Albayrak, C., Ozkan, N., and Dag, O.** (2011). Origin of lyotropic liquid crystalline mesophase formation and liquid crystalline to mesostructured solid transformation in the metal nitrate salt– surfactant systems. *Langmuir*, 27(3), 870-873. doi:10.1021/la1035932.
- [79] **Sakya, P., Seddon, J. M., Templer, R. H., Mirkin, R. J., and Tiddy, G. J. T.** (1997). Micellar cubic phases and their structural relationships: The nonionic surfactant system C12EO12/water. *Langmuir*, 13(14), 3706-3714. doi:10.1021/la9701844
- [80] **Sepulveda, A. F., Kumpgdee-Vollrath, M., Franco, M. K., Yokaichiya, F., and de Araujo, D. R.** (2023). Supramolecular structure organization and rheological properties modulate the performance of hyaluronic acid-loaded thermosensitive hydrogels as drug-delivery systems. *Journal of Colloid and Interface Science*, 630, 328-340. doi:10.1016/j.jcis.2022.10.064.
- [81] **Pang, Z., Deeth, H., and Bansal, N.** (2015). Effect of polysaccharides with different ionic charge on the rheological, microstructural and textural properties of acid milk gels. *Food research international*, 72, 62-73. doi: 10.1016/j.foodres.2015.02.009.
- [82] **Kujawa, P., Audibert-Hayet, A., Selb, J., and Candau, F.** (2006). Effect of ionic strength on the rheological properties of multisticker associative polyelectrolytes. *Macromolecules*, 39(1), 384-392. doi: 10.1021/ma051312v.
- [83] **Santos, L. R. B., Santilli, C. V., and Pulcinelli, S. H.** (1999). Sol–gel transition in SnO₂ colloidal suspensions: viscoelastic properties. *Journal of non-crystalline solids*, 247(1-3), 153-157. doi:10.1016/S0022-3093(99)00055-1.
- [84] **Cai, W., Hu, T., and Huang, Q.** (2021). A polysaccharide from *Lignosus rhinocerotis* sclerotia: Self-healing properties and the effect of temperature on its rheological behavior. *Carbohydrate Polymers*, 267, 118223. doi:10.1016/j.carbpol.2021.118223.
- [85] **Sacks, M. D., and Sheu, R. S.** (1987). Rheological properties of silica sol-gel materials. *Journal of non-crystalline solids*, 92(2-3), 383-396. doi: 10.1016/S0022-3093(87)80057-1.

- [86] **Razmkhah, S., Razavi, S. M. A., and Mohammadifar, M. A.** (2017). Dilute solution, flow behavior, thixotropy and viscoelastic characterization of cress seed (*Lepidium sativum*) gum fractions. *Food Hydrocolloids*, 63, 404-413. doi: 10.1016/j.foodhyd.2016.09.030.
- [87] **Zou, Y., Chen, C., Sun, Y., Gan, S., Dong, L., Zhao, J., and Rong, J.** (2021). Flexible, all-hydrogel supercapacitor with self-healing ability. *Chemical Engineering Journal*, 418, 128616. doi: 10.1016/j.cej.2021.128616.
- [88] **Corzo, I. J. M., da Fonsêca, J. H. L., and d'Ávila, M. A.** (2023). Influence of carboxymethyl cellulose solutions on rheological properties of Laponite dispersions. *Rheologica Acta*, 62(7), 393-404. doi: 10.1007/s00397-023-01401-3.
- [89] **Saxena, A., Kaloti, M., and Bohidar, H. B.** (2011). Rheological properties of binary and ternary protein-polysaccharide co-hydrogels and comparative release kinetics of salbutamol sulphate from their matrices. *International Journal of Biological Macromolecules*, 48(2), 263-270. doi: 10.1016/j.ijbiomac.2010.11.008.
- [90] **Dave, P. N., Macwan, P. M., and Kamaliya, B.** (2023). Synthesis and rheological investigations of gum-ghatti-cl-poly (NIPA-co-AA)-graphene oxide based hydrogels. *Materials Advances*, 4(14), 2971-2980. doi: 10.1039/d3ma00092c.
- [91] **Daniloski, D., McCarthy, N. A., Gazi, I., and Vasiljevic, T.** (2022). Rheological and structural properties of acid-induced milk gels as a function of β -casein phenotype. *Food Hydrocolloids*, 131, 107846. doi: 10.1016/j.foodhyd.2022.107846.
- [92] **Kundu, S. K., Yoshida, M., and Shibayama, M.** (2010). Effect of salt content on the rheological properties of hydrogel based on oligomeric electrolyte. *The Journal of Physical Chemistry B*, 114(4), 1541-1547. doi: 10.1021/jp906312f.
- [93] **Kwiatkowski, A. L., Molchanov, V. S., Orekhov, A. S., Vasiliev, A. L., and Philippova, O. E.** (2016). Impact of salt co- and counterions on rheological properties and structure of wormlike micellar solutions. *The Journal of Physical Chemistry B*, 120(49), 12547-12556. doi: 10.1021/acs.jpcb.6b09817.
- [94] **Dreiss, C. A.** (2007). Wormlike micelles: where do we stand? Recent developments, linear rheology and scattering techniques. *Soft matter*, 3(8), 956-970. doi: 10.1039/b705775j.
- [95] **Wu, Z., Ding, H., Tao, K., Wei, Y., Gui, X., Shi, W., ... et al.** (2021). Ultrasensitive, stretchable, and fast-response temperature sensors based on hydrogel films for wearable applications. *ACS Applied Materials & Interfaces*, 13(18), 21854-21864. doi: 10.1021/acsami.1c05291.
- [96] **Alaee, P., Kamkar, M., and Arjmand, M.** (2022). Fumed silica-based suspensions for shear thickening applications: a full-scale rheological study. *Langmuir*, 38(16), 5006-5019. doi: 10.1021/acs.langmuir.2c00591.

- [97] **Kotsilkova, R., and Tabakova, S.** (2023). Exploring effects of graphene and carbon nanotubes on rheology and flow instability for designing printable polymer nanocomposites. *Nanomaterials*, 13(5), 835. doi: 10.3390/nano13050835.
- [98] **Luo, X. J., Wei, B., Gao, K., Jing, B., Huang, B., Guo, P., ... et al.** (2023). Gas channeling control with an in-situ smart surfactant gel during water-alternating-CO₂ enhanced oil recovery. *Petroleum Science*, 20(5), 2835-2851. doi: 10.1016/j.petsci.2023.03.003.
- [99] **Wu, S., Lou, D., Wang, H., Jiang, D., Fang, X., Meng, J., ... et al.** (2022). One-pot synthesis of anti-freezing carrageenan/polyacrylamide double-network hydrogel electrolyte for low-temperature flexible supercapacitors. *Chemical Engineering Journal*, 435, 135057. doi: 10.1016/j.cej.2022.135057.
- [100] **Shabbir, A., Goldansaz, H., Hassager, O., Van Ruymbeke, E., and Alvarez, N. J.** (2015). Effect of hydrogen bonding on linear and nonlinear rheology of entangled polymer melts. *Macromolecules*, 48(16), 5988-5996. doi: 10.1021/acs.macromol.5b00757.
- [101] **Liu, S., Zhang, H., and Yu, W.** (2020). Simultaneously improved strength and toughness in κ -carrageenan/polyacrylamide double network hydrogel via synergistic interaction. *Carbohydrate Polymers*, 230, 115596. doi: 10.1016/j.carbpol.2019.115596.
- [102] **Liu, S., and Li, L.** (2017). Ultrastretchable and self-healing double-network hydrogel for 3D printing and strain sensor. *ACS applied materials & interfaces*, 9(31), 26429-26437. doi: 10.1021/acsami.7b07445.
- [103] **Basu, M., Hassan, P. A., and Shelar, S. B.** (2023). Modulation of surfactant self-assembly in deep eutectic solvents and its relevance to drug delivery-A review. *Journal of Molecular Liquids*, 375, 121301. doi: 10.1016/j.molliq.2023.121301.
- [104] **Yun, X. W., Tang, B., Xiong, Z. Y., and Wang, X. G.** (2020). Understanding self-assembly, colloidal behavior and rheological properties of graphene derivatives for high-performance supercapacitor fabrication. *Chinese Journal of Polymer Science*, 38(5), 423-434. doi: 10.1007/s10118-020-2411-0.
- [105] **Appel, E. A., Tibbitt, M. W., Webber, M. J., Mattix, B. A., Veisoh, O., and Langer, R.** (2015). Self-assembled hydrogels utilizing polymer-nanoparticle interactions. *Nature communications*, 6(1), 6295. doi: 10.1038/ncomms7295.
- [106] **Morini, M. A., Messina, P. V., and Schulz, P. C.** (2005). The interaction of electrolytes with non-ionic surfactant micelles. *Colloid and Polymer Science*, 283, 1206-1218. doi: 10.1007/s00396-005-1312-7.
- [107] **Ye, Z., Lu, H., Chai, G., Wu, C., Chen, J., and Lv, L.** (2023). Glycerol-modified poly (vinyl alcohol)/poly (ethylene glycol) self-healing hydrogel for artificial cartilage. *Polymer International*, 72(1), 27-38. doi: 10.1002/pi.6444.

- [108] **Brito-Oliveira, T. C., Moraes, I. C., Pinho, S. C., and Campanella, O. H.** (2022). Modeling creep/recovery behavior of cold-set gels using different approaches. *Food Hydrocolloids*, 123, 107183. doi: 10.1016/j.foodhyd.2021.107183.
- [109] **Krempel, E., and Khan, F.** (2003). Rate (time)-dependent deformation behavior: an overview of some properties of metals and solid polymers. *International Journal of Plasticity*, 19(7), 1069-1095. doi: 10.1016/S0749-6419(03)00002-0.
- [110] **Buitrago, C. F., Pressly, J. F., Yang, A. S., Gordon, P. A., Riggleman, R. A., Natarajan, B., and Winey, K. I.** (2020). Creep attenuation in glassy polymer nanocomposites with variable polymer–nanoparticle interactions. *Soft Matter*, 16(38), 8912-8924. doi: 10.1039/d0sm01247e.
- [111] **Pejkowski, Ł., Seyda, J., Nowicki, K., and Mroziński, D.** (2023). Mechanical performance of non-reinforced, carbon fiber reinforced and glass bubbles reinforced 3D printed PA12 polyamide. *Polymer Testing*, 118, 107891. doi: 10.1016/j.polymertesting.2022.107891.
- [112] **Mandlekar, N., Rana, B., Maurya, P., Butola, B. S., and Joshi, M.** (2023). Long-term prediction of creep and stress-relaxation behaviour in synthetic fabrics using the time–temperature superposition principle. *Fibers and Polymers*, 24(6), 2195-2207. doi: 10.1007/s12221-023-00181-0.
- [113] **Baron, R. I., Culica, M. E., Biliuta, G., Bercea, M., Gherman, S., Zavastin, D., ... et al.** (2019). Physical hydrogels of oxidized polysaccharides and poly (vinyl alcohol) for wound dressing applications. *Materials*, 12(9), 1569. doi: 10.3390/ma12091569.
- [114] **Starkova, O., Zhang, Z., and Zhang, H.** (2008). Effect Of Temperature, Moisture And Strain Rate On Limits Of Linear Viscoelastic Behaviour Of Polyamide 66 Filled With Tio2 Nanoparticles. *Materials Science and Engineering A*, 498(1-2), 242-247.
- [115] **Xu, Y. L., Xiong, S. B., Li, Y. B., and Zhao, S. M.** (2008). Study on creep properties of indica rice gel. *Journal of Food Engineering*, 86(1), 10-16. doi: 10.1016/j.jfoodeng.2007.09.002.
- [116] **Kurt, A., Cengiz, A., and Kahyaoglu, T.** (2016). The effect of gum tragacanth on the rheological properties of salep based ice cream mix. *Carbohydrate Polymers*, 143, 116-123. doi: 10.1016/j.carbpol.2016.02.018.
- [117] **Sharma, A., Naga, G. R. R., Kumar, P., and Raha, S.** (2022). Development of an empirical relationship between non-recoverable creep compliance & zero shear viscosity for wide-ranging stiffness of asphalt binders. *Construction and Building Materials*, 326, 126764. doi:10.1016/j.conbuildmat.2022.126764.
- [118] **Moučka, R., Sedláček, M., and Pátíková, Z.** (2023). Fractional viscoelastic models of porcine skin and its gelatin-based surrogates. *Mechanics of Materials*, 177, 104559. doi: 10.1016/j.mechmat.2023.104559.

- [119] **Tian, Z., He, J., Wang, Y., Zhao, W., and Duan, L.** (2022). Quantitative insights into rheology of self-crosslinking dialdehyde carboxymethyl cellulose/collagen solution: a comprehensive experimental and modelling investigation. *Mechanics of Materials*, 170, 104356. doi: 10.1016/j.mechmat.2022.104356.
- [120] **Liu, X., Xu, J., Li, Y., Zhao, H., and Guo, S.** (2023). Mechanism of the glucono- δ -lactone induced soymilk gelation: Enthalpy and entropy transformation in the cross-linking of protein molecules. *Food Research International*, 169, 112868. doi: 10.1016/j.foodres.2023.112868.
- [121] **Dolz, M., Hernández, M. J., and Delegido, J.** (2008). Creep and recovery experimental investigation of low oil content food emulsions. *Food Hydrocolloids*, 22(3), 421-427. doi: 10.1016/j.foodhyd.2006.12.011.
- [122] **Ghannam, M. T.** (2004). Creep–recovery experimental investigation of crude oil–polymer emulsions. *Journal of applied polymer science*, 92(1), 226-237. doi: 10.1002/app.13645.
- [123] **Sozer, N.** (2009). Rheological properties of rice pasta dough supplemented with proteins and gums. *Food Hydrocolloids*, 23(3), 849-855. doi: 10.1016/j.foodhyd.2008.03.016.
- [124] **Cofelice, M., Messina, M. C., Marconi, E., Cuomo, F., and Lopez, F.** (2023). Effect of the xanthan gum on the rheological properties of alginate hydrogels. *Food Hydrocolloids*, 142, 108768. doi: 10.1016/j.foodhyd.2023.108768.
- [125] **Hermida-Merino, C., Perez-Rodriguez, M., Pineiro, M. M., and Pastoriza-Gallego, M. J.** (2016). Evidence of viscoplastic behavior of exfoliated graphite nanofluids. *Soft Matter*, 12(8), 2264-2275. doi: 10.1039/c5sm02932e.
- [126] **Cash, J. J., Kubo, T., Dobbins, D. J., and Sumerlin, B. S.** (2018). Maximizing the symbiosis of static and dynamic bonds in self-healing boronic ester networks. *Polymer Chemistry*, 9(15), 2011-2020. doi: 10.1039/c8py00123e.
- [127] **Zhang, X., Wang, S., Jiang, Z., Li, Y., and Jing, X.** (2020). Boronic ester based vitrimers with enhanced stability via internal boron–nitrogen coordination. *Journal of the American Chemical Society*, 142(52), 21852-21860. doi:10.1021/jacs.0c10244.
- [128] **Wang, Q., Wang, X., Liu, B., Yu, G., Hou, X., Chen, D., and Shen, G.** (2013). NiCo₂O₄ nanowire arrays supported on Ni foam for high-performance flexible all-solid-state supercapacitors. *Journal of Materials Chemistry A*, 1(7), 2468-2473. doi: 10.1039/c2ta01283a.
- [129] **Li, M., Jia, C., Türker, Y., Özkaynak, M. U., Zhao, L., Zhang, D., ... et al.** (2023). Wide-temperature-range flexible micro-supercapacitors using liquid crystal gel electrolyte. *ACS Applied Energy Materials*, 6(10), 5230-5238. doi: 10.1021/acsaem.3c00144.

- [130] Yuan, C., Li, J., Hou, L., Zhang, X., Shen, L., and Lou, X. W. (2012). Ultrathin mesoporous NiCo₂O₄ nanosheets supported on Ni foam as advanced electrodes for supercapacitors. *Advanced Functional Materials*, 22(21), 4592-4597. doi: 10.1002/adfm.201200994.
- [131] Simon, P., and Gogotsi, Y. (2008). Materials for electrochemical capacitors. *Nature materials*, 7(11), 845-854.
- [132] Selvaraj, K., Arumugam, H., Muthukaruppan, A., Kannaiyan, S. K., Krishnan, S., Peethambaram, P., ... et al. (2022). Supercapacitor and high k properties of CNT–PbS reinforced quinoxaline amine based polybenzoxazine composites. *Soft Matter*, 18(46), 8779-8791. doi: 10.1039/d2sm00737a.
- [133] Goubard-Bretesché, N., Crosnier, O., Favier, F., and Brousse, T. (2016). Improving the volumetric energy density of supercapacitors. *Electrochimica Acta*, 206, 458-463. doi: 10.1016/j.electacta.2016.01.171.
- [134] Brezesinski, T., Wang, J., Tolbert, S. H., and Dunn, B. (2010). Ordered mesoporous α -MoO₃ with iso-oriented nanocrystalline walls for thin-film pseudocapacitors. *Nature materials*, 9(2), 146-151. doi: 10.1038/nmat2612.
- [135] An, L., Ren, Q., Li, W., Xu, K., Cao, Y., Ji, T., ... et al. (2015). Highly ordered mesoporous NiCo₂O₄ with superior pseudocapacitance performance for supercapacitors. *Journal of Materials Chemistry A*, 3(21), 11503-11510. doi: 10.1039/c5ta01746g.
- [136] Lu, Q., Chen, Y., Li, W., Chen, J. G., Xiao, J. Q., and Jiao, F. (2013). Ordered mesoporous nickel cobaltite spinel with ultra-high supercapacitance. *Journal of Materials Chemistry A*, 1(6), 2331-2336. doi: 10.1039/c2ta00921h.
- [137] Naveen, A. N., and Selladurai, S. (2015). Novel low temperature synthesis and electrochemical characterization of mesoporous nickel cobaltite-reduced graphene oxide (RGO) composite for supercapacitor application. *Electrochimica Acta*, 173, 290-301. doi: 10.1016/j.electacta.2015.05.072.
- [138] Hsu, C. T., and Hu, C. C. (2013). Synthesis and characterization of mesoporous spinel NiCo₂O₄ using surfactant-assembled dispersion for asymmetric supercapacitors. *Journal of power sources*, 242, 662-671. doi: 10.1016/j.jpowsour.2013.05.130.
- [139] Li, Y., Pan, J., Wu, J., Yi, T., and Xie, Y. (2019). Mesoporous NiCo₂O₄ nanoneedles@ MnO₂ nanoparticles grown on nickel foam for electrode used in high-performance supercapacitors. *Journal of energy chemistry*, 31, 167-177. doi: 10.1016/j.jechem.2018.06.009.
- [140] Wang, W., Kuai, L., Cao, W., Huttula, M., Ollikkala, S., Ahopelto, T., ... et al. (2017). Mass-production of mesoporous MnCo₂O₄ spinels with manganese (IV)-and cobalt (II)-rich surfaces for superior bifunctional oxygen electrocatalysis. *Angewandte Chemie*, 129(47), 15173-15177. doi: 10.1002/anie.201708765.

- [141] **Abidat, I., Bouchenafa-Saib, N., Habrioux, A., Comminges, C., Canaff, C., Rousseau, J., ... et al.** (2015). Electrochemically induced surface modifications of mesoporous spinels ($\text{Co}_3\text{O}_4-\delta$, $\text{MnCo}_2\text{O}_4-\delta$, $\text{NiCo}_2\text{O}_4-\delta$) as the origin of the OER activity and stability in alkaline medium. *Journal of Materials Chemistry A*, 3(33), 17433-17444. doi: 10.1039/c5ta04437e.
- [142] **Gao, X., Zhang, H., Li, Q., Yu, X., Hong, Z., Zhang, X., ... et al.** (2016). Hierarchical NiCo_2O_4 hollow microcuboids as bifunctional electrocatalysts for overall water-splitting. *Angewandte Chemie International Edition*, 55(21), 6290-6294. doi: 10.1002/ange.201600525.
- [143] **Dong, X., Yu, Y., Jing, X., Jiang, H., Hu, T., Meng, C., ... et al.** (2021). Sandwich-like honeycomb $\text{Co}_2\text{SiO}_4/\text{rGO}/\text{honeycomb Co}_2\text{SiO}_4$ structures with enhanced electrochemical properties for high-performance hybrid supercapacitor. *Journal of Power Sources*, 492, 229643. doi: 10.1016/j.jpowsour.2021.229643.
- [144] **Kumar, P. S., Prakash, P., Srinivasan, A. and Karuppiyah, C.** (2021). A new highly powered supercapacitor electrode of advantageously united ferrous tungstate and functionalized multiwalled carbon nanotubes. *Journal of Power Sources*, 482, 228892. doi: 10.1016/j.jpowsour.2020.228892.
- [145] **Amirzhanova, A., Akmanşen, N., Karakaya, I., and Dag, O.** (2021). Mesoporous MnCo_2O_4 , NiCo_2O_4 , and ZnCo_2O_4 thin-film electrodes as electrocatalysts for the oxygen evolution reaction in alkaline solutions. *ACS Applied Energy Materials*, 4(3), 2769-2785. doi: 10.1021/acsaem.1c00064.
- [146] **Shafique, M., Iqbal, T., Mahmood, H., Khan, M. A., Naeem, M., Ahmed, I., and Ahmad, P.** (2021). Surfactant-assisted synthesis of $\text{NiCo}_2\text{O}_4/\text{NiO}$ nanocomposite by facile atmospheric pressure microplasma electrochemical process with photocatalytic applications. *Journal of Materials Science: Materials in Electronics*, 32(13), 17865-17875. doi: 10.1007/s10854-021-06322-6.
- [147] **Pendashteh, A., Palma, J., Anderson, M., and Marcilla, R.** (2016). Facile synthesis of NiCoMnO_4 nanoparticles as novel electrode materials for high-performance asymmetric energy storage devices. *RSC Advances*, 6(34), 28970-28980. doi: 10.1039/c6ra00960c.
- [148] **Anandha Babu, G., Ravi, G., and Hayakawa, Y.** (2015). Microwave synthesis and effect of CTAB on ferromagnetic properties of NiO , Co_3O_4 and NiCo_2O_4 nanostructures. *Applied Physics A*, 119, 219-232. doi: 10.1007/s00339-014-8951-9.
- [149] **Wu, X., Li, Y., Zhao, S., Zeng, F., Peng, X., Xiang, Y., ... et al.** (2019). Fabrication of F-doped, C-coated NiCo_2O_4 nanocomposites and its electrochemical performances for lithium-ion batteries. *Solid State Ionics*, 334, 48-55. doi: 10.1016/j.ssi.2019.01.039.

- [150] **Avci, C., Aydın, A., Tuna, Z., Yavuz, Z., Yamauchi, Y., Suzuki, N., and Dag, O.** (2014). Molten salt assisted self assembly (MASA): synthesis of mesoporous metal titanate (CoTiO_3 , MnTiO_3 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) thin films and monoliths. *Chemistry of Materials*, 26(20), 6050-6057. doi: 10.1021/cm503020y.
- [151] **Çelik, Ö., and Dag, Ö.** (2001). A new lyotropic liquid crystalline system: oligo (ethylene oxide) surfactants with $[\text{M}(\text{H}_2\text{O})_n]^{Xm}$ transition metal complexes. *Angewandte Chemie International Edition*, 40(20), 3799-3803. doi: 10.1002/1521-3773(20011015)40:20<3799::aid-anie3799>3.0.co;2-i.
- [152] **Albayrak, C., Soylu, A. M., and Dag, O.** (2008). Lyotropic Liquid-Crystalline Mesophases of $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ -C12EO10-CTAB-H₂O and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ -C12EO10-SDS-H₂O Systems. *Langmuir*, 24(19), 10592-10595. doi: 10.1021/la8022453.
- [153] **Raza, H. A., Karakaya, I., and Dag, O.** (2023). Nanoarchitectonics of mesoporous CaFe_2O_4 thin-film electrodes from salt-surfactant lyotropic liquid crystalline mesophases and their OER performance. *ACS Applied Energy Materials*, 6(18), 9681-9697. doi: 10.1021/acsaem.3c01776.
- [154] **Amirzhanova, A., Karakaya, I., Uzundal, C. B., Karaoğlu, G., Karadas, F., Ülgüt, B., and Dag, Ö.** (2019). Synthesis and water oxidation electrocatalytic and electrochromic behaviours of mesoporous nickel oxide thin film electrodes. *Journal of Materials Chemistry A*, 7(38), 22012-22020. doi: 10.1039/c9ta07693j.
- [155] **Zhang, Y., Xue, Y., Yang, R., Zhang, K., Qin, A., and Chen, S.** (2022). Rational design of $\text{KCu}_7\text{S}_4@\text{NiCo}_2\text{O}_4$ in-situ growth on nickel foam for high performance supercapacitor electrode. *Journal of Alloys and Compounds*, 898, 162791. doi: 10.1016/j.jallcom.2021.162791.
- [156] **Cao, X. M., Sun, Z. J., Zhao, S. Y., Wang, B., and Han, Z. B.** (2018). MOF-derived sponge-like hierarchical porous carbon for flexible all-solid-state supercapacitors. *Materials Chemistry Frontiers*, 2(9), 1692-1699. doi: 10.1039/c8qm00284c.
- [157] **Xiao, J., Wan, L., Yang, S., Xiao, F., and Wang, S.** (2014). Design hierarchical electrodes with highly conductive NiCo_2S_4 nanotube arrays grown on carbon fiber paper for high-performance pseudocapacitors. *Nano letters*, 14(2), 831-838. doi: 10.1021/nl404199v.
- [158] **Wei, S., Wan, C., Zhang, L., Liu, X., Tian, W., Su, J., ... et al.** (2022). N-doped and oxygen vacancy-rich NiCo_2O_4 nanograss for supercapacitor electrode. *Chemical Engineering Journal*, 429, 132242. doi: 10.1016/j.cej.2021.132242.
- [159] **Matthews, T., Dolla, T. H., Gwebu, S. S., Mashola, T. A., Dlamini, L. T., Carleschi, E., ... et al., N. W.** (2021). Mn-ni-co-o spinel oxides towards oxygen reduction reaction in alkaline medium: $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4/\text{c}$ synergism and cooperation. *Catalysts*, 11(9), 1059. doi: 10.3390/catal11091059.

- [160] **Gao, J. S., Li, S., Wang, H., Zhou, Y., Zhang, L., Liu, Z., and He, Y.** (2021). Carbon nanotubes aerogels dispersed by thermal excitation on Ni Foam@ NiCo₂O₄ nanoneedles with enhanced properties for supercapacitor. *Journal of Alloys and Compounds*, 861, 157963. doi: 10.1016/j.jallcom.2020.157963.
- [161] **Zhao, D., Wu, X., and Guo, C.** (2018). Hybrid MnO₂@ NiCo₂O₄ nanosheets for high performance asymmetric supercapacitors. *Inorganic Chemistry Frontiers*, 5(6), 1378-1385. doi: 10.1039/c8qi00170g.
- [162] **Gopalakrishnan, A., and Badhulika, S.** (2021). Hierarchical architected dahlia flower-like NiCo₂O₄/NiCoSe₂ as a bifunctional electrode for high-energy supercapacitor and methanol fuel cell application. *Energy & Fuels*, 35(11), 9646-9659. doi: 10.1021/acs.energyfuels.1c00498.
- [163] **Zhou, Y., Li, J., Xiong, G., He, X., Huang, Z., and Wang, Y.** (2021). Synthesis of NiCo₂O₄ nanostructures with different morphologies for supercapacitor. *Synthetic Metals*, 282, 116954. doi: 10.1016/j.synthmet.2021.116954.
- [164] **Mary, A. J. C., Sathish, C. I., Vinu, A., and Bose, A. C.** (2020). Electrochemical performance of rGO/NiCo₂O₄@ ZnCo₂O₄ ternary composite material and the fabrication of an all-solid-state supercapacitor device. *Energy & Fuels*, 34(8), 10131-10141. doi: 10.1021/acs.energyfuels.0c01427.
- [165] **Km, D. K., Hong, J. G., Kweon, J., Saeed, G., Kim, K. H., Lee, D., and Kang, M. C.** (2022). Spinel NiCo₂O₄ nanowires synthesized on Ni foam as innovative binder-free supercapacitor electrodes. *Materials Chemistry and Physics*, 291, 126718. doi: 10.1016/j.matchemphys.2022.126718.
- [166] **Azizi, S., Seifi, M., Moghadam, M. T. T., Askari, M. B., and Varma, R. S.** (2023). High-capacity MnCo₂O₄/NiCo₂O₄ as electrode materials for electrochemical supercapacitors. *Journal of Physics and Chemistry of Solids*, 174, 111176. doi: 10.1016/j.jpcs.2022.111176.
- [167] **Mu, H., Su, X., Zhao, Z., Han, C., Wang, Z., and Zhao, P.** (2019). Facile synthesis of Ni_{0.5}Mn_{0.5}Co₂O₄ nanoflowers as high-performance electrode material for supercapacitors. *Journal of the American Ceramic Society*, 102(11), 6893-6903. doi: 10.1111/jace.16610.

CURRICULUM VITAE

Name Surname : Mert Umut ÖZKAYNAK

EDUCATION :

- **B.Sc.** : 1997-2001, Yıldız Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Metallurgical and Materials Engineering
- **B.Sc. (Double Major)** : 1999-2004, Yıldız Technical University, Faculty of Mechanical Engineering, Department of Mechanical Engineering
- **Executive MBA** : 2003-2004, Yıldız Technical University Faculty of Economics and Administrative Sciences, Department of Business Administration
- **M.Sc.** : 2002-2004, Istanbul Technical University, Faculty of Science and Letters, Department of Materials Science and Engineering
- **M.Eng.** : 2009-2012, Lehigh University, P.C. Rossin College of Engineering and Applied Science, Department of Mechanical Engineering and Mechanics

PROFESSIONAL EXPERIENCE

- 2018-Present CBDO, Sabancı University-SUNUM
- 2012-2018 Head of Business and Product Development, TEMSA, Sabancı Holding
- 2008-2012 Technology Transfer Specialist, Lehigh University
- 2004-2008 Research and Development Engineer, TEMSA, Sabancı Holding

PUBLICATIONS RELATED TO THE THESIS

Özkaynak, M. U., Türker, Y., Dönmez, K. B., Karatepe, N., and Güner, F. S. (2022). High-performance supercapacitor electrolytes based on high-mole-ratio phosphoric acid/lauryl ether surfactant liquid crystalline gel. *International Journal of Energy Research*, 46(14), 19980-19991. <https://doi.org/10.1002/er.8126>

Özkaynak, M. U., Kocaaga, B., Dönmez, K. B., Dağlar, S., Türker, Y., Karatepe, N., Güner, F. S., and Dag, Ö. (2024). Understanding the role of water in the lyotropic liquid crystalline mesophase of high-performance flexible supercapacitor electrolytes using

a rheological approach. *Journal of Molecular Liquids*, 394, 123705. <https://doi.org/10.1016/j.molliq.2023.123705>

Özkaynak, M.U., Türker, Y., Bahadır Dönmez, K., Dağlar, S., Çobandede, Z., Metin Çelenk, M., Karatepe, N., Seniha Güner, F., and Dag, Ö. (2024). Molten Salt Assisted Assembly (MASA) of novel mesoporous $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Co}_2\text{O}_4$ for high-performance asymmetric supercapacitors. *Electrochemistry Communications*, 168, 107811. <https://doi.org/10.1016/j.elecom.2024.107811>

Li, M., Jia, C., Türker, Y., **Özkaynak, M. U.**, Zhao, L., Zhang, D., Luo, Y., Luo, G., Wang, L., Xia, Y., Li, Z., Zhu, N., Yang, P., Dönmez, K. B., Boukherroub, R., and Jiang, Z. (2023). Wide-temperature-range flexible micro-supercapacitors using liquid crystal gel electrolyte. *ACS Applied Energy Materials*, 6(8), 5230–5238. <https://doi.org/10.1021/acsaem.3c00144>

Han, X., Wu, X., Zhao, L., Li, M., Jia, C., Li, Z., Xie, J., Luo, G., Yang, P., Boukherroub, R., Türker, Y., **Özkaynak, M. U.**, and Dönmez, K. B. (2024). Facile assembly of flexible, stretchable and attachable symmetric microsupercapacitors with wide working voltage windows and favorable durability. *Microsystems & Nanoengineering*, 10(1), 1-8. <https://doi.org/10.1038/s41378-024-00742-0>

PATENTS RELATED TO THE THESIS

European Patent EP4420146, titled ‘Gel Electrolyte for Use in an Energy Storage Device and Supercapacitor Cell,’ granted on 25.11.2024

PROJECTS RELATED TO THE THESIS

High-Performance Supercapacitors with Mesostructured Gel Electrolytes for Automotive Applications (Project Code: 4217024, TÜBİTAK 1702 Program, in collaboration with TEMSA)