



**RECOVERY OF TRANSITION METALS FROM ORTHODONTIC WASTES
AND DESIGNING COMPOSITES AS NEGATIVE ELECTRODE ACTIVE
MATERIALS FOR LITHIUM-ION BATTERY**

MSc Thesis

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By
Muhammad Humza Ashraf

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14 July 2023

We certify that we have read this dissertation and that in our opinion it is fully adequate,
in scope and in quality, as a dissertation for the degree of Master of Science.

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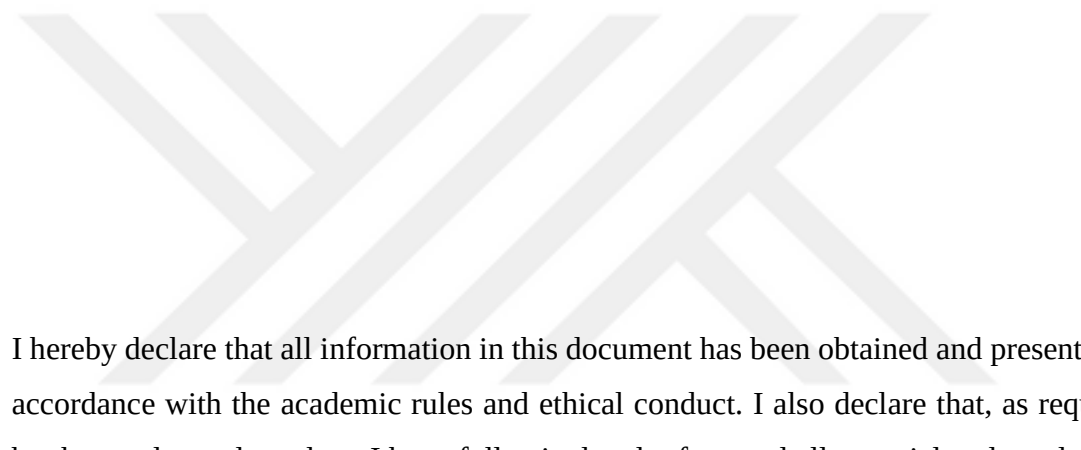
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CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT.....	iv
CONTENTS	v
LIST OF FIGURES	vii
LIST OF SYMBOLS	x
ABBREVIATIONS.....	xi
1. INTRODUCTION	1
2. LITERATURE REVIEW	4
2.1. Importance of secondary batteries in sustainability.....	4
2.2. Lithium ion batteries and working principle.....	7
2.3. Component of lithium ion battery.....	10
2.4. Anode materials used in LIBs.....	11
3. EXPERIMENTAL PART	28
3.1. Fabrication of metal oxide composite anodes from NiTi wires.....	28
3.1.1. Materials	28
3.1.2. Fabrication	29
3.1.2.1. Powder fabrication.....	29
3.1.2.2. Composite fabrication by ball milling	31
3.1.2.3. Electrode fabrication.....	32
3.1.3. Characterization	32
3.1.3.1. Powder characterization.....	32
3.1.3.2. Electrode characterization.....	33
3.2. Fabrication of metal oxide composite anodes from braces.....	34
3.2.1. Materials	34
3.2.2. Fabrication	35
3.2.2.1. Experimental design technique	35
a. Factorial design (FD).....	35
b. Fuzzy logic modeling.....	36
3.2.2.2. Powder fabrication.....	37
3.2.2.3. Electrode fabrication.....	39
3.2.3. Characterization	39
3.2.3.1. Powder characterization.....	39
3.2.3.2. Electrochemical characterization.....	39
4. RESULTS AND DISCUSSION	40
4.1. Fabrication and characterization of the composite powders from NiTi wires	40
4.1.1. Leaching of NiTi wires	40
4.1.2. Powder fabrication	40
4.1.2.1. Coprecipitation.....	40
4.1.2.2. Selective precipitation.....	41
4.1.3. Structural, morphological, and compositional analysis	42
4.1.4. Electrochemical analysis of powder from NiTi wires	47
4.2. Fabrication and characterization of iron oxide based anodes from orthodontic braces.	54
4.2.1. Leaching of braces	54
4.2.2. Hydrothermal reaction	54
4.2.3. Factorial design (FD).....	55
4.2.4. ANOVA analysis	59
4.2.5. Fuzzy Logic Modeling.....	61

4.2.5.1. Validation of fuzzy logic model	65
4.2.5.2. Validation through particle size	65
4.2.6. Structural and compositional analysis of the iron oxide rich powder.....	66
4.2.7. Electrochemical performances of the iron oxide rich anode vs Li	68
5. CONCLUSIONS AND FUTURE WORK.....	70
BIBLIOGRAPHY	71
CURRICULUM VITAE.....	86



LIST OF FIGURES

Figure 2.1: Contribution of different energy sources to total energy consumption [17]	5
Figure 2.2: Emission of greenhouse gasses over the 20th century in comparison with population growth [19]	5
Figure 2.3: Usage of LIBs in sectors of our daily life [2]	9
Figure 2.4: Energy production analysis by the US energy department [4]	9
Figure 2.5: Schematic representation of components of LIBs [6]	10
Figure 2.6: Manufacturing cost of LIB component [13]	11
Figure 2.7: Number of publications on LIB from 1990-2022	12
Figure 2.8: Number of publications on anode material of LIBs from 1990-2022	17
Figure 2.9: Usage of NiTi wire and SS braces [114]	20
Figure 2.10: Energy production analysis by US energy Department [115]	21
Figure 2.11: Representation of membership degree and fuzzy sets	23
Figure 2.12: Membership degree of an element in more than one fuzzy set	24
Figure 3.1: Orthodontic waste (NiTi wire and SS-braces)	28
Figure 3.2: Systematic setup of leaching in reflux system	29
Figure 3.3: Schematic flow chart of procedure followed.	30
Figure 3.4: High energy ball milling (VARSAN)	32
Figure 3.5: CR2032 standard battery component; 1-lower case; 2-spring; 3-stainless steel spacer; 4-lithium metal as cathode; 5-separator; 6-fabricated anode; 7-stainless steel spacer; 8-upper case.	33
Figure 3.6: a) Glovebox b) Gamry setup c) Battery analyzer	34
Figure 3.7: General structure of fuzzy logic model with three inputs and one output	36
Figure 3.8: The hydrothermal reactor and oven	38
Figure 3.9: Schematic flowchart of the procedure followed for synthesis and fuzzy logic application	38
Figure 4.1: Appearance of solution at different stages of co-precipitation a) Leachate solution b) pH adjustment at 10 c) After 24 h of phase separation d) Filtered clear solution showing the success of precipitation	41
Figure 4.2: Appearance of solution during different stages of selective precipitation a) pH adjustment at 1 b) After 24h of phase separation c) Filtered solution after precipitation at pH1 d) pH adjustment at pH10 e) After 24h of phase separation f) Filtered clear solution showing the success of precipitation.	42
Figure 4.3: XRD pattern of powder fabricated from NiTi wire leachate solution a) CS11 & CSA11, b) S1, S10, N3T1 & N6T1	44
Figure 4.4: SEM images of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f)	46
Figure 4.5: Capacity-cycle graphs of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f) N6T1	49
Figure 4.6: Voltage-capacity graphs of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f) N6T1	50
Figure 4.7: Cyclic voltammogram of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f) N6T1	53
Figure 4.8: a) Main effect plots from factorial design, b) the interaction plots	58
Figure 4.9: Factorial design cube with three factors and two levels	61
Figure 4.10: Evaluation of 27 fuzzy rule base in MATLAB	64
Figure 4.11: Particle size of a) 3 Repeated experiments & b) 8 experiments of 2 ³ factorial design (FD)	66
Figure 4.12: XRD pattern of samples fabricated by optimized condition from leachate of SS braces.	67

Figure 4.13: Electrochemical performance of iron oxide sample a) Voltage-Capacity curves b) Capacity-Cycle curves c) Cyclic voltammetry curves 69



LIST OF TABLES

Table 2.1: Literature examples of synthetically fabricated metal oxide as anode material in LIB.....	15
Table 3.1: The sample coding and the experimental details of coprecipitation.....	31
Table 3.2: Parameters and their levels of factorial design	35
Table 3.3: Factorial experimental design details	36
Table 3.4: Linguistic levels of Input and output of fuzzy logic model.....	37
Table 4.1: Samples code and experimental details of coprecipitated powders.....	41
Table 4.2: Sample coding and the experimental details of selective precipitated and the composite powders.....	42
Table 4.3: Chemical composition of the powder obtained by XRF.	47
Table 4.4: Leaching parameters optimization experiments	54
Table 4.5: Factorial experimental design and results.....	57
Table 4.6: Summary of factorial design.....	59
Table 4.7: ANOVA calculations for particle size of powder.....	59
Table 4.8: Revised ANOVA calculations for particle size of powder.....	60
Table 4.9: Fuzzy logic rule base.	62
Table 4.10: Results of 8 experimental data fitted in 27 fuzzy rules.	63
Table 4.11: Percentage relative error calculation	65

LIST OF SYMBOLS

θ	: Theta
α	: Alpha
β	: Beta
μ	: Micro
m	: Milli, Meter
A	: Ampere
g	: Gram
k	: Kilo
M	: Mega, Molar
W	: Watt
G	: Giga
°C	: Degree Celsius
°	: Degree
%	: Percentage
h	: Hour
min	: Minute
sec	: Second
n	: Nano
e⁻	: Electron
H	: Hydrogen
O	: Oxygen
Ni	: Nickel
Ti	: Titanium
Fe	: Iron
S	: Sulfur
Al	: Aluminum
Ag	: Silver
Sn	: Tin
Cr	: Chromium
C	: Carbon
Si	: Silicon
Li	: Lithium
Sb	: Antimony
Mg	: Magnesium
Cu	: Copper
Mn	: Manganese
Mo	: Molybdenum
Zr	: Zirconium

ABBREVIATIONS

NiTi	: Nickel Titanium
NaOH	: Sodium Hydroxide
SS	: Stainless Steel
NH₄OH	: Ammonium Hydroxide
H₂SO₄	: Sulfuric Acid
FD	: Factorial Design
ANOVA	: Analysis of Variance
LIBs	: Lithium Ion Batteries
WHO	: World Health Organization
CV	: Cyclic Voltammetry
TMO	: Transition Metal Oxide
NMP	: N-Methyl pyrrolidone
PVDF	: Polyvinylidene Difluoride
XRD	: X-Ray Diffraction
XRF	: X-Ray Fluorescence
SEI	: Solid Electrolyte Interface
AEA	: Atomic Energy Authority
UK	: United Kingdom
BC	: Before Christ
MD	: Membership Degree
AD	: Anno Domini
RPM	: Revolution Per Minute
SEM	: Scanning Electron Microscope
PRE	: Percentage Relative Error
HEB	: High Energy Ball-mill
i.e.	: Id est (that is)
DOE	: Design of Experiment
DOD	: Depth of Discharge
BMS	: Battery management System
PCA	: Process Control Agent

ORTODONTİK ATIKTAN GEÇİŞ METALLERİNİN GERİ KAZANILMASI VE KOMPOZİTLERİN LİTYUM İYON PİL İÇİN NEGATİF ELEKTROT AKTİF MATERYALLER OLARAK TASARLANMASI

ÖZET

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Biyomedikal Mühendisliği ve Biyoinformatik, Yüksek Lisans

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Son yıllarda biyomedikal endüstrisinde gerçekleştirilen, insanın yaşam kalitesini ve ömrünü arttırmaya yönelik yapılan araştırmalar hem bilimsel açıdan hem de tüketici bakış açısıyla heyecan verici bulunmaktadır. Bu noktada ortodonti alanında yapılmış araştırmalar sonucunda tasarlanmış diş telleri sayesinde hem hastanın diş diziliminde yaşanan problemlerin çözümünde hem de çeneler arası ilişkilerin ideal hale getirilmesinde önemli başarılar kazanıldığı bilinmektedir. Ortodontik tedaviler genelde birkaç yıl sürmekte, bu süreçte dişlerin pozisyonlarındaki gelişime bağlı olarak birçok kez tek kullanımlık olan bu teller hastanın ağzında yenilenmekte, eski kullanılmış teller tıbbi atık olarak değerlendirilip, bertarafa gönderilmektedir. Ortodontik tedavide kullanılan bu tellerin özel tasarlanmış NiTi alaşımlarından yapıldığı göz önüne alındığında, ortodontik tedavilerinin yaygınlaşması ile burada kullanılan tellerin geri dönüşümü ve yeniden değerlendirilmesi dikkat çeken bir konu haline gelmiştir.

Diğer taraftan metalik elementlerin yer kabuğunda sınırlı miktarda bulunması ve enerji fiyatlarındaki artış, küresel pazarda birincil kalite metallerin üretim maliyetinin sürekli ve katlanarak artmasına neden olmaktadır. Bu durum uzun vadede birincil kalite malzeme kullanarak elektrot malzemesi sentezi yapan lityum iyon batarya endüstrisinin gelişimine engel oluşturabilir. Bu sorunu çözmek için alternatif çözüm geliştirmek üzerine araştırma çalışmaları gerçekleştirilmektedir.

Bu çalışma kapsamında literatürde ilk defa lityum iyon pillerde kullanılacak elektrot malzemelerinin üretimi için biyomedikal endüstrisine ait atıkların başlangıç malzemesi olarak kullanılması önerilmiştir. Bu kapsamda ortodontik tedavide kullanılmış atık diş tellerinin farklı parçaları (NiTi teller ve çelik braketler) ayrı ayrı incelenerek özgün deney akış şemalarının tasarlanması suretiyle farklı iki başlık altında değişen özellikte kompozit malzeme üretimi için alternatif yöntemler önerilmiş, bu malzemelerin lityum iyon bataryalarda negatif elektrot malzemesi olarak kullanımları elektrokimyasal test sonuçları dikkate alınarak tartışılmıştır.

Tez kapsamında ilk başlıkta önce NiTi teller detaylı karakterize edilmiş sonrasında liç verimi optimize edilmiştir. Kompozit eldesi için iki farklı yaklaşım sergilenmiştir: İlk akış şemasında liç çözeltisinde bulunan Ni ve Ti iyonları beraber çöktürülmüş, ardından 400°C’de 4 saat hava ortamında ısıtılma işlemi yapılmıştır. Bu noktada şelatlayıcının kompozit oluşumuna etkisi ayrı olarak incelenmiştir (CS11 ve CSA11). Tasarlanmış diğer

yaklaşımında ise pH ayarlama yapılarak önce titanyum oksit ardından nikel oksit içeren tozlar ayrı ayrı üretilmiştir. Sonrasında her iki toz değişen NiO/TiO₂ oranlarında öğütme işlemine tabi tutularak kompozit üretimi gerçekleştirilmiştir (N3T1 ve N6T1). Bu noktada değişen bileşiminin kompozit özelliklerine etkisi detaylı incelenmiştir. Elde edilen tüm tozlar kimyasal, yapısal ve morfolojik olarak karakterize edildikten sonra elektrotlar üretilmiş ve Li'a karşı anot olarak sergiledikleri performanslar elektrokimyasal olarak incelenmiştir. Tezin ikinci başlığında ise dış tellerinde bulunan braketler öncelikle karakterize edilmiş, ardından sülfirik asitle liç verimi optimize edilmiştir. Liç çözeltisinden kompozit toz üretmek için hidrotermal prosesin koşulları ortogonal ve ortogonal olmayan deneysel tasarım yöntemleri kullanılarak, literatürde ifade edilen 150 nm kritik parçacık boyutuna sahip kompozit malzeme eldesi için optimize edilmiştir. Sonuçlar en uygun koşulların liç çözeltisinin pH'ı 10'a ayarlandıktan sonra 12 saat boyunca 150°C'de %100 reaktör doluluğunda malzemenin proses edilmesiyle elde edileceğini göstermiştir. Proses sonucunda, bulanık mantık modeli ile tahmin edilen 156 nm parçacık boyutu değerine yakın ortalama 153,8 nm parçacık boyutuna sahip kompozit toz elde edilmiştir. Bu toz daha sonra 730°C'de 5 saat ısıtılma işlemine alınmıştır. Sonrasında, elde edilen bu toz kimyasal, yapısal ve morfolojik olarak incelenmiş, Li'a karşı anot olarak sergiledikleri performanslar elektrokimyasal olarak karakterize edilmiştir.

Bu tezden elde edilen sonuçlar uygun bir malzeme seçimi ve proses tasarımı ile biyomedikal atıkların yüksek katma değerli lityum iyon bataryalarda kullanılacak elektrot sentezi için kullanılabilineceğini kanıtlamaktadır. Tez kapsamında yapılmış deneysel çalışmalar sonucunda NiTi tellerden sentezlenen NiO ve TiO₂ tozlarının birarada kullanılması ile üretilen N6T1 numaralı kompozit numunesinden elde edilen anodun günümüzde kullanılan grafitten daha yüksek kapasite sergilediği görülmüştür (1. Deşarj 517.9 mAsa g⁻¹, 50.deşarj:363 mAsa g⁻¹). Bu performans NiO'nin yüksek kapasite ve TiO₂'nin yüksek kapasite korunumu sergilemesi özellikleriyle ilişkilendirilmiştir. İlave, ortogonal ve ortogonal olmayan deneysel tasarım yöntemleri kullanılarak 153,8 nm partikül boyutunda kompozit toz eldesi 8 deney ile gerçekleştirilmiştir. Bu tozun anot malzemesi olarak kullanılması ile de günümüzde kullanılan grafitten daha yüksek performans sergileyen bir anot malzemesi sentezi gerçekleştirilmiştir (1. Deşarj 983 mAsa g⁻¹ 50.deşarj:408.7 mAsa g⁻¹). Elde edilen performans tozun kritik partikül boyutunun yanı sıra yapısal ve kimyasal özellikleri ile de ilişkilendirilmiştir. Sonuçlar gelecekte çalışmaların geliştirilmesi için ümit vaat edici bulunmuştur.

Anahtar sözcükler: Biyomedikal Atık, Metal Geri Kazanımı, Kompozit İmalat, Anot Malzemesi, Lityum İyon Piller.

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ABSTRACT

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In recent years, the research carried out in the biomedical industry to increase the quality of life and longevity of people is exciting for both scientists and consumer. At this point, the result of the researches on orthodontics enables significant benefits on the braces design as it solves the problems experienced in the patient's dental alignment and idealizes the relations between the jaws with success. Orthodontic treatments generally last for a few years, during this process, these single-use wires are renewed in the patient's mouth many times depending on the development in the positions of the teeth, and the old used wires are evaluated as medical waste and sent for disposal. Considering that these wires used in orthodontic treatment are made of specially designed NiTi alloys, recycling and re-evaluation of the wires used here has become a remarkable issue with the widespread use of orthodontic treatments.

In other respect, the limited availability of metallic elements in the earth's crust and the increase in energy prices cause the cost of primary metals to increase continuously and exponentially in the global market. This situation raises concerns about the acquisition of components to be used in the production of electrode materials of lithium-ion batteries in the long term, and research studies are carried out on developing an alternative solution to solve this problem.

Within the scope of this study, it has been proposed for the first time in the literature to use wastes from the biomedical industry as starting material for the production of electrode materials to be used in lithium-ion batteries. In this context, different parts of waste braces (NiTi wires and stainless steel brackets) used in orthodontic treatment were examined separately. Then, by designing original flow charts for each type of waste alternative waste treatment and composite fabrication methods were proposed. Finally, the use of these materials as negative electrode material in lithium-ion batteries was discussed considering their electrochemical test results.

Within the scope of the thesis, firstly, NiTi wires were characterized in detail and then the leaching efficiency was optimized. Two different approaches were studied for the composite production: In the first flow chart, Ni and Ti ions found in the leaching solution were chemically precipitated together, then heat treated (400°C 4h in air). At this point, the effects of chelating agent on composite formation were examined (CS11 and CSA11). In the other approach, powders containing titanium oxide and nickel oxide were produced separately by adjusting the pH of the leachate. Afterwards, both powders were grounded

together to produce composites (N3T1 and N6T1). At this point, the effect of the NiO/TiO₂ ratio on the composite properties was examined in detail. After all the obtained powders were characterized chemically, structurally, and morphologically, electrodes were produced and their performance as anode against Li was electrochemically investigated. In the second chapter of the thesis, the brackets in the braces were first characterized, then the leaching efficiency with sulfuric acid was optimized. Then, hydrothermal method was used to fabricate composite powder. Herein, the parameters of the hydrothermal method were studied using orthogonal (factorial design) and non-orthogonal (fuzzy logic) experimental design techniques to fabricate composite powder which had close to 150 nm particle size. Experimental results showed that when the leachate was hydrothermally treated at 150°C for 12 hours, with 100% reactor filling ratio, the obtained powder had 153.8 nm particle size in average which is close to 156 nm the predicted particle size value by fuzzy logic model. This powder was heat treated subsequently at 730°C for 5 hours. The chemical, structural morphological properties of the powder as well as the electrochemical behavior of the electrode made of this powder were analyzed.

This thesis demonstrates that with proper material selection and process design, biomedical waste can be effectively utilized for electrode synthesis. In this thesis five distinctive composites were produced and characterized from NiTi wires. The results show that sample N6T1 performs better capacity (1st discharge: 517.9 mAh g⁻¹ and 50th discharge: 363 mAh g⁻¹) than graphite. This performance is attributed to the high capacity of NiO and the high capacity retention of TiO₂. Moreover, successful applications of orthogonal and non-orthogonal experimental designs were realized to fabricate composite of 153.8 nm particle size, only with 8 experiments. Herein, a successful use of the fuzzy logic on material fabrication was also exemplified by using the brackets as the starting material. By using this powder as an anode material, the synthesis of an anode material exhibiting higher performance than graphite was also achieved (1st discharge: 983 mAh g⁻¹ and 50th discharge: 407.8 mAh g⁻¹). The obtained performance is attributed to the critical particle size of the powder as well as its structural and chemical properties. The results are promising for future development of the study.

Keywords: Biomedical Waste, Metal Recovery, Composite Fabrication, Anode Material, Lithium-Ion Batteries.

CHAPTER 1

1. INTRODUCTION

In the 20th century, the fast-growing population and economies need huge amounts of resources to fulfill the needs of consumers. And with the current growth rate of the population, it is expected that by 2040 many of the natural resources are going to be completely consumed [1]. Continuous decrease in natural energy resources and the occurrence of pollution due to conventional fossil fuels intrigued experts to explore green, environmentally friendly, and sustainable energy alternatives for the past several decades. This requisite necessitates the use of renewable green energies along with energy storage devices. Among such alternatives, lithium-ion batteries (LIBs) are the most renowned due to their lightweight, excellent energy density ($>150\text{Wh kg}^{-1}$), lack of memory effect, low self-discharge rate, and long cycle life of up to 5000 cycles with 80% depth of discharge [2], [3].

According to analysis, almost in each department/region of our daily usage routine LIBs are used such as in the transport sector (i.e., autocycles, cars, busses, forklifts, etc.), in electronic goods (i.e. laptops, personal care devices, phone, etc.) and stationary grid applications [2]. Experts say that LIBs will be utilized more in the future. A report issued in 2020, by the energy department, states that by 2030 the energy stored in LIBs will surpass 2 TWh collectively [4]. In another report, it is estimated that the growing market of LIB is going to expand up to \$300 billion by 2050, and per year power storage production requirement will be 4-12 TWh [5].

LIB consists of four basic components: electrolyte, separator, cathode, and anode [6], [7]. When the energy consumption of the LIB manufacturing process is considered, 163 kWh of energy is found to be utilized for the fabrication of LIB that stores 1kWh of energy [8], [9]. Detailed analysis reveals that 70-80% of that energy is used mainly for the electrode

active material fabrication [10], which results in approx. 150 kg CO₂ emission to store 1kWh of energy in LIB [11], [12]. Moreover, the cost of active material is noted to cover 65% of the total production cost of LIB simple battery management system (BMS) module/battery pack [13]. Here, keeping in mind the market forecast of LIB with the purpose of revenue generation, the motive is to reduce the production cost of active material without compromising environmental safety.

As a solution, some scientists have studied the recovery of metals from spent LIBs by pyro and hydrometallurgical processes [14]. Many people have worked on it but still, further improvement in efficiency is required. Alternatively, the recovery of valuable metals from various industrial wastes has also been studied. Mill scale, spent pickled acid, flue dust, and ash from different furnaces are utilized as the starting material, and valuable metals used in the electrode active material fabrication are recovered from them. As mentioned in these studies, the use of industrial waste in the synthesis of electrode-active materials not only provides a solution to the problems experienced during the disposal of the existing waste but also helps to reduce the damage to the environment caused by using primary quality raw materials in their production. This point of view will enable the formation of a system in which sectors can achieve mutual gains economically and the achievement of a sustainable world.

In recent years the biomedical field plays a paramount role in advancing healthcare, which involves diagnosis, treatment, prevention, and research about diseases and medical conditions. Its significance lies in improving human health and quality of life. By several years, the growth in biomedicine has been nothing short of remarkable, with revolutionary findings, innovative technologies, and state-of-the-art therapies that have reformed the medical. These progressions have brought about novel treatments, precise diagnostics with specified medicine, and promoting the potential to treat previously incurable family of deceases.

Yet, the rapid growth in the biomedical field has also brought about challenges, particularly concerning waste generation. The production of biomedical waste, which includes discarded materials from medical research, healthcare facilities, and pharmaceutical manufacturing, has increased substantially. Inadequate handling and abandoning these hazardous materials can set terrible risks to both human health and the environment. It demands strict regulations, appropriate waste management systems, and

increased awareness among practitioners to ensure the safe and eco-friendly disposal of biomedical waste. Recognizing and addressing these waste generation issues is crucial to maintaining the delicate balance between medical advancements and environmental preservation in the biomedical field. According to a report by the world health organization (WHO) in 2020, 144,000 tons of biomedical waste were generated collectively [15] and most of it was discarded. In the waste, 57%, 21%, and 6% amounts of Fe, Ti, and Ni are found. So far, a couple of research groups have made an effort to recover metals from biomedical waste but none of them have designed a procedure to manufacture LIB electrode materials out of it.

In this thesis innovatively, two types of orthodontic waste (nickel titanium (NiTi) wires and stainless steel (SS) braces) have been treated differently to design electrode materials for LIBs. Firstly, the leaching conditions of NiTi wires are optimized then selective metal recovery is applied to fabricate nickel oxide-rich and titanium oxide-rich powders, separately. Then, by high-energy ball milling of both in different ratios, composites of different compositions are fabricated. Moreover, in the second part of the thesis, to treat SS braces, firstly acidic leaching and then the hydrothermal reaction is utilized to fabricate composite powders. Herein, orthogonal, and non-orthogonal experimental designs are used to fabricate composite powder of 153 nm particle size. The fuzzy logic leads to produce 156 nm particle sized-composite powder when the leachate is hydrothermally treated at 150°C for 2 hours with 100% reactor filling ratio [16]. The heat treated (730°C 5h in air) powder is examined as anode material. In both cases, the results are found to be promising.

CHAPTER 2

2. LITERATURE REVIEW

2.1. Importance of secondary batteries in sustainability

The 20th century witnessed the industrial revolution and scientific advancement. Many crucial inventions were made that changed the whole point of view towards life. The astonishing development in the field of research and technology would not have been possible without one of the key factors i.e., conventional fossil fuels which include natural gas oil, and other organic fuels. More than the 85 % of the energy consumption in the world is coming through carbon based source **Figure 2.1** [17]. The extensive use of conventional fuels results in pollution on a deadly scale and bringing about the increasing global warming by emission of greenhouse gasses at large amount. According to a survey pollution caused by fossil fuels is killing 1 out of 5 people, globally. In a report issued in 2018, experts claim that 8.7 million human deaths were caused by pollution [18]. It can be seen in the **Figure 2.2** that in 20th century there is a dramatic increase in population and to satisfy the energy needs of them extensive carbonaceous foil consumption results in abrupt massive emission of greenhouse gasses (GHG) in late 20th century. These alarming analyses exhibit how they are causing adverse effects on human health and call for necessary measures. In this regard, many international efforts have been made by developed countries to put off or minimize fossil fuel consumption.

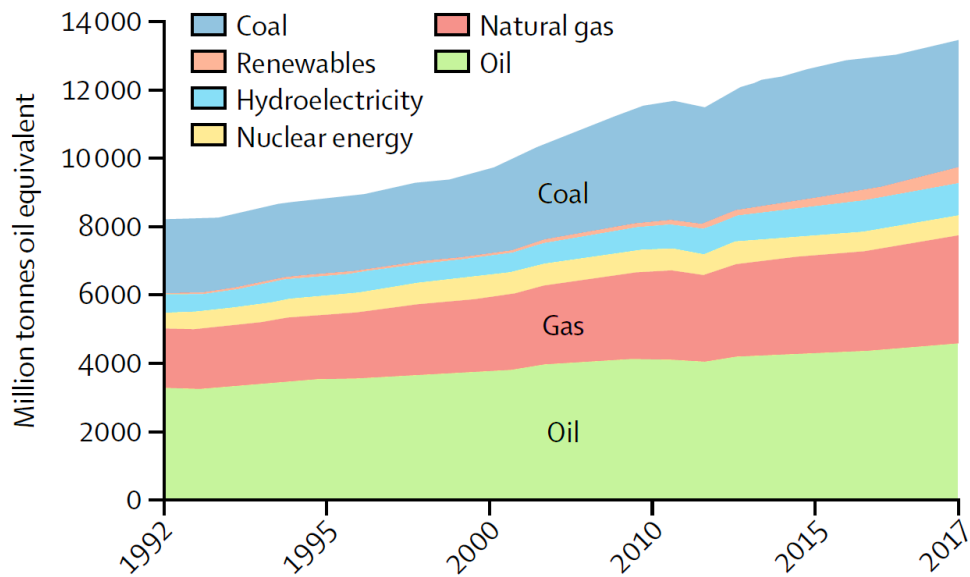


Figure 2.1: Contribution of different energy sources to total energy consumption [17]

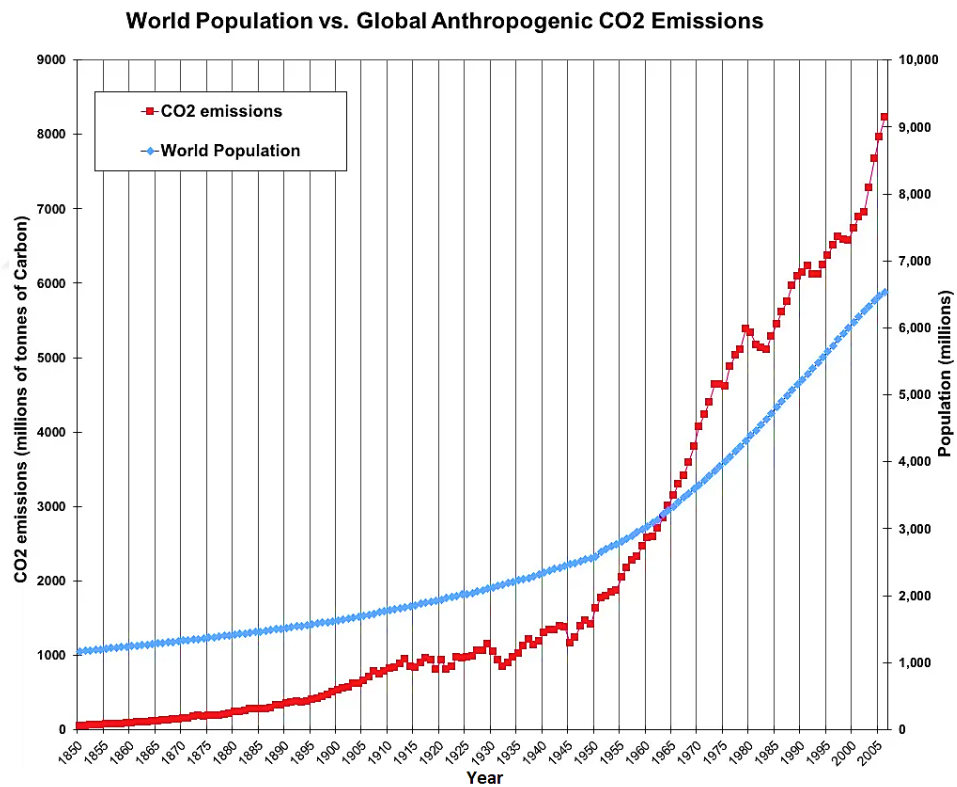


Figure 2.2: Emission of greenhouse gasses over the 20th century in comparison with population growth [19]

In 1997, an international treaty named Kyoto Protocol (also known as Kyoto Protocol to the United Nations Framework Convention on Climate Change) was agreed and signed by 41 developed countries and European union countries to lower the emission of greenhouse gasses. The list of six greenhouse gasses (i.e., methane, sulfur hexafluoride,

perfluorocarbons, nitrous oxide, carbon dioxide and hydrofluorocarbons) was subjected at that time. Mostly developed countries signed this treaty as they were main contributors in GHGs, and they decided to reduce their annual GHG emissions by an average of 5.2% till 2012. They will carefully monitor the annual GHG emission and will keep the record to follow this protocol mechanism. There were three key marketed mechanisms of Kyoto Protocol, to meet the target, i.e., International Emissions Trading, Clean Development Mechanism (CDM) and Joint implementation (JI) by which they are confined to reduce their GHG emission by replacing them with new clean energy projects. As a result, a good improvement from the members of EU was observed but it didn't affect the overall reduction of GHG because China and USA, the two bigger countries kept contributing to global warming. And an increase in emission was noted from 1990 to 2009 by 40 % [20]–[22].

After an approximate failure of the Kyoto protocol, another treaty called Paris Agreement (fully termed as Paris Agreement Under the United Nations Framework Convention on Climate Change or COP21). In 2015, during the United Nations climate change conference hosted by France in Paris a treaty was signed by 196 countries to cut short the extensive emission of GHG to the stage where it does not cause annual global temperature to rise of 2°C. This agreement emphasized the member countries to develop long term (5 years) action plan (also termed as nationally determined contributions (NDCs)) till 2020, to lower the emission of GHGs. And after each 5 year's-cycle monitoring the achievement of the countries and setting new goals for the next round. Unlike enforcement of mechanism to be followed in Kyoto protocol, this agreement underlined the cooperation between developed and developing countries, transparency in the actions taken especially financial aid, flexibility of application by adopting different strategies, and periodic reporting of achieved progress. Moreover, starting from 2024 countries will establish the enhanced transparency framework (ETF) which will enable countries to submit a report about their NDCs and progress of the journey in achieving them climate, and authentic statements about the facilitated or acknowledged. By means of this, international organizations can also review the reports submitted by countries and saving information global stock take to monitor an overall advancement towards the long-term objectives. This treaty ignited the countries to ascertain carbon reducing mindset. New marketing approaches such as low carbon solution and zero-carbon solution are getting prominent specially in the sector of transportation and power generation [22]–[25].

Another recent step taken towards climate change is the Green Deal or European Green Deal. This deal is a comprehensive set of guidelines or policies, towards risks as well as impact due to climate change on land, ecosystems, and natural resources in the European union. This gives a protocol to reduce the carbon emission in Europe by 55% of the 1990's quantity, till 2030. Planting at least 3 billion more trees by the end of 2030 in Europe and become first continent free of harmful effect of climate. This pact is majorly forced by French, German, and Spanish governments. As said, that it is comprehensive set of measures that why it focuses majority of the field to improve overall life style of a person in Europe [26]–[28].

All these efforts, agreements and treaties emphasize the adoption and utilization of green, sustainable, environmentally friendly, and renewable alternative energy sources. Such transformational steps taken by most countries, are incomplete without considering the role of energy storage batteries. All the aims set by countries to achieve carbon free climate till their specific deadline requires thorough attention on the area of batteries as they are biggest energy source for the portable and mobile devices. It is almost impossible to efficiently power the portable devices without their use. And modern electronic industry is completely based on these batteries.

2.2. Lithium ion batteries and working principle.

The roots of battery invention are found to be more than 2000 years. In 1983, archeologist found ceramic pots from the ruins of Khujut Rabu village in the capital Iraq. These pots are fitted with copper sheets around an iron rod conveying the idea that they were used as galvanic cells when filled with wine or vinegar. However, as found in the history first live phenomenon of the electricity was observed in 1786 by Italian researcher L. Galvani. His observation was further studied and examined by another Italian A. Volta and first battery by placing zinc and copper together in a saline solution. This battery was term as voltaic pile. This voltaic pile was further improved by other scientists over the period of time, but they were drained after all the chemicals reacted. In 1959, Gaston Planté invented the first rechargeable battery - the Lead-Acid battery which was further worked and improved by Camille Alphonse Faure. Then in 1866 first dry cell battery was developed by French scientist Georges Leclanché putting ammonium chloride paste inside zinc anode and carbon mixed magnesium oxide cathode. This idea was further improved and patented by Carl Gassner in 1886 and first time battery started getting used

in portable electric devices. In 1899, a Swedish scientist made first nickel cadmium battery by first time using alkaline solution, this new version of battery delivered improved energy density. This was further improved by famous scientist T. Edison and his improved batteries were extensively used in industries. In 1955 an engineer named L. Urry highlighted the advantages of alkaline batteries and replace the conventional zinc-carbon batteries for the regular use [29]–[31]. First time in 1958 Harris studied the interaction of lithium metal and its inorganic salts with several electrolyte and observe the formation of a passive layer that prevent the direct contact of the material with electrolyte but is permeable to ionic transportation. This finding coupled with the electrochemical properties of the metal make it a potential candidate to be used in battery. By 1969, lithium based batteries were introduced to the market comprising lithium sulfur dioxide based cathodes. Then in 1973, a known Japanese company Matsushita commercialized the based lithium–polycarbon monofluoride batteries. Later Sanyo introduced lithium–manganese oxide batteries in the market followed by the introduction of lithium–copper oxide based batteries. And by the development and usage of lithium-iodine battery in cardiac pacemaker, boost the development in lithium ion [31], [32]. Then many advancements in electrode material (anode and cathode) of LIB took place by many researchers and lithium ion batteries kept improving day by day. The progress in technology demands the light weight and high energy density delivering batteries and for this demand LIBs were the best candidate therefore, in 1990 LIBs completely took the attention of experts and its start getting involve in almost area of our daily life. Since then LIBs are incredibly the topic of discussion and got improved constantly [33]. Yet many research groups are constantly working on LIBs for further improvement, only in 2022, more than 12,500 scientific articles are published online. Analysis reveals that today, almost in each department/area in our daily usage routine LIBs are used **Figure 2.3**, such as in the transport sector (i.e., autocyces, cars, busses, forklifts, etc.), in electronic goods (i.e. laptops, personal care devices, phone, etc.) and stationary grid applications.

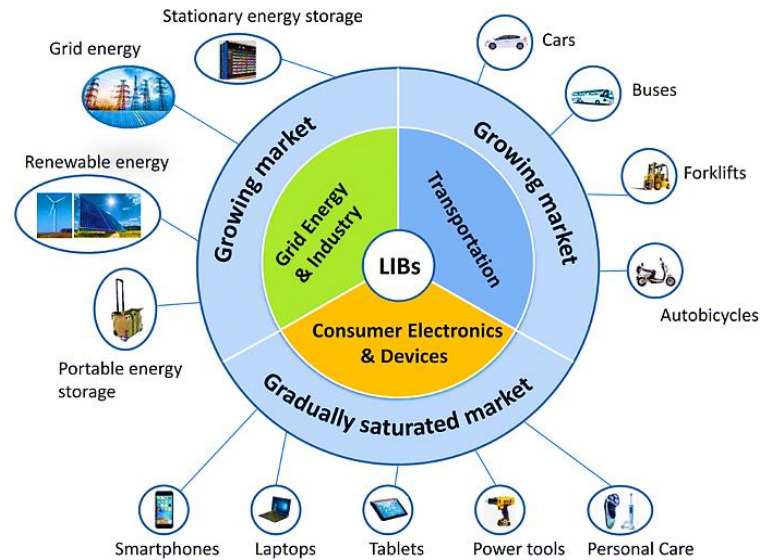


Figure 2.3: Usage of LIBs in sectors of our daily life [2].

According to experts' opinion this is still an unsaturated market and LIBs will be more utilized in the future. The states in a report issued by the energy department, states that by 2030 the energy stored in LIBs will surpass 2 TWh collectively [4] **Figure 2.4**. Likewise in another report, it is estimated that the growing market of LIB is going to expand up to \$300 billion by 2050 and per year power storage production requirement will be 4-12 TWh [5].

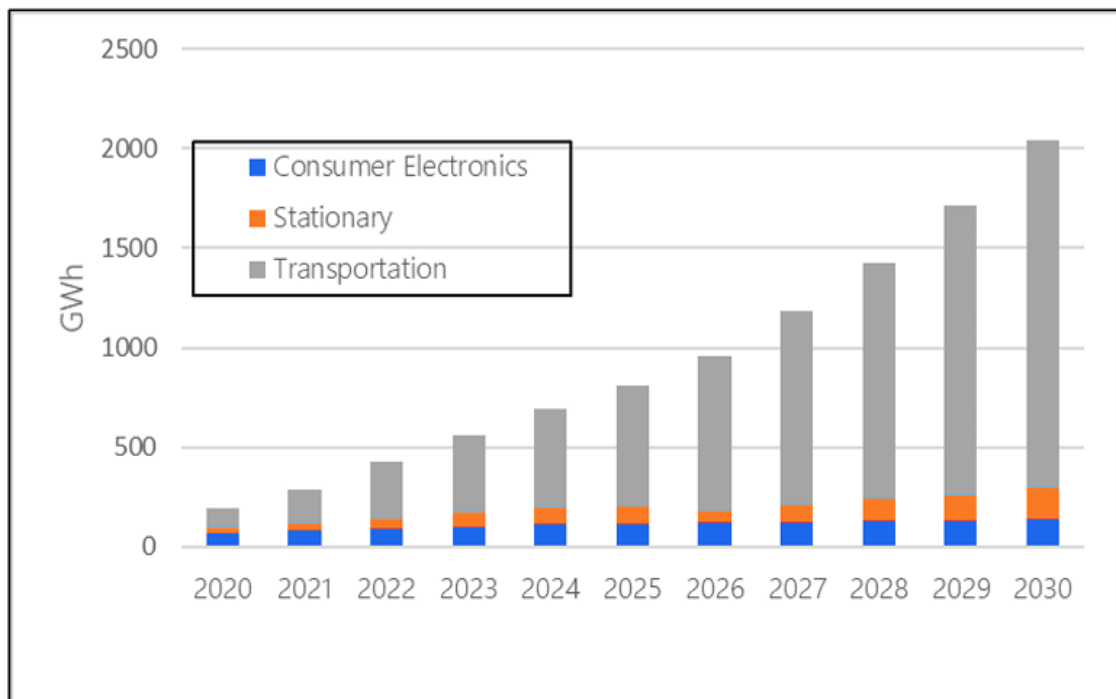


Figure 2.4: Energy production analysis by the US energy department [4]

2.3. Component of lithium ion battery

Like other battery cells, LIB consists of four basic components: electrolyte, separator, cathode, and anode [6], [7] as shown in **Figure 2.5**. The electrolyte provides an ionic conductive path between the anode and the cathode, which only permits the conduction of ions during the charging and discharging process. The separator is a partially permeable polymeric thin film that prevents direct electrical contact between the two electrodes from each other, but Li-ion conduction is permeable through it as it has small pores in it. The cathode is a positive electrode. It is approached by negative ions; its reduction takes place by receiving electrons. The anode is a negative electrode and has been approached by positive ions and its oxidation takes place by donating electrons to the cathode. During the charging-discharging cycle, the movement of lithium ions mainly takes place between the anode and the cathode and gets inserted in the active materials of both electrodes. Meanwhile, electrons get transferred from the anode to the cathode via an outer electrical circuit/connection [7].

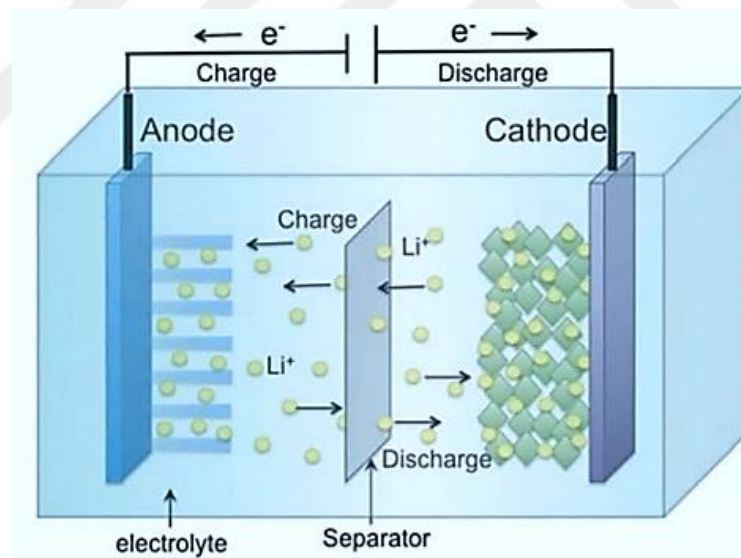


Figure 2.5: Schematic representation of components of LIBs [6]

The cost of active material used in fabrication of electrode is noted to cover 65% of the total production cost of LIB simple battery management system (BMS) module/battery pack [13] **Figure 2.6**.

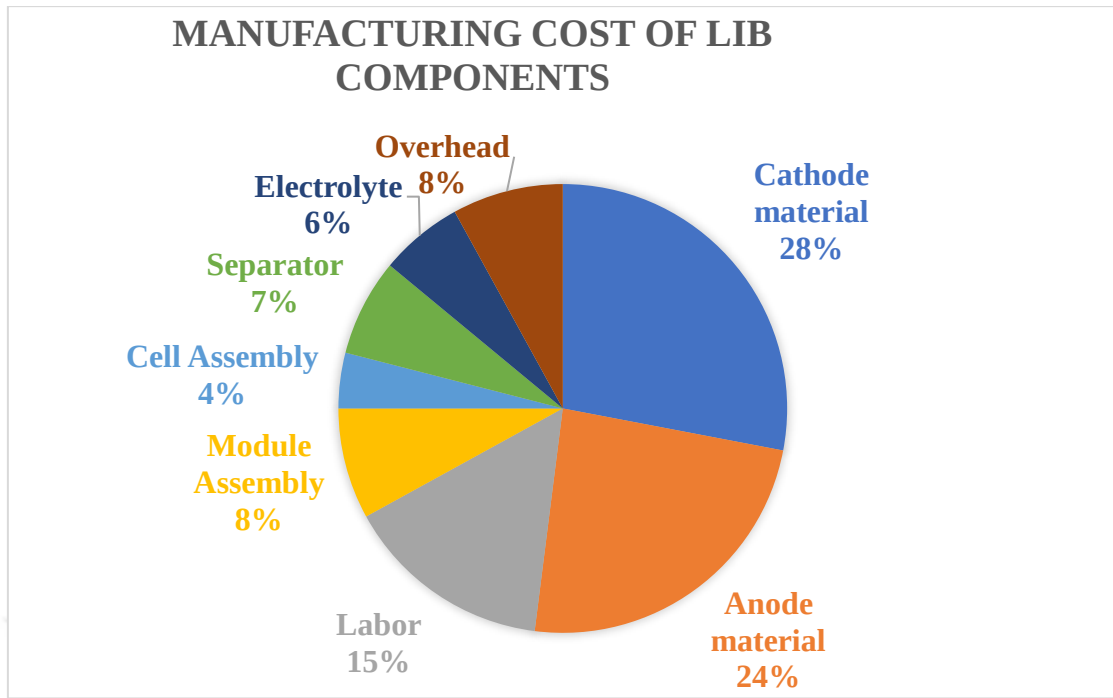


Figure 2.6: Manufacturing cost of LIB component [13]

2.4. Anode materials used in LIBs.

Literature review shows that from 1990 to 2022, the number of papers published on LIB has increased **Figure 2.7** [34], [35]. Then, among the ScienceDirect® indexed papers, 59.3% of these papers are found to be dedicated to the anode material. When these published articles are examined in a general framework, the general properties that the anode electrode active material should have can be listed below [36], [37]:

- High conductivity
- Low reaction potential vs Li
- Low polarization
- High capacity
- High mechanical strength
- Short diffusion length
- Small size to provide a high surface area.
- Insoluble in electrolyte

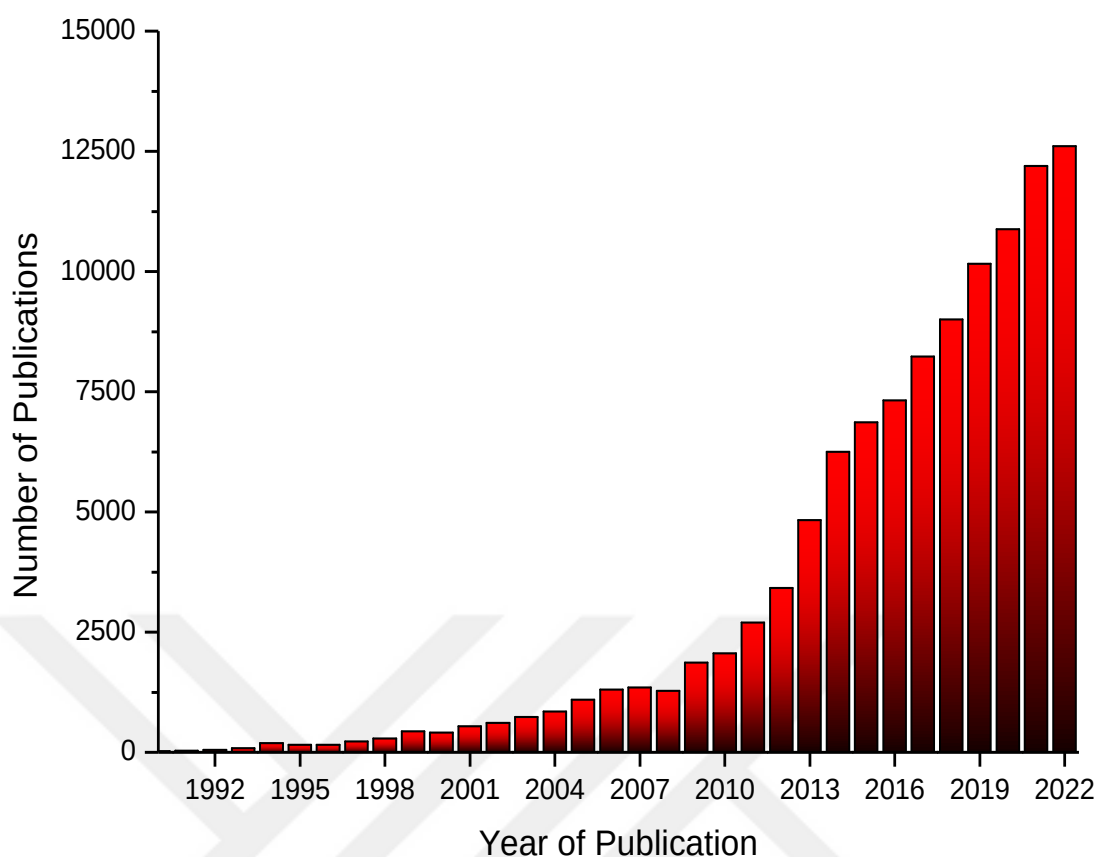


Figure 2.7: Number of publications on LIB from 1990-2022

As active material imparts two thirds of the cost of LIB it is worth considering the types of LIBs based on the active material used in it as an anode.

Initially graphite was used as anode material in LIBs and its lithium insertion mechanism was well explained in 1976 by Besenhard and Eichinger. Due to the absence of suitable electrolyte its usage in LIB was an open question. However, in 1978, Armand et al proposed the LIB containing polymer electrolyte that enabled researchers to investigate the likelihood of graphite as negative electrode. Further in 1970s, Armand put forward the rocking-chair battery concept, in which he used two different materials in both anode and cathode and explained their lithium intercalation materials for both materials. The rocking-chair battery was later termed as lithium ion battery and transportation of ion between the two electrodes of battery was further elaborated by Lazzari and co-worker [32].

Then commercialization breakthrough of LIBs was achieved by Sony when they introduced the LiCoO_2 /hard-carbon battery in 1991. Between 1990-2000, another anode

material for LIB was proposed with the spinel structure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It is expected that this anode material has potential to be an alternate option for graphite when high-power density is subjected [32]. After that many efforts are being reported on a daily basis. Only in 2022, more than 3200 scientific articles are being published online in different journals. Present day, commercially available LIBs are of three types i.e., Graphite based, silicon-based, and metal oxide based. In graphite-based LIBs, Li gets intercalated between the plans of graphite, this category of battery shows good cyclic life, and is relatively safe to use. But there are some demerits of graphite-based LIBs that they deliver lower capacity, Plus, CO_2 emission during the production of graphite involves environmental concern, and the sustainability of graphite is also in danger. Moreover, China is the biggest graphite produce in the world and up to 45% of its graphite production goes to export of graphite for LIBs to be used in electric vehicles. It is expected that by 2030, demand of Chinese graphite will increase 18% [38]

Carbonaceous material exists in two forms, one is crystalline and the other is amorphous. Amorphous carbon could be graphitic or non-graphitic. In graphitic material, carbon atoms are in hexagonal structures consisting of sp or sp hybridized state, and the whole structure comprise layered graphene planes stacked over each other. Normally, six carbon atoms get attached to one lithium atom to form LiC_6 . The naturally occurring graphite (as mined) is flaky in microstructure containing and more crystalline in nature. However, graphite used in LIB is not used directly after mining. As mined graphite is treated at very high temperature of 3000°C to convert that flaky structure into more homogenized nodular or spherical structure. This graphite is also termed synthetic graphite. After the spheroidizing process the graphite possess better packing density, uniform in size and morphology, and make Li intercalation and de-intercalation easier and rapid [39]. The theoretical capacity of 372 mAhg^{-1} of carbon anode is mainly due to the presence of LiC_6 . The lithium intercalation and de-intercalation of carbon can be given by the following equation 1.1 [40], [41]:



Alternatively, silicon-based LIBs are studied. Metals like Silver (Ag), Tin (Sn), Aluminum (Al), Antimony (Sb), Magnesium (Mg), and their alloys come under this type of anode material. As silicon is the 2nd most abundant element in earth's crust, a geographical restriction is not valid for the fabrication of Si, which promotes its use as

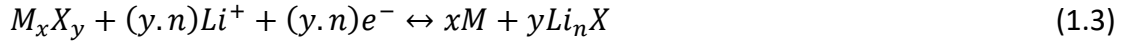
anode material. Moreover, in lithiation, lithium reacts with silicon to form alloys and delivers high capacity (around 10 times larger than that of graphite). But these anodes possess some drawbacks including poor electrical conductivity, and dramatic volumetric expansion during insertion/extraction of lithium ions giving rise to irreversible capacity loss prominently in the first cycle and rapid capacity loss in successive cycles. Moreover, such materials are used in LIB in form of thin film not as bulk material and the fabrication of nanosized film electrodes (especially Si) is complex and often involve steps like chemical vapor deposition, acid etching and high temperature treatment. Such steps in the production methods increases the cost of the production and also involvement of high energy endangers the process of being environmentally friendly [42]. Besides that the alloying and dealloying of such kind of materials are expressed by the reaction represented by equation 1.2 [43], [44]:



For years, many research groups have made mechanistic investigations about why silicon-containing anode materials degrade in a short time. The results obtained are briefly summarized below [40], [45]:

- There is an electrical disconnection due to intense volume change during the charge-discharge cycle.
- A permanent capacity loss takes place because due to the low electrical conductivity of the material. And due to continual reduction in the concentration of Li-ions as they get trapped in between the structural defects of the material and due to the formation of side products of lithium.
- Such anode material experiences decrease in capacity due to annihilation and revival of SEI onto their surface.

Another most common mechanism of lithium storage, shown by anode materials, is the conversion reaction. In this mechanism, a redox reaction takes place between lithium ion and the anode material, usually a transition metallic compound. Such kind of material possesses high theoretical specific capacity, and compounds of transition metals e.g., oxides, selenides, phosphides, fluorides, sulfides, and nitrides exhibit this manner of Li-ion storage. This type of storage mechanism was first observed and illustrated by Lu et al [46] (Equation 1.3).



The merits of such material, over other anode materials, are that their production cost is relatively lower, no dramatic change in volume occurs. However, their reaction potential with lithium is around i.e., 0.5V to 1V. When the mechanism of conversion reaction is studied in detail, thermodynamically, formation of Li_nX is possible, and reversal of this reaction is also achievable due to the presence of highly active nano M particles. But such materials do have demerits as well e.g., they possess large volume expansion (<200%), poor conductivity (both electronic and ionic), and electrolyte decomposition [40], [46].

Table 2.1: Literature examples of synthetically fabricated metal oxide as anode material in LIB

Ref.	Anode Material	Production Method	Morphology and Particle Size (nm)	Current Density (mA g^{-1})	1 st Discharge Capacity (mAh g^{-1})	Cycle	Capacity (mAh g^{-1})
[47]	Co_3O_4	Template based	Nanotubes, 20-40 μm x 200 nm	50	850	100	500
[48]	Co_3O_4 @ graphene	Chemical precipitation on graphene	Nano particle, 10-30 nm	50	1097	30	935
[49]	CoO-Co-C	Carbothermal reduction	Nano spheres, 20-30 nm	45	800	80	700
[50]	Ti-doped CoO/C	Solvothermal reaction	Octahedral, 300-400 nm	200	1749	150	1180
[51]	MnO_2/CNT	CVD with vacuum infiltration	Nanotubes, ~250 nm ϕ	50	2170	15	500
[52]	Mn_3O_4	Chemical precipitation	Sponge like, 80 nm	30	1320	40	800
[53]	MnO@C	Carbothermal reduction	Nano-disc, 400 nm ϕ , 150 nm thick	200	~1140	100	858
[54]	CuO (NP)	Chemical precipitation	Irregular inter-connected, 30-40 nm	100	1208	40	505
[55]	$\text{Co}_3\text{O}_4/\text{CuO}$	Substrate grown precipitation	Nanowires on Ni-foam, 40 nm ϕ , 5-10 μm length	100	1633	200	1191

[56]	CuO-Fe ₂ O ₃ /C	HEB	Microbeads, few hundred nanometers	121	~1000	100	500
[57]	CuO@NiO	Microwave- assisted metal- organic frame	Microspheres, 0.9-1 μ m	100	1218	200	1061
[58]	NiO	Liquid phase deposition	Flake like strips, 5 nm	100	1100	35	260
[59]	NiO	Simple precipitation	Global particles, 100 nm	100	1000	50	380
[60]	TiO ₂	Sol-gel method	Polygon shaped, 15-25 nm	100	150	100	107 (at 1 Ah g ⁻¹)
[61]	TiO ₂	Hydrothermal reaction	Nanotubes, 10 nm ϕ , 200- 400 nm length	36	290	20	205
[62]	NiTiO ₃	Solvothermal reaction	Micro-rods, 2 μ m length, 600 nm ϕ	100	750	90	200
[63]	NiTiO ₃	Solvothermal reaction	Irregular nanoparticles, 40-50 nm	50	613	50	184
[64]	α -Fe ₂ O ₃	Hydrothermal reaction	Nanowires, 300 nm ϕ	100	1303	100	456
[65]	α -Fe ₂ O ₃	Hydrothermal reaction	Micro and nano particles, 40- 200 nm	100	1190	50	228
[66]	α -Fe ₂ O ₃	Hydrolysis	Polygons, 25 nm	100	1290	50	1000
[67]	α -Fe ₂ O ₃	Hydrothermal reaction	Irregular, 122-226 nm	100	1320	200	200
[67]	α -Fe ₂ O ₃ /C	Hydrothermal reaction	Globular, 10 nm	100	1200	200	800

The history shows that the number of papers on anode electrode active material has increased from 1990-2022 **Figure 2.8**, where the use of transition metal oxides (TMO) as anode material has received a particular interest once their mechanism was disclosed by Poizot et al. [68], [69]. In order to solve the problems of TMO anodes and extend their uses, chemical and morphological improvements have been proposed and well elaborated in literature [69]. In this scope, metal doping (Cr [70]–[72], Mn [70], [73]–[75], Ni [70], [76], [77] etc.), composite formation (with C based materials [78]–[81], with another

metal oxide [55], [56], [82], [83], etc.) and morphological alteration (nanometer sized spherical particles [84]–[86], flower shaped micron sized particle [87]–[89], core-shell design [90]–[92], etc.) have been realized.

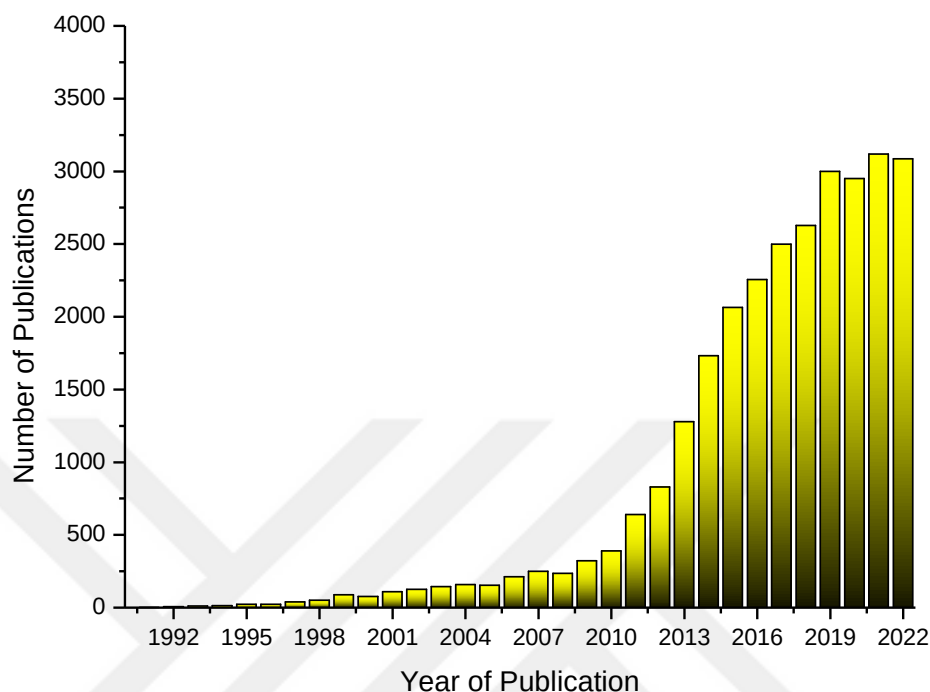


Figure 2.8: Number of publications on anode material of LIBs from 1990-2022

Among alternatives, NiO (cubic), a p-type semiconductor having a broad band gap (3.6 eV – 4 eV [93]) is becoming attractive anode material because the high specific theoretical capacity of 718 mAhg⁻¹ owing to a reversible conversion reaction between NiO and Li-ion and lithium gets in to the octahedron sites within the cubic structure and after lithiation the cubic structure changes to tetrahedral structure [94]. Despite having high theoretical capacity, the overall electrochemical performance of NiO needs improvement as compared to another conversion type of TMO. The inferior performance of the said metal oxide is due to several reasons including poor electronic conductivity (<10⁻¹³ Ω⁻¹cm⁻¹) [93] and volumetric expansion [95]. Many research studies have been reported in which scientists have synthetically fabricated the oxide material and applied some carbon coating and/or composite formation with carbon to benefit the advantages of carbon atoms as buffer and electron conductive pathways in the structure **Table 2.1**.

When the lithiation potential mechanism of transition metal oxides are studied, it is observed that the lithiation potentials of different metal oxides differ. At this point TiO₂ anode receives attention because upon the lithiation of anatase Li gets around 1.5V (above

1V) which is way above then the potential where SEI is formed therefore, there will be no SEI formation and because of its absence there will be no loss of lithium due to SEI during lithium insertion and extraction [96]. Moreover, TiO_2 has non-toxicity, safety, high power density, cost effectiveness, high retention, and relatively high electrochemical conductivity than other TMOs [97]. TiO_2 exists in different polymorphs (i.e., anatase-tetragonal-I41/amd, brookite-orthorhombic, rutile-tetragonal-P42/mnm, and β - TiO_2 -monoclinic-C2/m). the theoretical capacity of them is 335 mAh g^{-1} but based on the structurally available sites for lithiation the reversible capacity can vary for each polymorph i.e., 200 mAh g^{-1} for both anatase and β - TiO_2 , 170 mAh g^{-1} for brookite and 185 mAh g^{-1} for rutile [98]. This fact shows that, anatase phase performs better than the other phases **Table 2.1**.

Increase in prices of the electrode active material becomes very crucial for the sustainability of the business. At this point, iron oxide has also become the subject of many studies. Fe_2O_3 anodes have received considerable interest from audiences as next generation anode material candidates thanks to their properties such as low cost, abundant occurrence, the high theoretical capacity (1006 mAh g^{-1}), and non-toxicity. It has also been explained by the researchers that the reversible capacity of iron oxide increases by decreasing the particle size to nano-meter range [67], [99]. Moreover, researcher has doped iron oxide with other element or made composite with dopped carbon sources and tried to enhance the electrochemical performance of the anode material in several aspects [100]–[102]. **Table 2.1** summarizes the performances of synthetically fabricated NiO , TiO_2 and Fe_2O_3 .

The use of metal salts produced by primary methods in all these improvement studies shows that the carbon footprint of the product to be obtained in the improvement processes is not taken into account. Unlikely, in this thesis, the necessity of synthesizing low carbon footprint electrode material in all improvement efforts has been taken into consideration. Because the use of fossil fuel in the manufacturing process of metal salts increases the carbon footprint of the final product. Moreover, the continual depletion of metal reserves and increased energy cost have raised the per ton production costs of metal through primary routes. Thus, to reduce both the price and the carbon footprint of the electrode active material recycling metals from waste is widely studied. In the recovery of metals from spent LIBs involves pyro and hydro-metallurgical processes [14]. Many

patents on hydrometallurgical recovery of valuable metals (e.g., cobalt) show that hydrometallurgical processes prevail because they are practical, economical, environment friendly, and highly effective to recover the element selectively [103]. Moreover, hydrometallurgical processes don't need high investment costs. Up to now, many companies have patented hydrometallurgical methods to be used to recover elements from LIB waste. For instance, in 1998 Toxco process was patented by W. McLaughlin [104] where water and sulfuric acid are used subsequently to recover, lithium hydroxide and cobalt. Alternately, Sonny also had a patent where high temperature has been proposed to recover cobalt. Herein, the patent of atomic energy authority (AEA) of UK attracts attention as they propose low temperature simple mechanical process leading to recover most of the LIB components i.e., cobalt and lithium with less energy consumption [14]. Those studies are not only limited by LIB wastes but also industrial and/or domestic wastes are also considered to be used as the initial raw material to recover an element or synthesize a product with low energy consumption [105], [106].

Our research group has used scale as an industrial waste and treat it with different carbon sources to use it as anode material [107]. Moreover, Luo et al [67] utilized, spent pickled acid as raw material to obtain iron oxide based anode material and evaluate its use in LIB [67], [108]. Furthermore, recovery and development of silicon based anode material has also been studied by researchers using waste of photovoltaic industry [109]. In addition, flue dust from arc furnace was also processed with carbon source via pyrolysis in order to valorize this hazardous waste in batteries [110].

Waste generation during mass production is a known and accepted fact. However, the disposal of those waste is not fully possible due to the restriction of landfill, contamination of land and generation of land pollution or lack of resources to deal with the complete disposal of huge amount of waste [111]. Therefore, evaluating the possible use of the waste for different applications is very crucial in terms of circular economy and sustainability of the world we live in.

In this thesis, our focus is to valorize typical wastes of biomedical industry such as orthodontic braces and wires. NiTi wires are shape memory wire that are majorly used in dentistry for the alignment of teeth and ss braces are the attachments which get attached with the teeth and on them NiTi wires get attached or tied as shown in **Figure 2.9**. The SS braces used in the orthodontic can be made of different grade of stainless steel and use

of specific grade depends on the type of application, corrosive conditions, and duration of application. But majority of them are manufactured according to AISI 304L SS grade, which specifically contains chromium around 18%, 10% nickel and almost 0.03% carbon. Besides this, other grades like 316L SS, 17-4PH SS, Super SS (SR-50A) and 2205 duplex SS. In medical field stainless steel braces are used among mentioned grades and each of them has different but standard chemical composition [112]. For NiTi wires nitinol 55 medical grade alloy is used which is manufactured and produced according to the ASTM standard 2063-18 for shape memory alloy this contains almost 55% nickel, 0.04% carbon and oxygen, 0.012% iron and the rest of 44% is titanium [113]. In this study stainless steel braces of 304L SS grade and NiTi of nitinol 55 alloy of ASTM standard 2063-18 for shape memory alloy has been used.

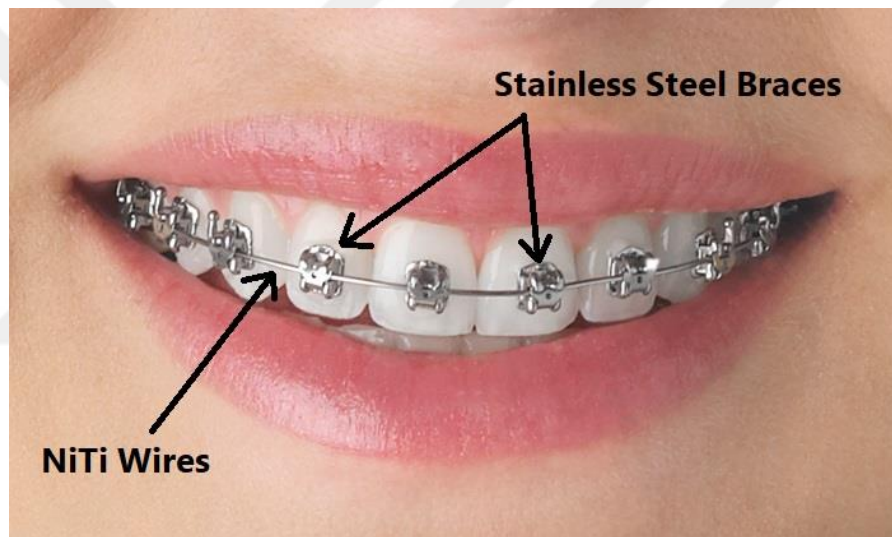


Figure 2.9: Usage of NiTi wire and SS braces [114]

The survey of J. Maida from Technavio Research, shows that the total amount of metals used in the biomedical application, constitutes more than 57% of iron, 21% of titanium, and 6% of other metals like nickel [115] **Figure 2.10.**

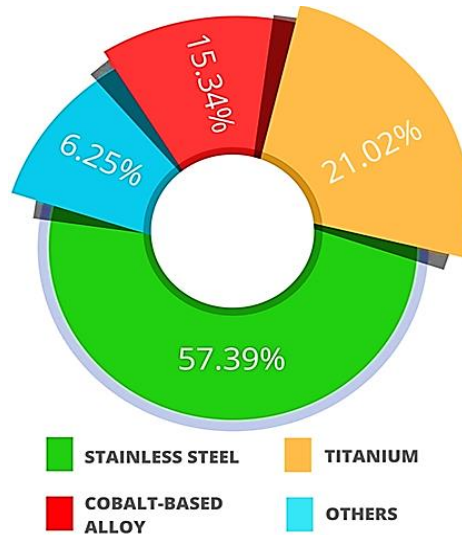


Figure 2.10: Energy production analysis by US energy Department [115]

Considering this fact, some flowcharts have been designed over the years to recover Ni and Ti as metals or in their oxide states. Additionally, the braces used in orthodontic applications are made of stainless steel and represent another biomedical waste that may be used to recover iron oxides.

Recently a couple of research groups had done an effort to recover metals (NiO and TiO₂) from biomedical parts but didn't evaluate their uses as electrode material. Özgün et al [116] has recovered titanium dioxide and nickel oxide by chemical precipitation, at two different pH values, from the leached solution of orthodontic waste. Ans et al [117] in their study has also recovered nickel from the orthodontic waste by leaching.

Herein, our motivation is to use the metal solution recovered from waste treatment as the precursor in the fabrication of electrode active material for LIBs. This fact strengthens production both financially and ecologically. Because literature analysis demonstrates that up to now various metal oxides (such as NiO, TiO₂, Fe₂O₃) have been utilized as electrode active material in LIBs. The properties as well as the performance of those materials are given in **Table 2.1**.

At this point, while planning the experimental studies in the leaching process of braces and fabricating iron oxide rich particles with small particle size, fuzzy logic was used innovatively to examine the effect of changing experimental conditions on the particle size, hence maximizing the efficiency. At this point, the main reason for choosing fuzzy

logic is that the interrelations among the independent parameters that are the subject of the research do not affect the output in a single direction and at a one degree.

Indeed, in the field of science, traditional ways of computation, analysis, or interpretation of most of the things involve precision or certainty. This certainty is normally ascribed with two extreme phenomena i.e., true, or false: yes or no etc. In terms of mathematics or computational area the two extremes are denoted by 1 and 0. According to orthodox logic, a statement can be true (1) or false (0). There is no existence of anything uncertain in between these two extreme ends, such logic is also called crisp logic or two valued logics. This logic was originated by Aristotle-a Greek philosopher, early in 4th century B.C. that's why some time also termed as Aristotelian logic. For a long period of time, Aristotelian logic was well used and was core of scientific thinking all over Middle East and Europe, as it helps the way of handling the problem, in an easier and practical way. However, the real situation is not that simple, and found to be mostly vague and uncertain in many ways. In most of the events in practical life there is no absolute existence of being entirely true or entirely false. Many renowned European philosophers and mathematician realized and emphasized that crisp logic is unable to explain or contain all kind of occurring events, even Aristotle himself believed that there is possible degree of being true or false which is also called as membership degree (MD). The logic of ambiguity or vagueness was first devised by a polish philosopher J. Lukasiewicz in 1920. He first made the three subdivisions of 0, $\frac{1}{2}$ and 1 in order to manage the vague occurrence of events. Later extended it to infinite values between 0 to 1. Then in 1937, another work came to surface when Max Black from Cornell university, relates the object based on their likeliness of usage with particular set. The relation was termed as membership of usage and by this he proceeded with the concept of vagueness. These couple of efforts proved to be the foundation of the comprehensive invention of fuzzy logic, in later years. Theory of fuzzy logic and fuzzy logic set was set and conceived by an American native Lofti Zadeh in 1965. His theory is the combination of two valued logic and concept used by Lukasiewicz, by defining more division or degree of belonging. The tool or theory devised by Zadeh provides a way to link or to handle real time events using mathematics. So, fuzzy logic sets enable the construction of models close to realistic situation by using words linked with mathematical values [118], [119].

As mentioned by many philosophers and researchers, fuzzy logic set or simply fuzzy set, is an extension of the conventional Aristotelian two valued logic. The crisp logic only enables us to decide that either a certain object is among the two categories i.e., yes, or no, true, or false, 0 or 1, ON or OFF. However, fuzzy logic defines a greater number of divisions between the two values or ends, by using the degree of belonging also called membership degree. The value of membership degree ranges between 0 to 1. Here, membership degree 0 shows the exclusion of an element from the fuzzy set and membership degree 1 implies that element completely belongs to the fuzzy set. In fuzzy logic, the element can belong to two fuzzy sets that are overlapping but here the membership degree comes into play and determines to which fuzzy set the element has more influence and based on greater membership degree an element is considered to be from that fuzzy set. Relation between membership degree and fuzzy sets is graphically represented by membership degree on vertical axis and fuzzy set along with their range of values on horizontal axis as shown in **Figure 2.11**. A fuzzy set is usually triangular, trapezoidal and gaussian in shape. They may or may not overlap with each other. An element can be part of more than one fuzzy set, but membership degree determines from which set has its strong influence on the output. As it can be seen in **Figure 2.12**, that an element x belongs to both set **A** and **B**, but its membership degree is higher (i.e., 0.45) in set A than the membership degree in set B (i.e., 0.23). Therefore, while calculating its effect on output, higher MD is considered and due to this that fuzzy set will be considered effecting the output in this case.

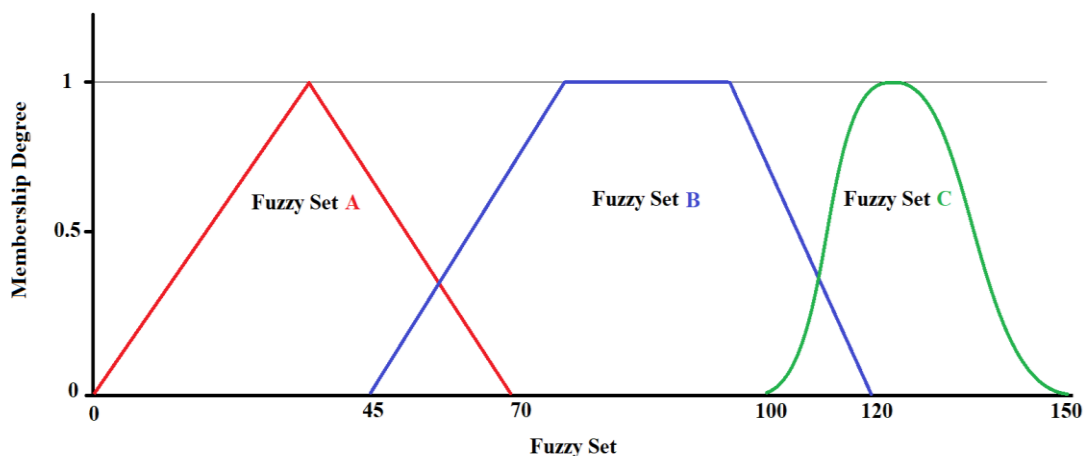


Figure 2.11: Representation of membership degree and fuzzy sets

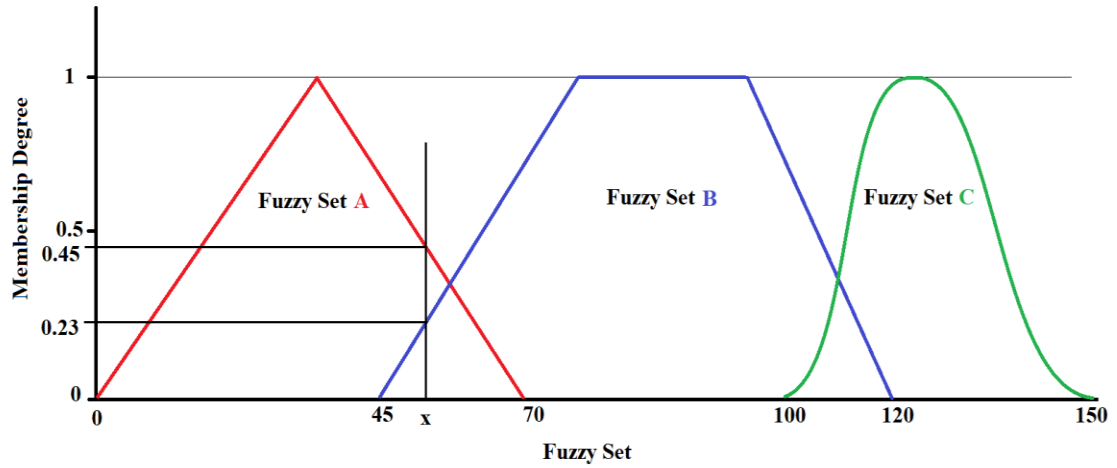


Figure 2.12: Membership degree of an element in more than one fuzzy set

Then another important thing in fuzzy logic is fuzzy control system or also known as fuzzy interference. This is the way of processing the data from fuzzified inputs and then generating output. The inputs can be divided into several linguistic fuzzy sets with different shapes and input value ranges as described earlier. Then these fuzzy sets of different inputs are connected with each other using logical operations i.e., AND, OR, NOT etc. Afterwards fuzzy rules are formed by linking these logically connected input fuzzy sets with output by using IF, THEN statements. Fuzzy interference uses these fuzzy rules to form an output as a result. Formation of number of fuzzy rules is decided by number of fuzzy sets of input variables for example if there are two input variables of a system and each of them is fuzzified in three fuzzy sets then number of fuzzy rules will be $3 \times 3 = 9$.

The very first practical development of fuzzy interference system was done by a British engineer Ebrahim Mamdani in 1974 A.D. for the automation of a steam engine of a laboratory [120]. Mamdani fuzzy interference system evaluates the fuzzy rules, aggregates the output of each fuzzy rules and forms one fuzzy output then a single value is obtained from the aggregated fuzzy output by different approach such as centroid method, maximum membership degree, maximum average MD, center of weight etc. Another known fuzzy interference is Sugeno fuzzy interface which was developed by Japanese researchers T. Takagi and M. Sugeno in 1985 [121]. In such a fuzzy system generation of output is in manner of two valued logic or crisp number. The major difference between the two fuzzy interference systems is that Mamdani fuzzy system involves a full fuzzified system. It processes the fuzzified inputs and produces results in

a fuzzified way. But Sugeno fuzzy system is semi fuzzy system because it processes fuzzy input but gives results in form of one valued constant or in form of linear polynomial equation [122]. Beside these, there is another fuzzy system named fuzzy relational system proposed by W. Pedrycz [123] has been reported as well. Because of the ease of handling the complex system by fuzzy logic, it has been utilized all around the globe very successfully. Famous Japanese companies are like Sony, Nissan, Mitsubishi and Matsushita are using fuzzy logic based control system in production and smooth operation of their products [118]. Among these reported fuzzy interference systems Mamdani type is very convenient to use and to apply the most realistic and practical application where inputs are vaguer in nature. For the application of Mamdani type fuzzy interference system following steps are followed:

- i. Identification of input(s) and output(s) variable- first of all for the application of fuzzy logic system on a particular system input variables and output variables are decided first.
- ii. Fuzzification- Then these selected input and output variables are fuzzified into fuzzy subgroups. Linguistic fuzzification is done and numerical range of values is assigned.
- iii. Development of fuzzy logic rule base- here a rule base is developed using IF...THEN, AND, OR, NOT etc. operations to link the input fuzzy set with output fuzzy sets.
- iv. Fuzzy interference system- here, by using a suitable software, an appropriate fuzzy system (Mamdani/Sugeno) is selected, and the fuzzy rules are fed into it.
- v. Fuzzy result- this involves aggregation of the output in fuzzy form.
- vi. Defuzzification- this final stage involves the generation of a single value from the fuzzy output obtained in previous step.

Since the invention of fuzzy logic, the enthusiasm of researchers towards the use of this tool in the field of science is worth appreciating. As mentioned earlier, the Mamdani fuzzy system is the easiest to apply, that's why in area of practical performance of the experiment, this type has been mostly utilized by the researchers and reported in the literature. Here are the few examples which are most analogous to present study; Majmudar et al [124] has used fuzzy logic in measuring and studying the size and shape of the fabricated gold particle using C-mean clustering approach on TEM images. Shetty

et al. [125] has used Taguchi method with fuzzy logic modeling to optimize and predict surface roughness of composite. Hosseini et al. [126] has used fuzzy logic model. This AI-based approach enabled them to develop a relation between Cr (VI) removal efficiency (as output) and pH, contact time, initial Cr (VI) concentration and absorbent dose as input variables by applying Mamdani interface.

Another well-known classical design of experiment (DOE) technique for evaluation of effect of variables, on to the system or response, is factorial design. Different numbers of variables with 2 or more levels are taken into consideration and their individual as well as their joint effect on output response and a regression model is generated which represents the combine effect of the variable. Based on the number of factors and their sub level, the number of experiments that must be carried out are calculated using the formula M^n , here M is number of levels and n is number of factors taken [127]. Being an attractive easier approach, it's been applied by researchers in all fields of research. Zhao et al. [128] has used full factorial design to optimize the four factors with 2 levels to achieve minimum particle size of the nano particles. Rangappa and co-worker [129] has full factorial DOE for the cooling of the LIBs by optimizing the 3 factors with 3 levels. Besides these there are many examples found in literature where researchers have used full factorial design for optimization of their process parameters.

In this study, two types of biomedical (orthodontic) waste (NiTi wires and SS braces) have been leached with sulfuric acid. In the first part of the thesis, the first leaching optimization was achieved with 100% efficiency then selective metal recovery and co precipitation, though chemical precipitation, was done at different pHs for NiTi waste wire. Afterward, the composite was fabricated by high-energy ball milling and electrodes were fabricated to test their performances. Then, in the second part of the thesis both factorial design and fuzzy logic are utilized to develop a relation between input variables and output dependent on the variables. For SS based waste material, powder was fabricated by hydrothermal reaction and innovatively for the first time in open literature factorial coupled with fuzzy logic was applied to optimize the hydrothermal parameters to achieve minimum particle size to ultimately have high capacity. Hydrothermal reaction parameters i.e., time, solid to liquid ratio and temperature were used as gaussian input function and by using Mamdani fuzzy interface was used to link with particle size as a

gaussian output function. Then these fabricated powders were used as anode material in lithium-ion batteries and other characterizations were made.



CHAPTER 3

3. EXPERIMENTAL PART

3.1. Fabrication of metal oxide composite anodes from NiTi wires

3.1.1. Materials

Orthodontic waste (NiTi wire) **Figure 3.1** was provided by Dr Halenur Bilir (Istanbul Medipol Mega Hospital), Dr. Ekram Emirerim (Biruni University Hospital), Dr Serdar Ayyıldız, and Prof. Dr. Tülin ARUN. Leaching of waste had been made with Merck quality sulfuric acid (1.00713.2500). For selective metal precipitation and co-precipitation, 14M NaOH and 14M NH₄OH of analytical grade are utilized. Deionized water and NH₄OH are of analytical grade.



Figure 3.1: Orthodontic waste (NiTi wire and SS-braces)

For fabrication of electrode, slurry was prepared with technical grade polyvinylidene fluoride (PVDF) as binder and conductive carbon as conductor. N-Methyl-2-pyrrolidone (NMP) Merck quality (8.06072.2500) is used as a solvent in slurry preparation. 10 μ m thick electrical grade highly pure copper foil (>99.95%) has been used as current collector.

3.1.2. Fabrication

3.1.2.1. Powder fabrication

NiTi wires were leached out and then the leached solution was subject to co-precipitation, selective precipitation, and composite fabrication. The procedure of each sample is described later in detail and the flowchart in **Figure 3.3** shows the complete set of procedure followed with NiTi wires.

First orthodontic waste (NiTi wires) was washed with distilled water at 60°C for 2 h. Then acidic leaching of wire was carried out at 90°C with 5 M H₂SO₄ for 4 h with a solid to liquid ratio 1/50 in the reflux system shown in **Figure 3.2**. The selective precipitation of TiO₂ and NiO from the leachate was accomplished at pH 1 (S1) and pH 10 (S10), respectively, by using 14 M NaOH. The pH adjustment was realized in 6 hours and 24 hours aging duration was given for phase separation. The precipitates were filtered then washed multiple times centrifugally at 4500 RPM for 30 min. After drying of precipitates at 100°C for 12 h each precipitate was dried again at high temperature 300°C for 2 h separately to ensure complete removal of any chemically attached water.

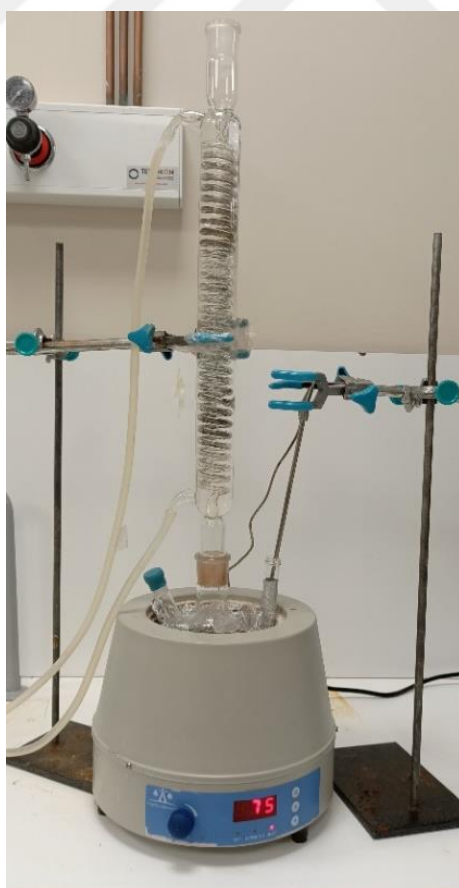


Figure 3.2: Systematic setup of leaching in reflux system

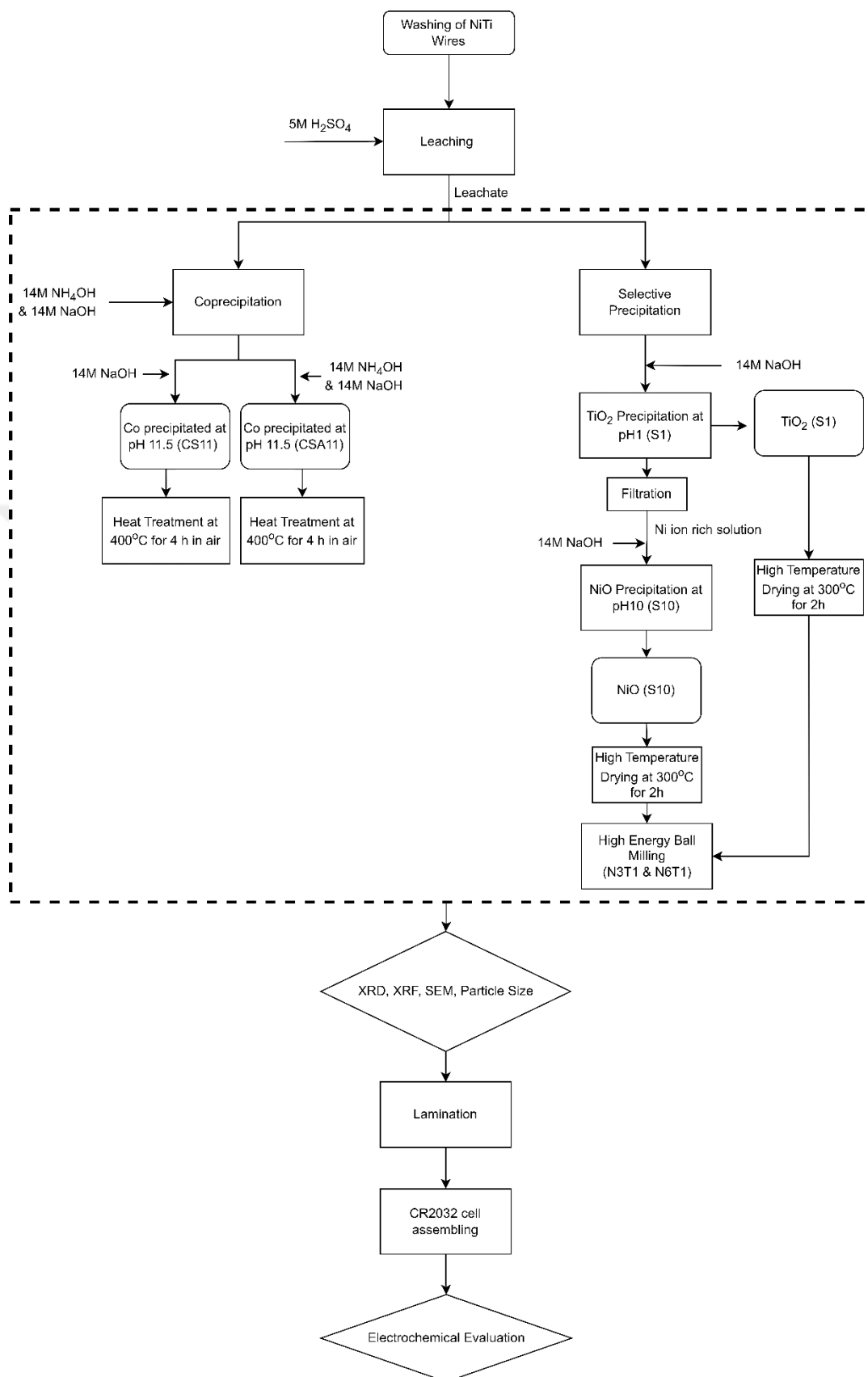


Figure 3.3: Schematic flow chart of procedure followed.

Co precipitation of the NiTi-wires leachate solution was done at pH 11.5 with 14 M NaOH solution (CS11) and at pH 11.5 (CSA11) with 14 M of NH_4OH and NaOH.

The pH adjustment was realized for 6 hours. After 24 hours of phase separation, the precipitates were separated from the solution by centrifuge and the precipitate was washed multiple times then centrifuged at 4500 RPM for 30 min. After drying precipitates at 100°C for 12 h they were heat treated at 400°C for 4 h in air atmosphere. To reduce the amount of the sulfur detected in CS11, the sample was washed several times in water at 90°C, at S/L ratio 1:10, for one hour and then dried. **Table 3.1** shows the sample coding and the experimental details.

3.1.2.2. Composite fabrication by ball milling

Composite from the selectively precipitated powder was made by using high energy ball milling (VARSAN) shown in **Figure 3.4**. The two selectively precipitated powders were treated in ball milling in different two weight ratios i.e., 1:3 and 1:6 (titanium oxide rich: nickel oxide rich) at 300 RPM for 2 hours in Ar. Ethanol was added as process control agent (PCA) 5% by the weight of the powder charge and the ratio between grinding media and the dust mixture was kept at 20:1. Next, the milled powders were dried overnight at 80°C, in vacuum.

Table 3.1: The sample coding and the experimental details of coprecipitation

Sample code	Precipitation agent	Chelating agent	pH value	Temp	RPM
CS11	NaOH	-	11.5	RT	600
CSA11	NaOH	NH_4OH	11.5	RT	600



Figure 3.4: High energy ball milling (VARSAN)

3.1.2.3. Electrode fabrication

Anodes were fabricated by coating the mixture of active material, conductor, and binder in an organic solvent. The mixture or slurry was prepared by mixing 60% powder sample (CSA11, S1, S10, N3T1, and N6T1) as active material, 25% carbon black as conductor and 15% PVDF as binder in Thinky ARE-250 (for washed CS11 sample the lamination was carried out with 80% active material, 10% binder, and 10% conductor). Then lamination was prepared by coating the slurry on copper foil by Dr. Blade technique. Then coated foil/ lamination was dried at 70°C for 12 hours then at 120°C for 12 h. Then, the dried foils were rolled down to achieve anode with 30 μm thickness by using a roller.

3.1.3. Characterization

3.1.3.1. Powder characterization

To analyze the structural phases, X-ray diffractometer (XRD, Bruker D2 Phaser) had been carried out between 10°-90° by Cu K α with 0.02°/sec scanning rate. Morphological investigation of samples had been performed by scanning electron microscope instrument (SEM, Zeiss Gemini 500). The chemical composition of the fabricated powder has been examined by applying X-ray fluorescence (XRF, Rigaku - ZSX Primus II). For determination of particle size, Malvern-Mastersizer 3001 had been utilized.

3.1.3.2. Electrode characterization

Electrochemical evaluation of the fabricated anodes was realized by assembling CR2032 standard coin cells **Figure 3.5**. All the cell assembly had been carried out in argon filled glovebox (MBRAUN, Labmaster (<1 ppm O₂, <1 ppm H₂O)). The electrolyte contains 1M LiPF₆ (in EC: DMC (1:1) solution). The separator was Celgrad 2400. Galvanostatic assessments were made at load of 50 mA g⁻¹ between voltage range of 10 mV - 3 V (vs Li/Li⁺) using MTI BST8-WA. Lithiation mechanisms had been examined by performing cyclic voltammetry using Gamry Interface1000E. First 4 cycles CV curvatures of each electrode were retrieved by cycling the electrodes between said voltages with a scan rate of 0.2 mV/sec **Figure 3.6**.

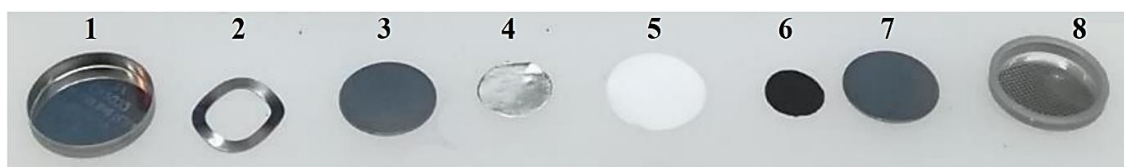


Figure 3.5: CR2032 standard battery component; 1-lower case; 2-spring; 3-stainless steel spacer; 4-lithium metal as cathode; 5-separator; 6-fabricated anode; 7-stainless steel spacer; 8-upper case.



Figure 3.6: a) Glovebox b) Gamry setup c) Battery analyzer

3.2. Fabrication of metal oxide composite anodes from braces

3.2.1. Materials

Orthodontic waste (SS-braces) **Figure 3.1** was provided by Dr Halenur Bilir (Istanbul Medipol Mega Hospital), Dr. Ekram Emirerim (Biruni University Hospital), Dr Serdar Ayyıldız, and Prof. Dr. Tülin ARUN. Leaching of waste had been made with Merck quality sulfuric acid (1.00713.2500). For metal precipitation 14M NH_4OH of analytical grade was utilized. Deionized water and NH_4OH are of analytical grade.

For fabrication of electrode, slurry was prepared with technical grade polyvinylidene fluoride (PVDF) as binder and conductive carbon as conductor. N-Methyl-2-pyrrolidone (NMP) Merck quality (8.06072.2500) was used as a solvent in slurry preparation. 10 μm thick electrical grade highly pure copper foil (>99.95%) had been used as current collector.

3.2.2. Fabrication

3.2.2.1. Experimental design technique

Knowing that stainless steel braces are made of 314 low carbon stainless steel, the experimental design was realized in order to co-precipitate iron oxide along with other transition metal oxides together, in submicron sized since the literature revealed that iron oxide would perform better electrochemical performance when its size was ~150 nm and in the form of a composite rather than its pure oxide state [16], [99].

To get 150 nm particle sized composite powder hydrothermal method was chosen as a fabrication method. There, the reaction time, temperature, and filling ratio were optimized. Herein both orthogonal (factorial design) and non-orthogonal (fuzzy logic) systems were studied, and the results were discussed. Factorial design and ANOVA analysis were performed on MINITAB v20. For the application of fuzzy logic, Fuzzy Logic toolbox of MATLAB was used.

a. Factorial design (FD)

Composite powder was fabricated by using hydrothermal reaction. The significance and influence of the hydrothermal process parameters (time, temperature, and filling ratio), on the particle size of the powder formed, was investigated by factorial design. **Table 3.2** gives the number of experiments and their parameters. **Table 3.3** shows each parameter and levels for every experiment.

Table 3.2: Parameters and their levels of factorial design

Symbols	Parameters	Coded Levels	
		-1	+1
A	Temperature (°C)	150	200
B	Time (h)	12	24
C	Filling ratio	0.5	1

Table 3.3: Factorial experimental design details

No. of Experiment	A	B	C
1	-1	-1	-1
2	-1	-1	1
3	-1	1	-1
4	-1	1	1
5	1	-1	-1
6	1	-1	1
7	1	1	-1
8	1	1	1

b. Fuzzy logic modeling

Alternatively, a non-orthogonal experimental design named fuzzy logic was used to define the experimental parameters required for the fabrication of 150 nm particle sized composite powders. For this purpose, three input variables i.e., time, temperature and filling ratio were used. These three inputs were connected to the one output, i.e., particle size, with Mamdani type fuzzy interface as shown **Figure 3.7**. Each of three input and output were fuzzified in to three linguistic sets or levels as shown in **Table 3.4**. These three inputs with three levels make 27 rules. Among them only 8 experiments were chosen and were realized. The results obtained from fuzzy, and FD were compared at the end.

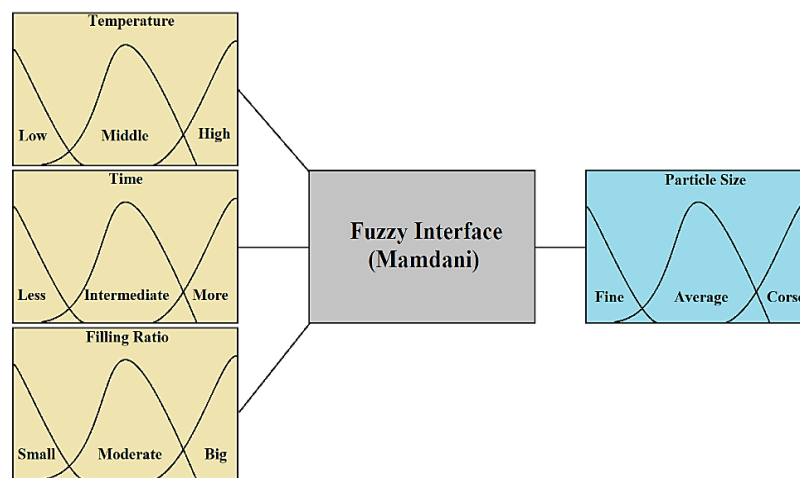
**Figure 3.7:** General structure of fuzzy logic model with three inputs and one output

Table 3.4: Linguistic levels of Input and output of fuzzy logic model

Variable	Linguistic Levels	Range
Temperature (°C)	Low	140-173
	Middle	157-205
	High	173-230
Time (h)	Less	0-22
	Intermediate	15-26
	More	18-36
Filling ratio	Small	0-0.64
	Moderate	0.3-0.8
	Big	0.6-1.2
Particle size (nm)	Fine	100-220
	Average	160-410
	Corse	300-530

3.2.2.2. Powder fabrication

First waste stainless steel braces were washed with distilled water at 60°C for 2 h. Then leaching of braces was carried out at 90°C with 4 M H₂SO₄ for 4 h with a solid to liquid ratio of 1/50 in the reflux system shown in **Figure 3.2**.

Later, pH was adjusted at 10 by using 14 M NaOH. After pH adjustment, the solution was transferred in hydrothermal reactor and the reaction was realized at different durations, temperatures and reactor filling ratios as shown in **Figure 3.8**. Once, the reaction was done, the precipitates were filtered and then washed multiple times by centrifuge at 4500 RPM for 30 min. After drying of precipitates at 100°C for 12 h the precipitates were heat treated at 730°C for 5 h in air atmosphere. The whole schematic flowchart of the procedure followed is given in **Figure 3.9**.

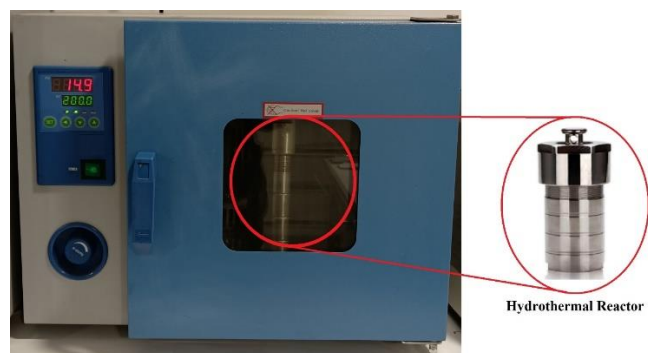


Figure 3.8: The hydrothermal reactor and oven

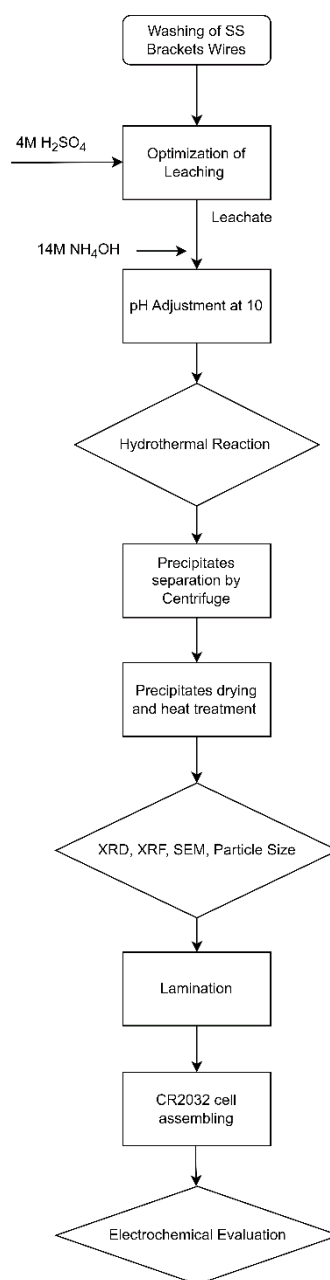


Figure 3.9: Schematic flowchart of the procedure followed for synthesis and fuzzy logic application

3.2.2.3. Electrode fabrication

Anodes were fabricated by coating the mixture of active material, conductor, and binder in an organic solvent. The slurry mixture was prepared by mixing 60% powder sample as active material, 25% carbon black as conductor and 15% PVDF as binder in Thinky ARE-250. Then, the lamination was prepared by coating the slurry on copper foil by Dr. Blade technique and the coated foil/ lamination was dried at 70°C for 12 hours then at 120°C for 12 h. Finally, the dried foils were rolled to achieve anode with 30 μm thickness by using a roller.

3.2.3. Characterization

3.2.3.1. Powder characterization

To analyze the structural phases, X-ray diffractometer (XRD, Bruker D2 Phaser) was used between 10°-90° by Cu K α with 0.02°/sec scanning rate. Morphological investigation of samples was performed by scanning electron microscope instrument (SEM, Zeiss Gemini 500). The chemical composition of the fabricated powder was examined by applying X-ray fluorescence (XRF, Rigaku - ZSX Primus II). For determination of particle size, Malvern-Master sizer 3001 was utilized.

3.2.3.2. Electrochemical characterization

Electrochemical evaluation of the fabricated anodes was realized by assembling CR2032 standard coin cells, **Figure 3.5**. All the cell assembly was carried out in argon filled glovebox MBRAUN, Labmaster (<1 ppm O₂, <1 ppm H₂O). The electrolyte contained 1M LiPF₆ (in EC: DMC (1:1) solution). The separator was Celgrad 2400. Galvanostatic assessments were made at load of 50 mA g⁻¹ between voltage range of 1 mV - 3 V (vs Li/Li⁺) using MTI BST8-WA. Lithiation mechanisms were examined by performing cyclic voltammetry using Gamry Interface1000E. First 4 cycles CV curvatures of each electrode were retrieved by cycling the electrodes between said voltages with a scan rate of 0.2 mV/sec, **Figure 3.6**.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1. Fabrication and characterization of the composite powders from NiTi wires

In this section, NiTi wires had been used as the initial material to fabricate composite powders. After leaching the precursor material two different methodologies had been studied. Firstly, a coprecipitation method had been applied to form nickel titanate. Then secondly selective precipitation with ball milling had been used to fabricate a composite made of NiO-TiO₂. The use of these different composite materials, which had been obtained by different methods, as electrode material in the lithium ion battery is also examined.

4.1.1. Leaching of NiTi wires

Once the NiTi wires were washed with distilled water, they were leached with sulfuric acid in the reflux system. In leaching, molarity of acid, temperature, solid to liquid ratio and time were the most important factors. Özgün et al [116] had disclosed the molarity of acid and temperature of leaching at 5M and 80°C, respectively and they achieved 60% efficiency. Taking these values as starting point leaching was carried out in reflux with solid to liquid ratio of 1/50. As a result, 100% leaching was achieved. Özgün et al [116] had recovered titanium dioxide and nickel oxide by chemical precipitation, at two different pH values, from the leached solution of orthodontic waste. Ans et al [117] in their study had also recovered nickel from the orthodontic waste by leaching.

4.1.2. Powder fabrication

4.1.2.1. Coprecipitation

In this work the aim was to coprecipitate Ni-ions and Tiions together, hoping to fabricate composite material with improved structural characteristics of anode material for better

lithium diffusion kinetics. For this purpose, the Pourbaix diagram was examined. Ni and Ti ions in the sulfate-containing aqueous solution could only precipitate above pH 10. Therefore, coprecipitation was carried out at pH 11.5 to precipitate both metals. Moreover, to discuss the effect of chelating agent 2 different experiments were designed. **Table 4.1** shows the sample coding and the experimental details.

Table 4.1: Samples code and experimental details of coprecipitated powders

Sample code	Precipitation agent	Chelating agent	pH value	Temp	RPM
CS11	NaOH	-	11.5	RT	600
CSA11	NaOH	NH ₄ OH	11.5	RT	600

The precipitation was carried out at room temperature, while the solution was magnetically stirred at 600 rpm continuously during precipitation. Once the pH was stabilized, the mixture was left for ageing for 24 hours, then the precipitate was filtered **Figure 4.1**.

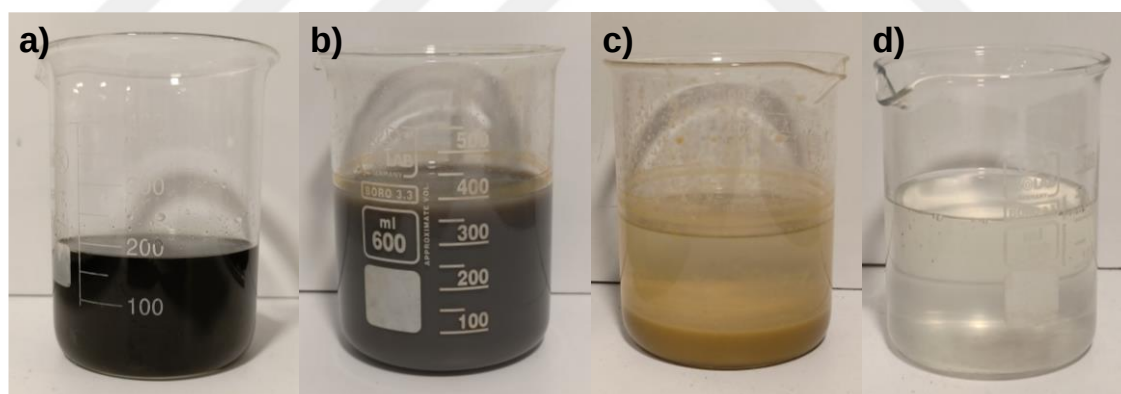


Figure 4.1: Appearance of solution at different stages of co-precipitation a) Leachate solution b) pH adjustment at 10 c) After 24 h of phase separation d) Filtered clear solution showing the success of precipitation.

4.1.2.2. Selective precipitation

Nickel and titanium were selectively precipitated at pH 1 and 10 by using 14 M NaOH, based on the information given in the Pourbaix diagram [116]. And it was later proved by XRF results **Table 4.3** that both metals were successfully recovered from the leachate independently as shown in **Figure 4.2**.

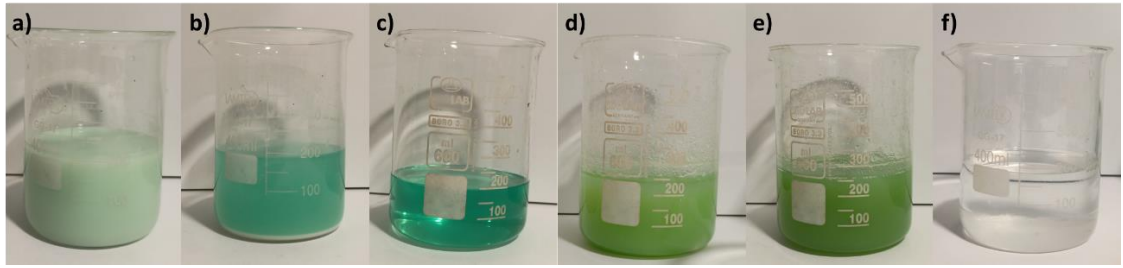


Figure 4.2: Appearance of solution during different stages of selective precipitation a) pH adjustment at 1 b) After 24h of phase separation c) Filtered solution after precipitation at pH1 d) pH adjustment at pH10 e) After 24h of phase separation f) Filtered clear solution showing the success of precipitation.

Once the selective precipitation was realized, to study the effect of composite composition, by using HEB the composites were fabricated by mixing these selectively precipitated powders at two different weight ratios (1:3 and 1:6 titanium oxide: nickel oxide) **Table 4.2.**

Table 4.2: Sample coding and the experimental details of selective precipitated and the composite powders

Sample code	NiO	TiO ₂	Time	RPM	Filling Ratio%	BPR
S1	-	Only	-	600	-	-
S10	Only	-	-	600	-	-
N3T1	3 wt. fraction	1 wt. fraction	2 h	300	60%	20:1
N6T1	6 wt. fraction	1 wt. fraction	2 h	300	60%	20:1

4.1.3. Structural, morphological, and compositional analysis

XRD was performed the co-precipitated (CS11 and CSA11), selectively fabricated (S1 and S10) and composite powders (N3T1 and N6T1) to study their structural properties.

Figure 4.3 (a) demonstrated that XRD pattern of co-precipitated powders (CS11 and CSA11) were very similar. Addition of chelating agent increased nanosized particle formation as the bump noted at $2\theta = 36^\circ$, 44° , and 63.5° became widen. On the other hand, in the absence of the chelating agent sulfur peaks became more prevalent because of the fact that the NaOH is a strong base, and it reacted with sulphate ions to resulted in sulfur based species [130]. The peaks appeared at the vales were co-residing with NiO

and nickel titanate. But because of the coprecipitation and post formation heat treatment, it was more probable that the peaks at $2\theta = 36^\circ$, 44° , and 63.5° were assigned to nickel titanate formation rather than NiO. Then in order to remove peaks related to sulfur in CS11, an improvement in the washing procedure is applied: washing at 95°C with 1/10 solid/liquid ratio for couple of hours repeating it 3 times. **Figure 4.3 (a)** showed that the peaks of S disappeared as expected, and the XRD of CS11 revealed nanocrystalline structure formation as CSA11 did.

Moreover, **Figure 4.3 (b)** showed that the S1 consist of only titanium dioxide (anatase phase), and the sample S10 selectively precipitate nickel oxide. Some amount of sulfur was also detected in the powder as the leachate solution contained sulfate ions (and its reaction with NaOH). The XRD result indicated that selective metal recovery was realized and NiO, and TiO_2 powders had fabricated successfully. Then XRD revealed that upon ball milling of these two powders at different ratios, a partial phase transformation was noted in N3T1 and N6T1 samples. Some peaks of sulfur ($2\theta = 22.6^\circ$, 23.6° , 46.2°) got vanished and new peaks related to sulfur (at $2\theta = 28.3^\circ$, 29.4°) appeared in both composite powders. This reflected that high energy ball milling assisted partial phase transformation of sulfur peaks, in fabricated composite powder. Here the broad peaks appearing at $2\theta = 36^\circ$, 44° , and 63.5° were overlapping with nickel oxide of S10 and nickel titanate. But it was thought that these peaks ($2\theta = 36^\circ$, 44° , and 63.5°) belong to nickel oxide and high energy balling milling just promoted the through mixing of the two constituents.

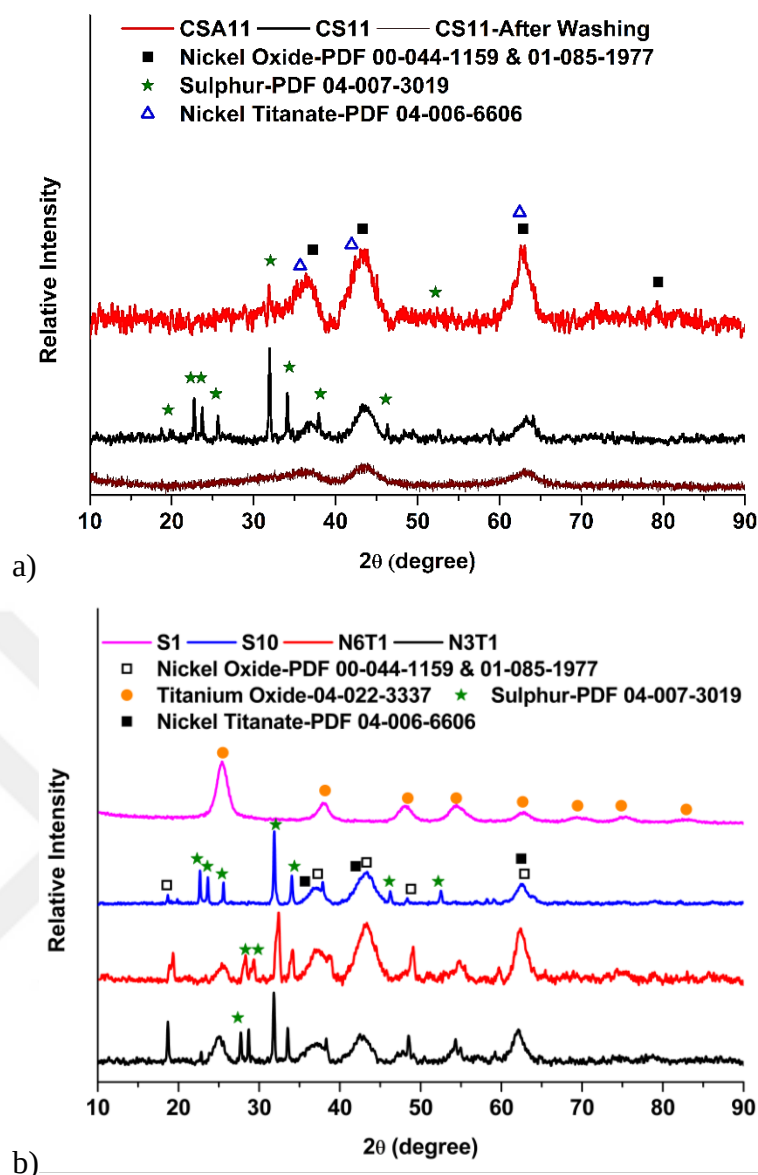


Figure 4.3: XRD pattern of powder fabricated from NiTi wire leachate solution a) CS11 & CSA11, b) S1, S10, N3T1 & N6T1

To attain morphological insight of the fabricated powders, SEM was carried out and their corresponding images were provided in **Figure 4.4** (a-f). All the fabricated samples are comprised of irregular shaped nano sized particles. Then, **Figure 4.4** (a-b) demonstrated that by using chelating agent the particles tended to precipitate with small primary particles, but these particles got agglomerated to form bigger dense particles. Hwang et al. [131] found in their study that upon precipitation, NH_4OH promoted precipitates with a smaller particle size as compared to precipitates formed with NaOH . On the other hand, scientists [132] have concluded that NaOH tended to promote multi-nuclei precipitation- whilst the addition of NH_4OH promoted slower growth leading to the formation of spherical shaped particles leading to big denser particles. Further, Malanova et al. [133]

highlighted that the precipitation rate with NaOH was much higher than that of the precipitation rate of NH_4OH . Crystal nucleation then growth occurred very rapidly in the case of NaOH. But in the case of NH_4OH , crystal nucleation and growth were slower process. Additionally, it is mentioned in literature that different alkaline reagents precipitate different phase compositions due to their different precipitation rate, this reflected that all precipitating agents didn't favor the precipitation of different species equally. This could be because of the extent of their nature, which means that NaOH is a strong base, its dissociation constant is 5.8 it completely dissociates completely in water. But NH_4OH is a weak base, its dissociation constant is 1.76×10^{-5} , and it dissociates partially and slowly [133].

Therefore, in sample CSA11 (co-precipitated by ammonium hydroxide & sodium hydroxide at pH 11.5) the small particles densely adhered to each other forming big dense agglomerates **Figure 4.4** (a). On the other hand, sample CS11 (co-precipitated by only sodium hydroxide at pH 11.5) had interconnected morphology and it did not show densely packed morphology, **Figure 4.4** (b). As mentioned by Yamashita et al. [132] higher molar solution of ammonium hydroxide resulted in dense bigger particles. Thus, upon the absence of NH_4OH , abrupt growth with more nucleation sites had occurred, resulting in less dense particle formation. By comparing **Figure 4.4** (a) & (b), it can be concluded that along with ammonium hydroxide the primary particles were small in size but they got densely adhered to each other to form much bigger secondary particles and with only NaOH the size of the agglomerates was smaller with less dense compaction, same results had been disclosed by S. Riaz et al. [134] and by this surface area increased which was beneficial to had as it directly affected the capacity delivered.

Likewise, SEM analysis of S1 and S10 **Figure 4.4** (d) & (e) respectively, demonstrated that powders were comprising of nano-sized, irregular-shaped particles which tended to agglomerate and form relatively bigger particles. And a large fluctuation in the range of size of particles could be observed, which was expected to lead weaker cycle performance. However, it was examined that after producing the composite of these two powders at two different weight compositions by milling, the particle size significantly got reduced to the size of their parent constituents **Figure 4.4** (f) & (g). This relatively smaller size was one of the key advantages to achieve higher electrochemical performance. **Figure 4.4** (g) depicted that in N6T1 sample, particles were more uniform in shape and comparatively much homogenized in size than N3T1 and the two

constituting powders. These two attributes of nano sized anode material were beneficial to had as they shorten the lithium diffusion path, provided greater number of sites for the reaction of lithium due to their high surface area, and hence enhanced contact interface of powder with electrolyte. So, the effect of milling can be conclusively observed that milling resulted in the reduction in the particle size.

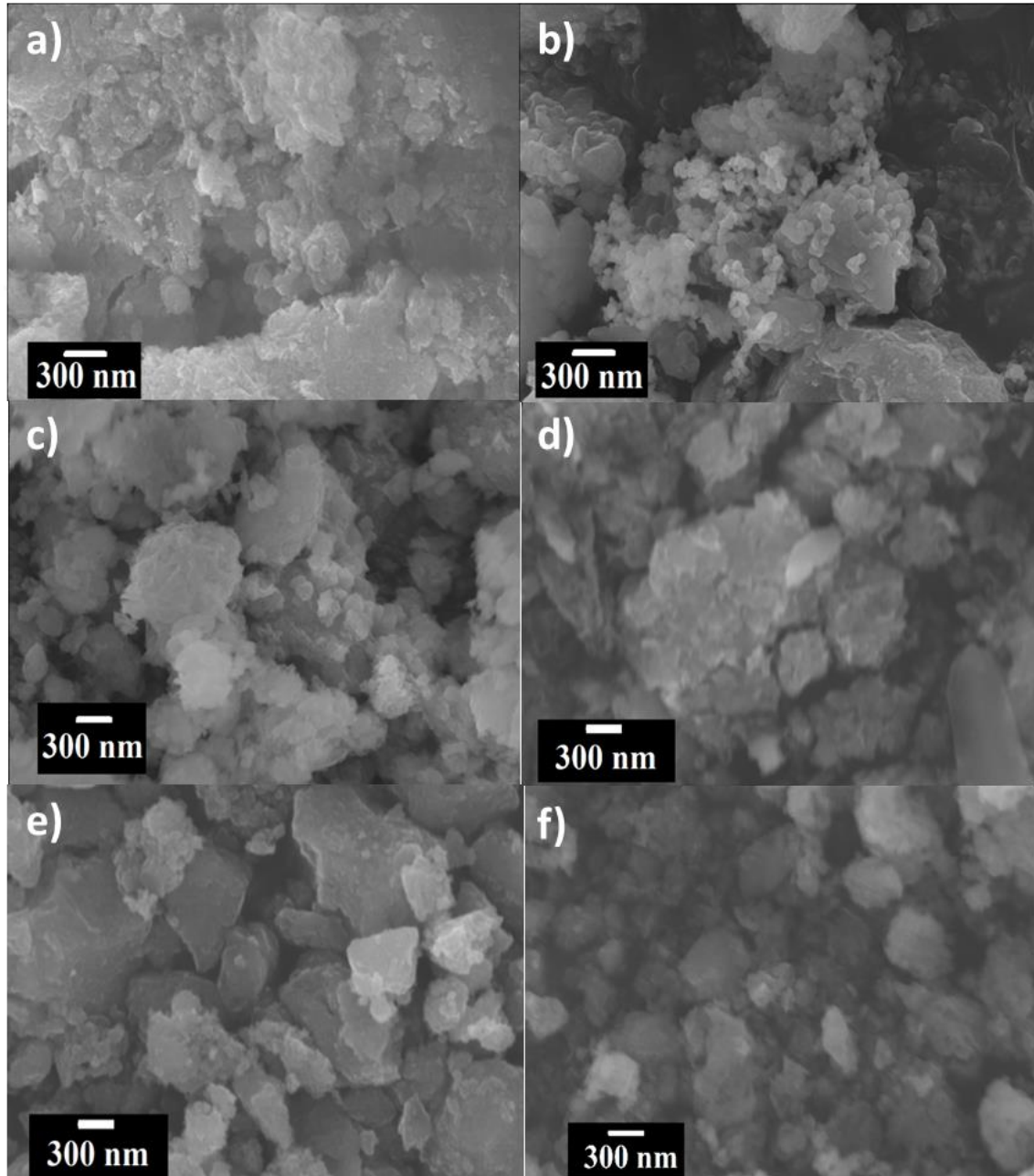


Figure 4.4: SEM images of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f)

The chemical composition of the fabricated powders was examined by XRF analysis, and the compositional results were disclosed in **Table 4.3**. It showed that the NiTi wire contained 49 % Ti and almost 47 % Ni as their major elements. Powders selectively precipitated at different pHs showed that the Ni and Ti recovery was successfully realized. Herein, its worthy to note that by using chelating agent the coprecipitation efficiency of Ni and Ti was also improved.

Table 4.3: Chemical composition of the powder obtained by XRF.

Powder	Ni	Ti	S	Fe	Cr	Mo	Zr	Mn
NiTi Wires	46.91	49.02	-	-	-	2.25	1.21	-
CS11	56.85	28.96	12.63	1.02	0.25	-	-	-
CSA11	51.98	33.56	8.58	0.90	1.98	0.02	-	0.16
S1	0.17	94.55	3.55	1.4	0.17	-	-	-
S10	84.76	0.5	12.2	1.28	0.36	-	-	-

4.1.4. Electrochemical analysis of powder from NiTi wires

Fabricated anodes were punched and CR2032 standard half-cells were assembled for their electrochemical assessment, between the cutoff voltages of 10 mV-3 V and current load of 50 mA g⁻¹. **Figure 4.5** (a-g) showed the capacity-cycle performance of the fabricated powders. The 1st discharge capacities, of the CSA11 and washed CS11 were found to be 279.29 mAhg⁻¹ and 933.8 mAhg⁻¹, respectively. An obvious irreversible capacity loss after 1st cycle was due to SEI formation. After the 50th cycle the capacities delivered by the samples were 138 mAhg⁻¹, and 313 mAhg⁻¹. The relatively better capacity of CS11 coprecipitated could be due to less dense particles found in SEM analysis but overall higher, less discharge capacity was due to the poor electronic conductivity of the metal oxide based powders.

For S1, S10, N3T1 and N6T1, 1st discharge capacities were: 281 mAhg⁻¹, 331 mAhg⁻¹, 389.9 mAhg⁻¹ and 517.9 mAhg⁻¹, respectively. Each sample exhibited considerable capacity loss as documented in the literature [135], [136]. After 50 cycles the capacities delivered by three electrodes were 147 mAhg⁻¹, 187.9 mAhg⁻¹, 180 mAhg⁻¹ and 363 mAhg⁻¹, respectively. Pure nickel oxide had high theoretical capacity (718 mAh g⁻¹) but caused by its low lithiation kinetics of conversion type reaction, poor ionic and electrical conductivity, and immense volumetric expansion, it could not achieve that value in LIBs

[137]. In contrast, titanium oxide had good retention of capacity with higher coulombic efficiency due to low volumetric expansion (<4%), and faster Li intercalation kinetics thanks to presence of feasible sites for reaction accompanied with better electric conductivity [137]–[139]. Therefore, to overcome the short comings of the pure metal oxide powders composite fabrication of these two powders was carried out and this proved to be a valuable effort as composite delivered higher capacity with enhanced capacity retention. This was because in the composite titanium oxide improved electronic conductivity, prevent aggregation of particle, and endorsed diffusion of Li^+ by effecting SEI layer formation [137]. In addition it improved structural stability by upholding volumetric change in nickel oxide which eventually enhanced electrochemical performance [139], [140]. When the performances of the two composite powders were compared, the superior performance of N6T1 was related to the chemical and the morphological properties.

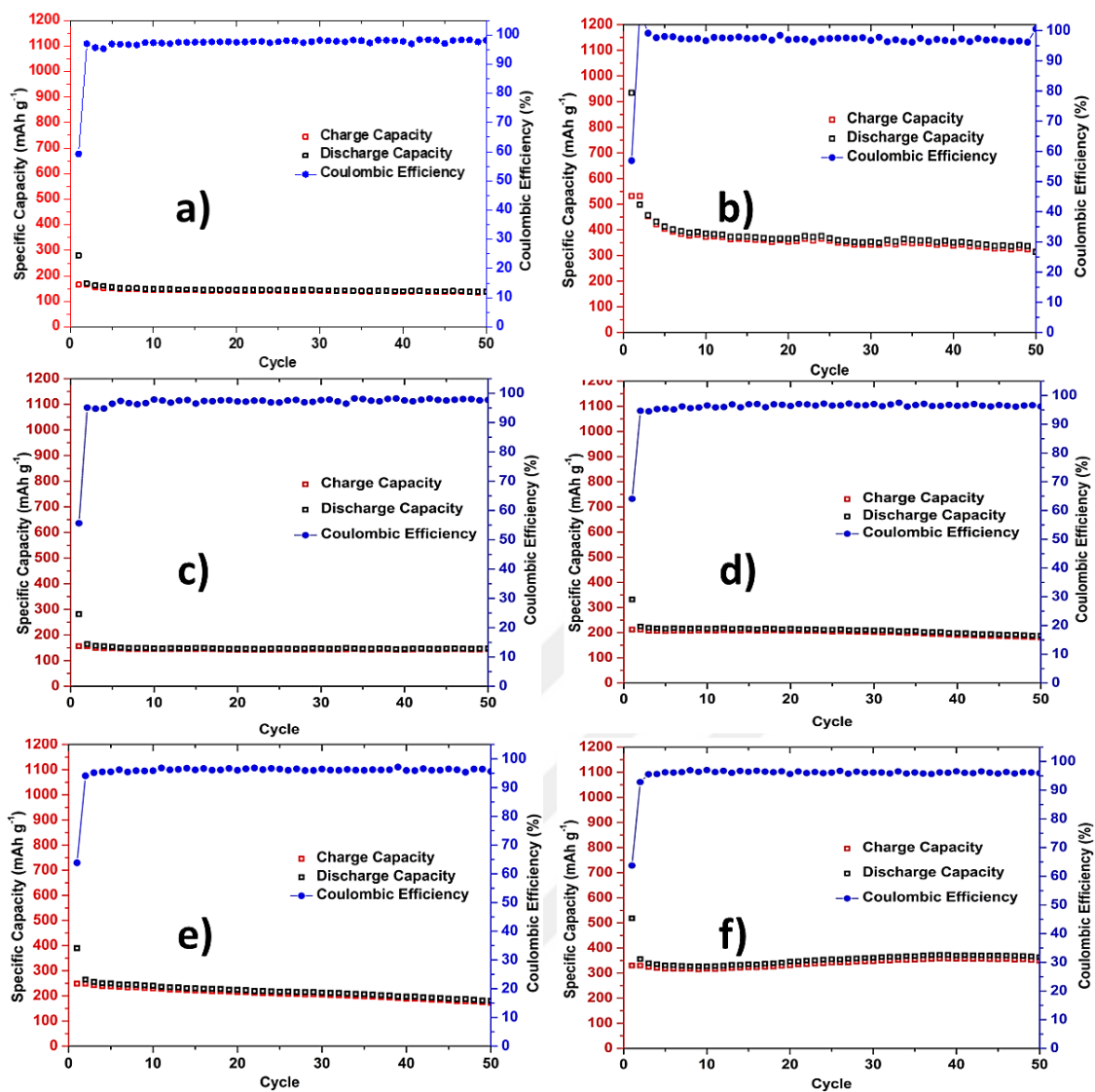


Figure 4.5: Capacity-cycle graphs of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f) N6T1

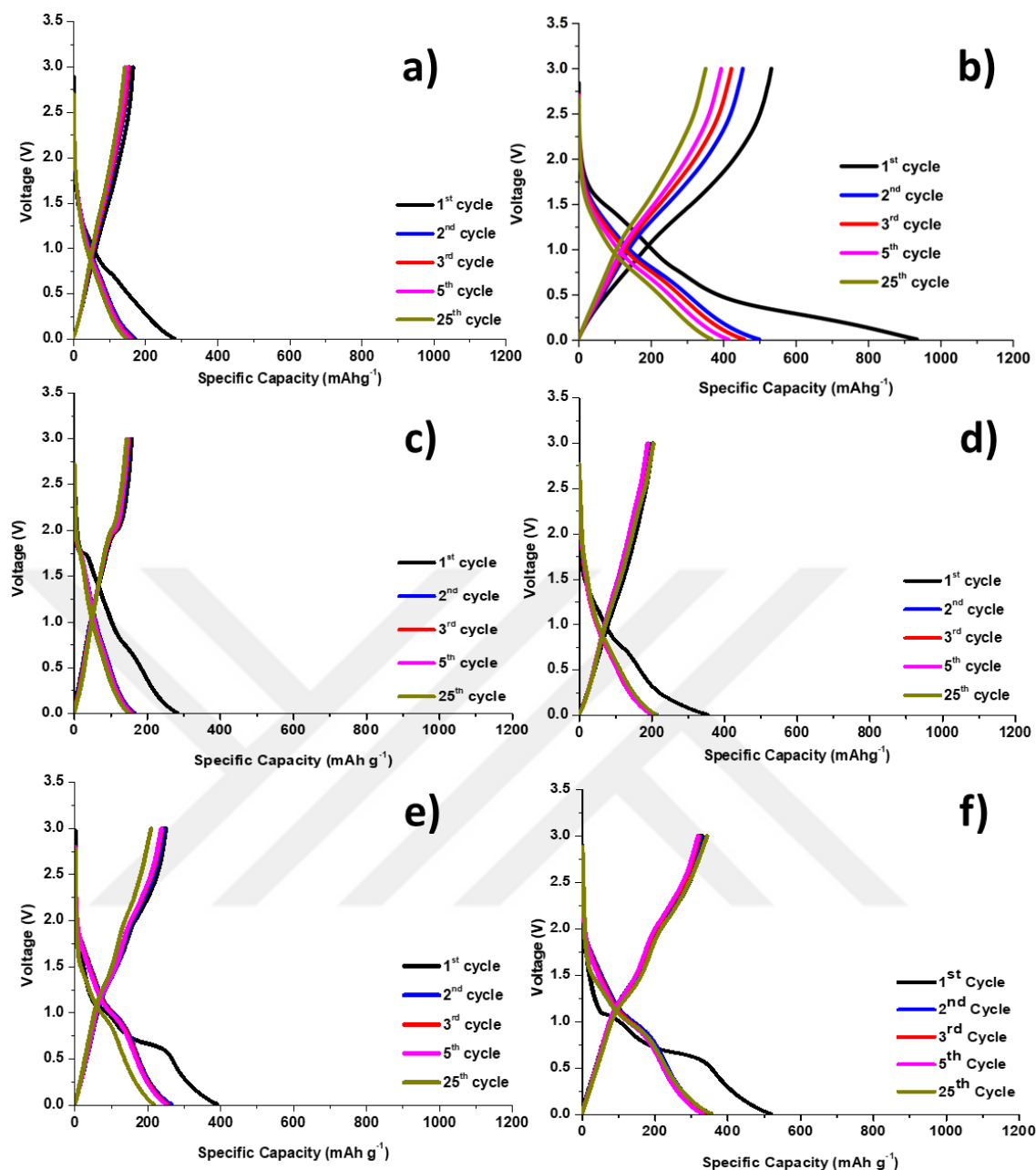


Figure 4.6: Voltage-capacity graphs of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f) N6T1

Figure 4.6 (a-f) summarized the voltage capacity profiles of the fabricated samples. In voltage-capacity curves of coprecipitated samples (a-b), a slight plateau appearing just above 0.5 V was assigned to irreversible SEI formation and reduction of the metal oxide present and in charging curves almost straighter curve without any significant plateau was observed. In titanium oxide rich powder (S1) two plateaus were observed at 1.75V on discharge curve and 2V in charge curves. The first peak represented the intercalation of Li^+ in tetrahedral site of TiO_2 and formation of octahedral Li_xTiO_2 . The second represented the deintercalation of Li^+ from octahedral sites of Li_xTiO_2 . The overall reversible reaction of lithium with TiO_2 is shown by equation (4.1) [141], however, there

existed a minute turn at around 0.75V disappearing in succeeding cycles. This bend could be ascribed to SEI formation [142]. For the nickel oxide-rich sample, a notable plateau was noted around 0.75V in its maiden discharge curve attributed to the conversion reaction of nickel oxide mentioned by equation (4.2), and SEI formation [136]. This plateau shifted to almost 1V in the following cycles due to polarization. Further, in the charge curve, two bends at 2.25V and 1.45V were due to reduction reaction of Li₂O with Ni and SEI decomposition [143]. These findings were consistent with the previously reported researches [136], [141]. By the scrutiny of voltage capacity curves of the two composites, it was found that nearly all plateaus which were noticed in the curves of pure metal oxide are also in the curves of composite powders, but the performance of nickel oxide powder was more dominant as its weight ratio was larger than that of TiO₂.



Figure 4.7 (a-f) exhibited the cyclic voltammogram of the powders. The first two graphs belong to CSA11 (a), CS11 (b). These samples displayed almost the same shape, peaks, and their positions due to the fact that they consist of the same phase (NiTiO₃) as found in the XRD. It can be seen that in the cathodic scan of these sample, a peak appeared at around 0.7V was due to SEI formation and reduction of nickel oxide following the reaction given by equation (4.2) [136][144], another small broad peak appeared at the voltage value of ~1.25V representing the lithium intercalation in TiO₂, following the reaction shown by equation (4.1), present in NiTiO₃ [144]. In an anodic scan a slight curve can be observed at ~1.4V representing the oxidation of nickel metal by reacting with lithium oxide, the reverse of the reaction given in equation (4.2) and reversal of reaction given by equation (4.1). These peaks got vanish due to the irreversible capacity loss. Here it is worth highlighting that although these were co precipitated powders, here nickel oxide based character was more dominant due to relatively higher amount of nickel oxide phase found in XRD and XRF. **Figure 4.7** (c) represent the CV result of titanium oxide rich powder S1. In its cathodic scan of a sharp peak at 1.75V appeared which showed the lithium insertion in tetra TiO₂ by the reaction given in equation 4.1, and due to formation of irreversible SEI, second peak in cathodic scan appeared at lower voltage value of around 0.75V, which disappeared in successive cycles. On anodic curve, just one abruptly

occurring peak at 2V was due to lithium extraction from Li_xTiO_2 [135], [141]. **Figure 4.7 (d)**, the CV curves of nickel oxide rich powder S10, the only cathodic trough forming at 0.7 V was the significance of SEI formation and nickel oxide by reacting with lithium by following the equation 4.2. This trough got shifted at 1V with relatively flat appearance because of polarity [136]. However, two humps were visible in anodic scan of the sample i.e., at 1.45V and 2.25V. The first bump was due to the electrolyte decomposition and the second bump showed the oxidation of nickel with lithium oxide [143]. The conclusions of cyclic voltammogram were consistent with the voltage capacity curves of the corresponding samples. In the same manner, the cyclic voltammogram of the composite powder samples (N3T1 and N6T1) **Figure 4.7 (e & f)** included all those characteristic peaks that were found in the CVs of titanium oxide rich and nickel oxide rich powder. But the nickel oxide character was more influential due to its relatively higher amount.

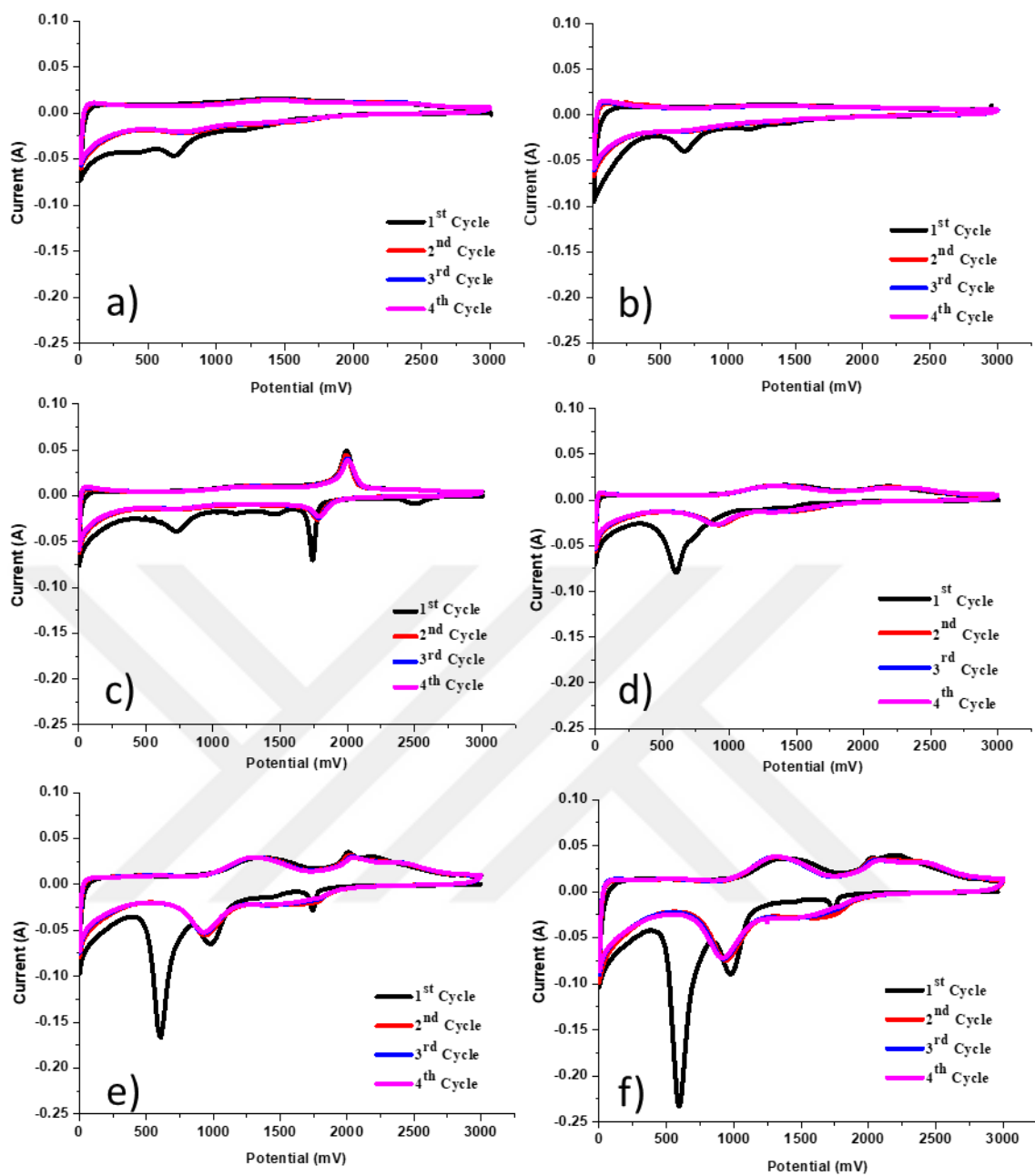


Figure 4.7: Cyclic voltammogram of a) CSA11 b) CS11 c) S1 d) S10 e) N3T1 f) N6T1

4.2. Fabrication and characterization of iron oxide based anodes from orthodontic braces.

In this section, composite powders had been fabricated by leaching stainless steel braces then hydrothermally treating them.

4.2.1. Leaching of braces

Rashed et al. [145] found in their study that sulfuric acid with molarity between 4-6 M was highly corrosive and dissolve max amount of stainless steel. Similar to current study, Gülcan et al. [146] performed the leaching of ferrochrome alloy using sulfuric acid and found the optimum leaching conditions in rotary vapor. Therefore, the leaching of stainless steel braces was carried out in reflux system and 100% efficiency was achieved by optimizing molarity of acid, temperature, solid to liquid ratio and time **Table 4.4**. The results showed that the parameters of the 5th experiment give the best efficiency.

Table 4.4: Leaching parameters optimization experiments

Experiment	Molarity (M)	S/L	Temperature (°C)	Time (h)	Efficiency (%)
1	2	1/30	80	4	69.1
2	2	1/50	80	4	85.5
3	2	1/100	80	4	92
4	4	1/30	80	4	89.3
5	4	1/50	80	4	100

4.2.2. Hydrothermal reaction

The pH of leachate was adjusted (using 14M NH₄OH) to 10, before the initiation of hydrothermal reaction, for the recovery of iron ion. The pH adjustment was crucial for the complete recovery of iron ions because addition of NH₄OH or any other base, facilitates the supply of (-OH) ions. These hydroxyl ions reacted with iron during hydrothermal reaction to form iron oxide as reported in literature [147]. Moreover, pourbaix diagram showed that higher pH (10 or above) not only precipitated iron, but also

other iron group metal ions e.g., both Cr^{+3} and Ni^{+2} get precipitated at pH 5 or more [148], [149]. Furthermore, higher pH also promoted the mesoporous round/spherical structural morphology [150].

Then in the subsequent hydrothermal reaction, hydroxides then got together to form nanoparticles. In this stage, the oxidation of iron ions took place by reaction between iron ions and hydroxide ions. The hydroxide ions were generated either by the ionization of water (at high temperature and pressure) or because of NH_4OH . As a result of the reaction iron hydroxide ($\text{Fe}(\text{OH})_3$) forms equation 4.3 [150]–[152].



Then oxidation of the formed iron hydroxide took place, which converted $\text{Fe}(\text{OH})_3$ into iron oxide Fe_2O_3 . The oxidation of iron hydroxide incorporated the removal of water molecules and the relocation of iron and oxygen atoms. The reaction is given by equations 4.4 and 4.5 [150]–[152].



To adjust the parameters that had to produce 150 nanometer particles size an orthogonal and non-orthogonal experimental system had been studied independently.

4.2.3. Factorial design (FD)

Used stainless steel braces were first washed and then leached out by using sulfuric acid. Oxide was fabricated by pH adjustment at 10 by using 14 M NaOH. Followed by hydrothermal reaction at different duration and temperatures **Table 4.5**. Hydrothermal reaction parameters strongly influenced the particle size of the powder. And the capacity delivered by the material depends on the particle size. So, it was necessary to optimize the reaction parameters to achieve the critical particle size (~150 nm) which will eventually deliver good cyclability.

So far in literature, many studies had been reported to minimize the particle size in hydrothermal methods. They had selected reaction time, reaction temperature, internal pressure, or filling ratio as parameters because as described by many researchers that

these were the most important factor in hydrothermal reaction to control the morphology and size of forming precipitates [153]–[156].

Here in the significance and the influence of the hydrothermal process parameters (time, temperature, and filling ratio), on the particle size of the powder formed, had been studied and the conditions had been optimized by factorial design. Three parameters with two levels of each, had been chosen and the number of experiments had been calculated according to the formula given earlier in the literature section. According to which in total $2^3 = 8$ experiments had been required to be carried out. The results of the experimental design can be seen in **Table 4.5**. By using Minitab, main effect plots had been constructed given in **Figure 4.8**. It can be clearly seen that temperature and filling ratio have pronounced effect on the particle size with temperature. **Figure 4.8** (b) represented the two way interaction of two factors on the particle size. Upon observing the plots, it can be concluded there was an expected effect of factors on the particle size. If we take A (Temp)* B (Time) interaction, we can see that at higher time or higher temperature, particle size got increased. But when both were at a higher level the particle size got increased more dramatically. Because when the temperature rose, the kinetic energy of the molecules increased, leading to more frequent and energetic collisions. Moreover, at higher temperatures, not only does the rate of nucleation got increased, resulting in a greater number of particles formation, but also the thermal motion of the molecules was more rapid, leading to faster diffusion rates, hence particle growth. At elevated temperatures, the kinetic energy of the particle and their collision with each other got enhanced. As a result, the odds of particle colliding, sticking together, and forming larger aggregates or agglomerates, also increased [156]. And when this phenomenon occurred for longer time, there was an obvious particle size increment. In A (Temp)* C (f. ratio) two way interaction, the increase in filling ratio promoted smaller particle reason due to the fact that at high filling ratio the pressure generated during hydrothermal reaction was very high that inhibit the further growth of particles [155]. For B (Time)* C (F ratio) two way interaction, high filling ratio lead to lower particle size whilst longer duration resulted in bigger particle size. The coded regression equation of the model generated through the software is given below:

$$\begin{aligned} \text{Particle Size} = & 274.52 - 78.03 \text{ A(Temp)}_{-150} + 78.03 \text{ A(Temp)}_{+200} \\ & - 37.30 \text{ B(time)}_{-12} + 37.30 \text{ B(time)}_{+24} \\ & + 56.22 \text{ C(f ratio)}_{-0.5} - 56.22 \text{ C(f ratio)}_{+1.0} \end{aligned}$$

+ 34.80 A(Temp)*B(time)_150 12- 34.80 A(Temp)*B(time)_150
 24 - 34.80 A(Temp)*B(time)_200
 12+ 34.80 A(Temp)*B(time)_200 24
 - 30.73 A(Temp)*C(f ratio)_150 0.5
 + 30.73 A(Temp)*C(f ratio)_150 1.0
 + 30.73 A(Temp)*C(f ratio)_200
 0.5- 30.73 A(Temp)*C(f ratio)_200 1.0
 + 17.05 B(time)*C(f ratio)_12 0.5- 17.05 B(time)*C(f ratio)_12
 1.0 - 17.05 B(time)*C(f ratio)_24 0.5
 + 17.05 B(time)*C(f ratio)_24 1.0

Table 4.5: Factorial experimental design and results

No. of Experiment	A	B	C	Particle Size (nm)
1	150	12	0.5	230
2	150	12	1	158
3	150	24	0.5	214
4	150	24	1	184
5	200	12	0.5	391
6	200	12	1	169.9
7	200	24	0.5	488
8	200	24	1	361.3

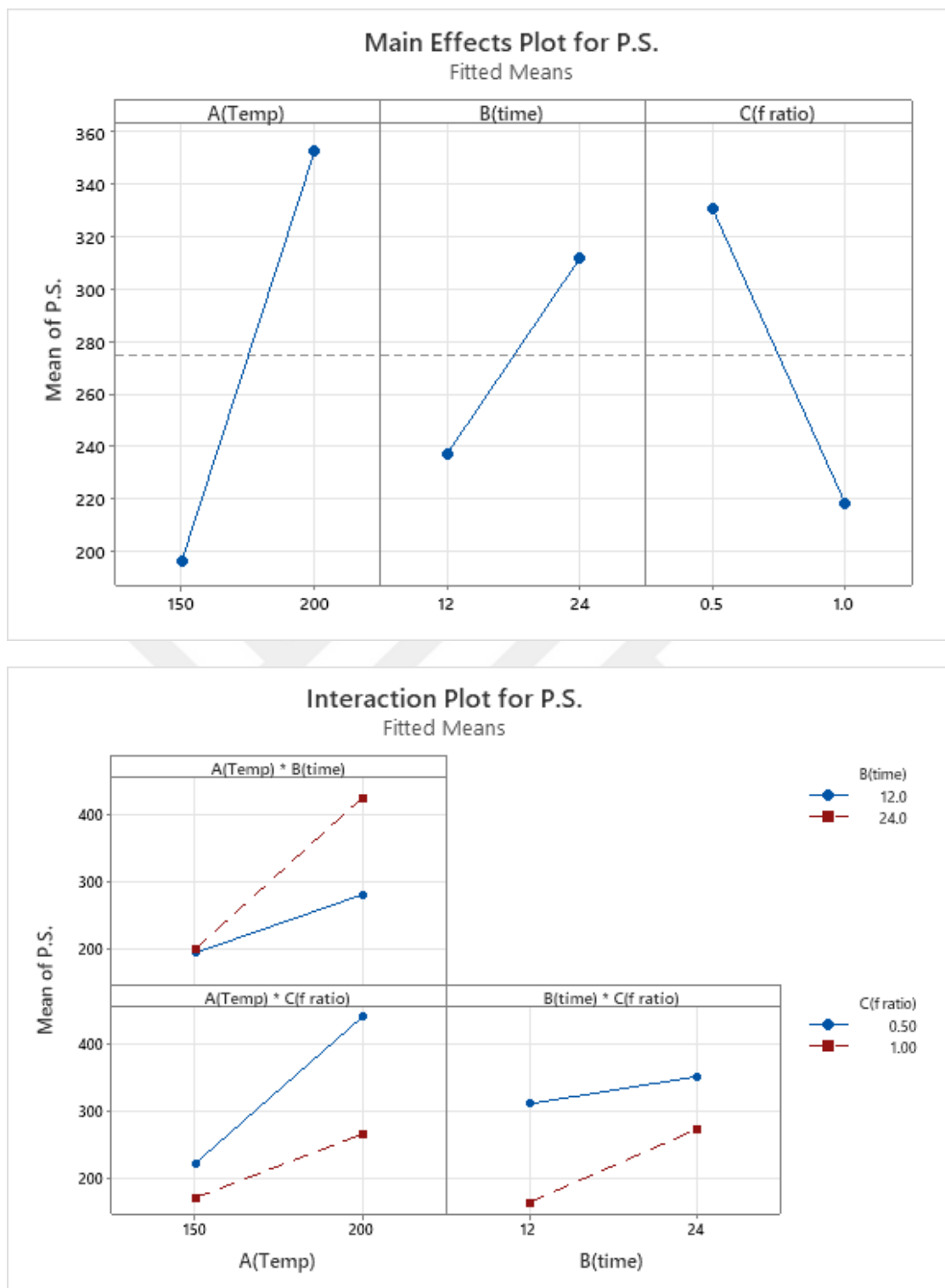


Figure 4.8: a) Main effect plots from factorial design, b) the interaction plots

It can be seen in **Table 4.6** that the R-sqr and R-sqr (adjusted) values were close to each other and near to 100% this showed that the prepared regression model was well fitted with the numerical data of the particle size and goodness of fit for this model in the current experimental values was high.

Table 4.6: Summary of factorial design

S	R-sq	R-sq (adj)	R-sq (pred)
18.5262	99.67 %	97.71 %	79.09%

4.2.4. ANOVA analysis

Using MINITAB software v.20, ANOVA analysis had been performed to study the individual as well as combined interaction of the parameters on to the particle size and to investigate the most effecting parameter of the hydrothermal on to particle size of the precipitates, here considering the dealing with waste and the attempt to recover the values from it by precipitation, therefore the significance level of 0.1 (alpha, $p < 0.1$) was taken, which means that willingness of accepting was 10% error in the system and results were displayed in **Table 4.7**.

Table 4.7: ANOVA calculations for particle size of powder

Source	DF	Adj SS	Adj MS	F-Value	P-Value
A (Temp)	1	48703	48703.2	-	-
B (time)	1	11130	11130.3	-	-
C (f ratio)	1	25290	25290.0	-	-
2-Way Interactions					
A (Temp)*B (time)	1	9688	9688.3	-	-
A (Temp)*C (f ratio)	1	7552	7552.2	-	-
B(time)*C (f ratio)	1	2326	2325.6	-	-
3-Way Interactions					
A (Temp)*B (time)*C (f ratio)	1	343	343.2	-	-
Error	0	-	-		
Total	7	105033			

The calculation revealed that the 3-way interaction of the parameters had the less effectiveness on to the final product as its sum of square value was too low. Therefore, this was taken as error and ANOVA calculation had been revised and given below in **Table 4.8**.

Table 4.8: Revised ANOVA calculations for particle size of powder

Source	DF	Adj SS	Adj MS	F-Value	P-Value
A (Temp)	1	48703	48703.2	141.90	0.053
B (time)	1	11130	11130.3	32.43	0.111
C (f ratio)	1	25290	25290.0	73.68	0.074
2-Way Interactions					
A (Temp)*B (time)	1	9688	9688.3	28.23	0.118
A (Temp)*C (f ratio)	1	7552	7552.2	22.00	0.134
B (time)*C (f ratio)	1	2326	2325.6	6.78	0.233
Error	1	343	343.2	-	-
Total	7	105033			

According to the calculation the most effective parameter, based on the F-value, was the temperature as it had the biggest F-value, after that filling ratio was the 2nd most effective parameter and temperature was the least effective parameter among these three. Likewise, the two way interaction of parameters also had considerable effect on the particle size. It was further verified by ANOVA analysis that previously described interaction of parameters (single and two way) satisfactorily explained the ongoing phenomenon.

In orthogonal design, experiments are positioned in different parts of the cube. The factorial design (FD) is like a cube with the three axes corresponding to the three factors and the corner of cubs are the combination of the extreme conditions of the factors **Figure 4.9**. While changing any parameter the point (combination of level of factors) moves/get shift in straight line mostly either on edges or faces of the cubes. Based on the literature survey, it can be considered that the entire set of experimental conditions /combinations within the FD cube refers to the volume of FD cube. This volume of cube increases exponentially by the increase in number of factors or/and their levels.

Although, the large volume of FD cube allowed for a comprehensive examination of all possible factor combinations, providing a complete understanding of how different factors interact and their impact on output. High number of experiments requirement causing too much time and money consumption limit its practical use

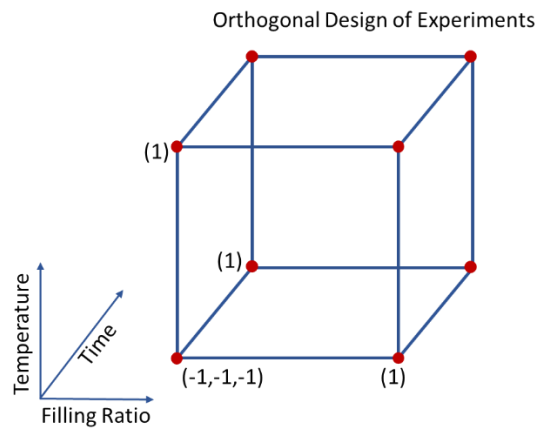


Figure 4.9: Factorial design cube with three factors and two levels

4.2.5. Fuzzy Logic Modeling

Fuzzy logic involved the subdivision of important factors affecting the process (called input) and possible outcome (output), into linguistic fuzzy sets (e.g., low, medium, high). Then, a logical relation of each subdivision of input variables, with subdivision of output variable was developed. This was one of the biggest reasons to use fuzzy logic, as factorial design being an orthogonal array system and only enables to study the effect of parameters on the corner of the cubes (or at two extreme values) but fuzzy logic enabled us to create and study the effect of intermediate value.

There are two famous types of fuzzy system Mamdani and Sugeno system. As Mamdani fuzzy system was more appropriate to apply on practical experimental work, in the optimization of hydrothermal parameters to fabricate particle size around 150 nm, Mamdani system was utilized. For the application of fuzzy logic system, the steps and procedure, described in literature section, was applied. The steps followed are mentioned below:

- i. Identification of input(s) and output(s) variable- first of all the input and output variables were decided. The aim was to optimize hydrothermal reaction parameters so the important parameters are time, temperature, and filling ratio. Therefore, these three parameters were taken as input parameters and the objective was to reduce the particle size that's why it was taken as output.

- ii. Fuzzification- Then these selected input and output variables were fuzzified into fuzzy subgroups. Linguistic fuzzification was done and numerical range of values were assigned these fuzzy sets and their values were given in **Table 3.4**.
- iii. Development of fuzzy logic rule base- then a rule base was developed using IF...THEN and AND operations to link the input fuzzy set with output fuzzy sets. As there are three inputs and each input had three fuzzy set therefore total rules were $3 \times 3 \times 3 = 27$. These 27 rules are shown in **Table 4.9**.

These were 27 rules or in other words 27 number of possible combinations of input variables which may affect the results in terms of output. Upon analysis it was found that each of those 8 experiments triggered any of the above mentioned rules. The data and results obtained from the 8 experiments of 2^3 factorial design was fitted into 27 rules shown in **Table 4.10**.

Table 4.9: Fuzzy logic rule base.

	Time		Temperature		Filling Ratio
Rule 1	Less	AND	Low	AND	Small
Rule 2	Intermediate		Low		Small
Rule 3	More		Low		Small
Rule 4	Less		Middle		Small
Rule 5	Intermediate		Middle		Small
Rule 6	More		Middle		Small
Rule 7	Less		High		Small
Rule 8	Intermediate		High		Small
Rule 9	More		High		Small
Rule 10	Less		Low		Moderate
Rule 11	Intermediate		Low		Moderate
Rule 12	More		Low		Moderate
Rule 13	Less		Middle		Moderate
Rule 14	Intermediate		Middle		Moderate
Rule 15	More		Middle		Moderate
Rule 16	Less		High		Moderate
Rule 17	Intermediate		High		Moderate
Rule 18	More		High		Moderate
Rule 19	Less		Low		Big
Rule 20	Intermediate		Low		Big
Rule 21	More		Low		Big
Rule 22	Less		Middle		Big
Rule 23	Intermediate		Middle		Big
Rule 24	More		Middle		Big
Rule 25	Less		High		Big
Rule 26	Intermediate		High		Big

Rule 27	More		High		Big
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- iv. Fuzzy inference system- here by using MATLAB fuzzy logic tool, Mamdani fuzzy inference system was used and above mentioned 27 rules were fed into the software **Figure 4.10**.
- v. Fuzzy result- after feeding the 27 rules then their results were realized. Parameters of the 8 experiments were inserted in the model trained with 27 rules and outputs were noted.
- vi. Defuzzification- then one value was obtained by centroid based defuzzification of the output, through software.

Table 4.10: Results of 8 experimental data fitted in 27 fuzzy rules.

		Time		Temperature		Filling Ratio		Particle Size
Rule 1	IF	Less	AND	Low	AND	Small	THEN	Average
Rule 2		Intermediate		Low		Small		Average
Rule 3		More		Low		Small		Average
Rule 4		Less		Middle		Small		Corse
Rule 5		Intermediate		Middle		Small		Corse
Rule 6		More		Middle		Small		Corse
Rule 7		Less		High		Small		Corse
Rule 8		Intermediate		High		Small		Corse
Rule 9		More		High		Small		Corse
Rule 10		Less		Low		Moderate		Average
Rule 11		Intermediate		Low		Moderate		Average
Rule 12		More		Low		Moderate		Average
Rule 13		Less		Middle		Moderate		Corse
Rule 14		Intermediate		Middle		Moderate		Corse
Rule 15		More		Middle		Moderate		Corse
Rule 16		Less		High		Moderate		Corse
Rule 17		Intermediate		High		Moderate		Corse
Rule 18		More		High		Moderate		Corse
Rule 19		Less		Low		Big		Fine
Rule 20		Intermediate		Low		Big		Fine
Rule 21		More		Low		Big		Fine
Rule 22		Less		Middle		Big		Fine
Rule 23		Intermediate		Middle		Big		Corse
Rule 24		More		Middle		Big		Corse
Rule 25		Less		High		Big		Fine
Rule 26		Intermediate		High		Big		Corse
Rule 27		More		High		Big		Corse

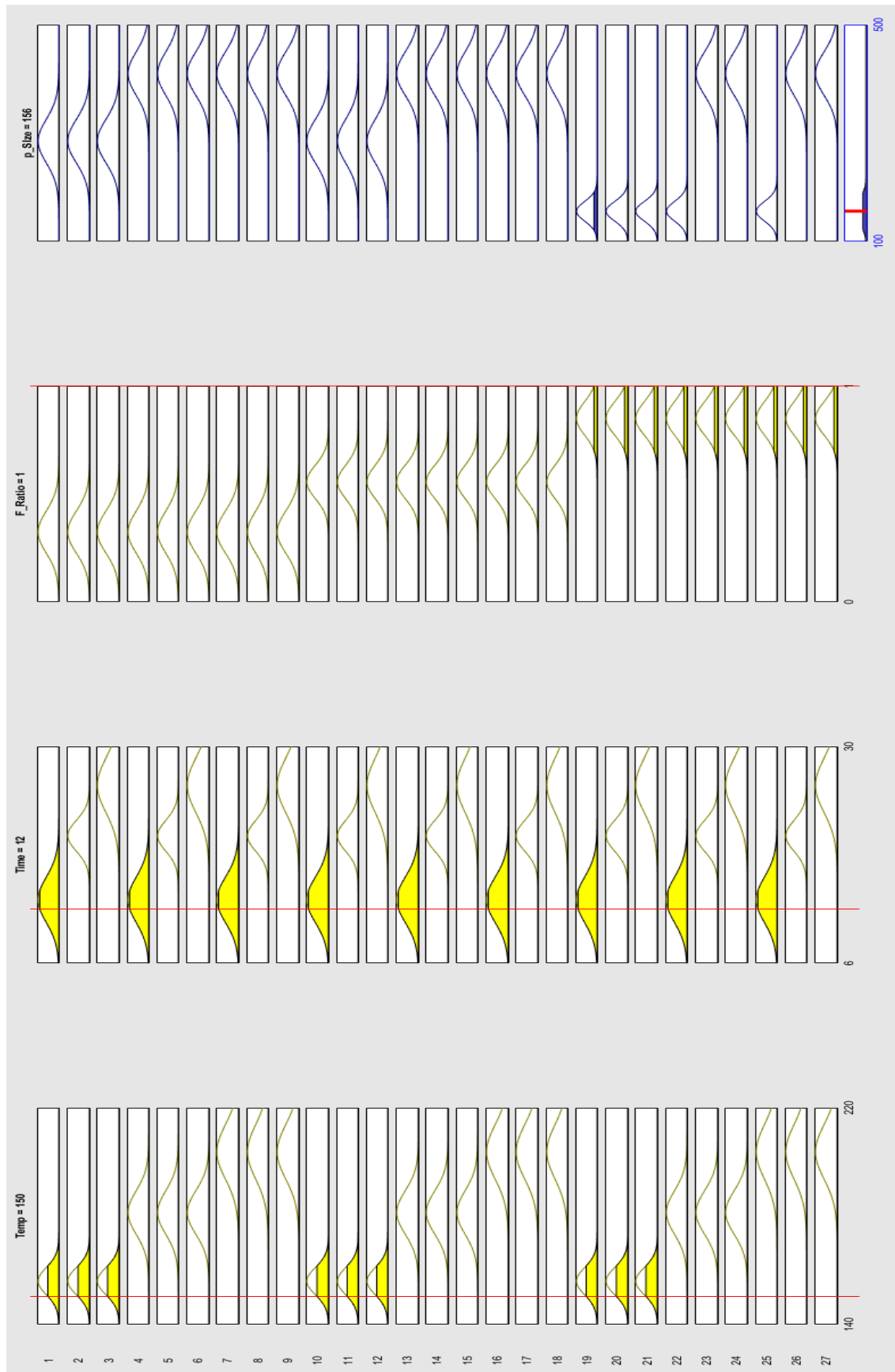


Figure 4.10: Evaluation of 27 fuzzy rule base in MATLAB

4.2.5.1. Validation of fuzzy logic model

The devised fuzzy logic model was validated by calculating the percentage relative error (PRE) between the value predicted by model and experimental value using the following formula:

$$\text{Percentage Relative Error (PRE)} = \frac{(V_E - V_C)}{\max(V_E, V_C)} \times 100 \quad (4.6)$$

Here V_E is experimental particle size value and V_C is calculated particle size value through fuzzy logic model. The error percentage of the model was found to be -2.48% which is well within the engineering limit of $\pm 5\%$. So, the model is well designed and acceptable. The following **Table 4.11** shows the all the experimental values, calculated values, and error calculation.

Table 4.11: Percentage relative error calculation

	Temperature (°C)	Time (h)	Filling Ratio	Experimental Particle Size (nm)	Calculated Particle Size (nm)	PRE (%)
Exp. 1	150	12	0.5	230	285	-19.2982
Exp. 2	150	12	1	158	156	1.26582
Exp. 3	150	24	0.5	214	285	-24.9123
Exp. 4	150	24	1	184	158	14.1304
Exp. 5	200	12	0.5	391	409	-4.40098
Exp. 6	200	12	1	169.9	156	8.18128
Exp. 7	200	24	0.5	488	409	16.1885
Exp. 8	200	24	1	361.3	406	-11.0099
Average percentage relative error =						-2.48

4.2.5.2. Validation through particle size

By using fuzzy logic model the optimized parameters, giving minimum particles size, indicated by the model were temperature 150°C, time 12 hours and filling ratio 1. For the confirmation and validation of these optimized parameters, three experiments were conducted for the verification, and the particle size of these experiments were measured and found to be 145.7 nm, 146 nm, and 169 nm as given in **Figure 4.11**.

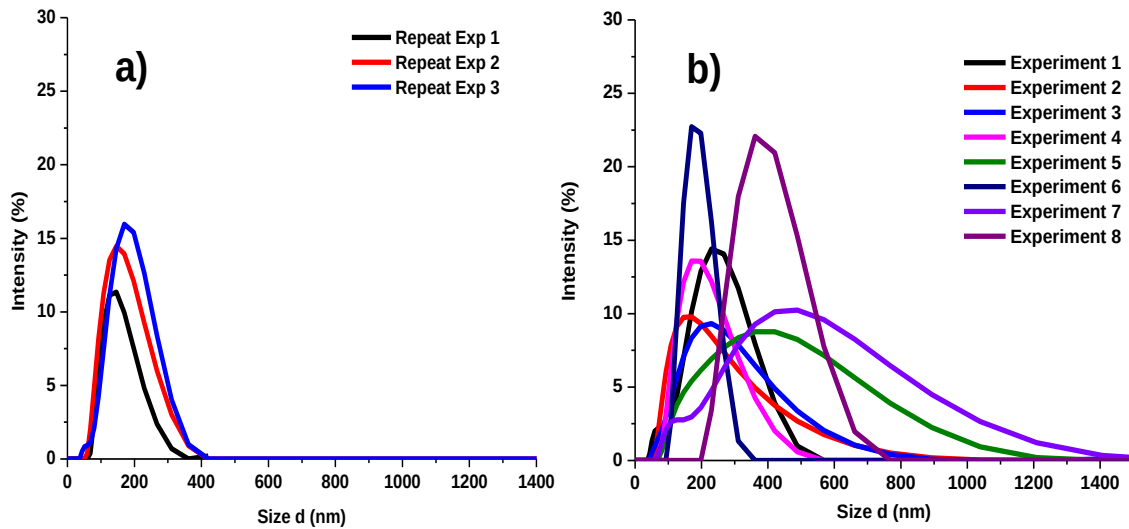


Figure 4.11: Particle size of a) 3 Repeated experiments & b) 8 experiments of 2^3 factorial design (FD)

The smallest particle size predicted by the model was 156 nm. However, the average of the 3 experiments is 153.8 nm which was much closer to the 156 nm predicted by the model with percentage relative (PRE) of -1.9 %, the value of PRE was well in the range of -2.48% of value for entire model.

This study proved that fuzzy logic was successfully applied for the tuning of the hydrothermal parameters for particle size refinement. And the set of levels suggested by fuzzy logic modeling resulted in almost the required or targeted particle size of anode material.

4.2.6. Structural and compositional analysis of the iron oxide rich powder

The chemical composition of the fabricated powder after the heat treatment had been examined by XRF analysis, and the compositional results showed that the material had been made of Fe, Cr, Ni as expected since the braces were 304L. These results show that pH adjustment was accurate, and the fabrication of composite oxide was successful.

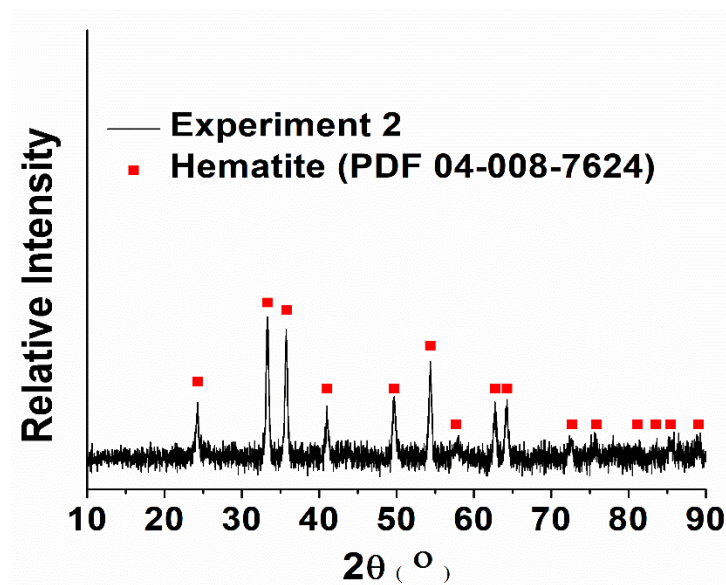


Figure 4.12: XRD pattern of samples fabricated by optimized condition from leachate of SS braces.

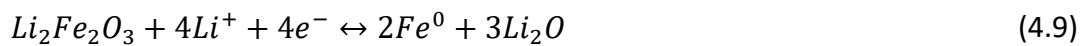
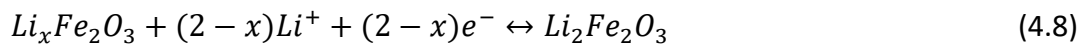
The obtained precipitates were heat treated at 730°C for 5 h to ensure the conversion of hydroxide (if any) into oxide. **Figure 4.12** shows the XRD pattern of the powder fabricated at the optimized hydrothermal conditions. It showed that the powder contained hematite as the only phase as all the peaks were the characteristic peaks of hematite. So, Cr and Ni were considered to form solid solution as they have similar structure as of iron. In the study of Janin et al [157] they disclosed that at pH above 10, iron and chromium got precipitated together from a leachate, along with nickel also got precipitated and the fact that Fe and Cr have similar ionic radii (Fe^{+3} 0.67 Å; Cr^{+3} 0.64 Å), after the calcination of this precipitate a tendency to form a solid solution of iron oxide at any concentration level due to the same crystal structure [158] was increased. Therefore, although XRF revealed that high amount of Cr and Ni existence along with Fe in the powder, no further or additional peak related to chromium/nickel oxide was observed in XRD analysis.

Such a solid solution was expected to perform better electrochemically because solid solution imparted the interference crystals defects and imperfections that might lead to contribution in lithium reaction sites and shortened its diffusion pathway. Moreover, solid solution formation also enhanced structural stability. Pure oxide experienced immense volumetric shift while charging-discharging cycle, but solid solution generated internal stresses in the structure that helped to alleviate the volumetric change without any compromise in structural integrity [157]. To prove the reliability of the experimental

setup and the consistency of the data, the same procedure had been repeated 3 times. All powders revealed the same chemical, structural, and morphological properties.

4.2.7. Electrochemical performances of the iron oxide rich anode vs Li

Fabricated anodes were punched and CR2032 standard half-cells were assembled for their electrochemical assessment, between the cutoff voltages of 10 mV-3 V and current load of 50 mA g⁻¹. **Figure 4.13** (a-c) showed the electrochemical performance of the iron oxide sample. The voltage-capacity curve showed that the slope changed at 1.3 V (slightly) and 0.7V in the first discharge reaction showing the lithiation of metal oxide and SEI formation respectively. As reported in the literature, this reduction of hematite follows 3 step chemical reaction given by equation (4.7 - 4.9) [159]–[161]. Following the first reaction a small amount of lithium got inserted in iron oxide solution and formed hexagonal $Li_xFe_2O_3$ without any prominent change in structure. However, there was a change in crystal structure during the during the second reaction from hexagonal $Li_xFe_2O_3$ to cubic $Li_2Fe_2O_3$. And in the last, third reaction brought about complete reduction of iron oxide and formed reduced elemental iron cluster in Li_2O matrix. While charging, the elemental iron got converted to iron oxide as its more stable when nanosized (eq 4.10). [159], [160], [162], [163].



Knowing that the theoretical capacity of hematite is 1006 mAhg⁻¹, the small size and homogenous morphology of the fabricated powder delivered 983 mAhg⁻¹ as the 1st discharge capacity. This performance decreased down to 408.7 mAhg⁻¹ after 50th cycle. Low electrical conductivity of the metal oxide may explain it.

The CV curvatures of the electrode were given in **Figure 4.13** (c). The obtained results were consistent with literature [159], [164], [165], a characteristic behavior of hematite can be observed in cathodic profile, the peak at 0.7 V and a wide slight hump appeared at 1.3 V, signified the irreversible SEI formation and the reduction of hematite by reacting with lithium during, resulting formation of Li_2O and Fe^0 (eq 4.7 - 4.9). This peak shifted

to 0.8-0.9V in subsequent cycles. In the anodic profile, only a broad peak appeared at about 1.65 V, which was attributed to the oxidation of iron to Fe^{+3} and extraction of lithium [159], [162]–[164].

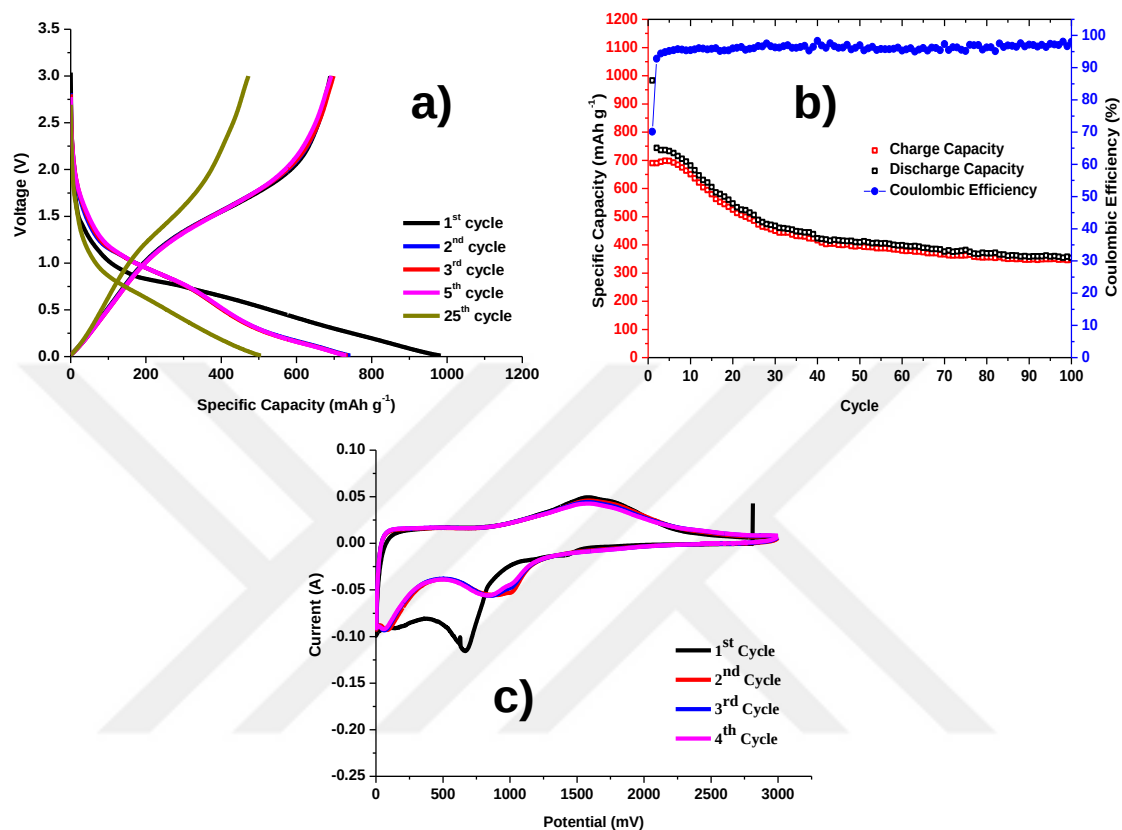


Figure 4.13: Electrochemical performance of iron oxide sample a) Voltage-Capacity curves b) Capacity-Cycle curves c) Cyclic voltammetry curves

CHAPTER 5

5. CONCLUSIONS AND FUTURE WORK

This study sets an example and provides the economical solution for the sustainability of the initial material used in the production of electrode materials of lithium ion batteries. Herein a recovery of values from the biomedical waste is suggested and fabrication of high value add electrode material for lithium ion battery has been proposed. Under the scope of this research following key findings can be documented:

1. Biomedical orthodontic waste has been leached out with 100% efficiency.
2. In coprecipitation the existence of chelating agent affects the particle density and the size of the precipitates. The inferior performance of CSA11 is because of NH_4OH , which promoted big dense agglomerates formation leading to slower Li diffusion kinetic.
3. From NiTi wires, in total 5 different composite materials were fabricated: Titanium oxide-rich (S1) and nickel oxide-rich (S10) powders were acquired by selective precipitation at different pHs, and the composite was developed by ball milling of them in two weight ratios 1:3 (N3T1) and 1:6 (N6T1). Results show that the composites exhibited better electrochemical performance than their constituent powder due to combined electrochemical properties of nickel oxide and titanium oxide based powders. As pure nickel oxide has high theoretical capacity (718 mAh g^{-1}) and titanium oxide has good retention of capacity with higher coulombic efficiency, their combination leads to better cycle performance.
4. For stainless steel braces, hydrothermal reaction parameters optimized by fuzzy logic model were verified by experimental finding, the average particle size obtained in verification experiment was 153.8 nm which is in close proximity of 156 nm size predicted by fuzzy model. Further, the optimized parameters (i.e., temperature 150°C , time 12 h, and filling ratio 1) suggested by fuzzy logic model,

found consistent with factorial design of experiment as well. Fuzzy logic is an important emerging practice which makes handling of realistic problems easier by dividing them in linguistic fuzzy words and making a logical connection with subjected output effect.

5. The sample obtained from SS braces contains precipitated chromium and nickel in hematite structure when precipitated at pH 10. Then the sample was heat treated at 730°C for 5 h, upon electrochemical evaluation powder as anode, it delivered 983 mAhg⁻¹ as the 1st discharge capacity and 408.7 mAhg⁻¹ after 50th cycle.

In future, the proposed methodology can be further improved to solve the problem of material's sustainability for the production of LIBs following these suggestions:

- Morphology and size control: this can be accomplished by careful literature survey, choosing appropriate precipitating agent, selecting appropriate molarity of agent, and carefully selecting the parameters of the fabrication to control, alter and target the specific structural phase, morphology, and particle size of the material to achieve a handsome set of electrochemical properties.
- Electrochemical conductivity: The increase in the capacity can be achieved up to a certain point due to the fact that the resulting powder will be metal oxide based and they have poor electrochemical conductivity. As a solution for this, developing a physical or chemical carbon based composite of these powders can be one of the possible ways to proceed with in order to enhance the electrochemical conductivity, hence electrochemical performance.
- Coating: electron conductive pathway within the material can also be developed by doing the coating or developing the coating of the more conductive material such as Ni coating.
- Doping: another way to enhance electrochemical performance is by creating structural defects by the doping of elements like nitrogen that impart imperfections in crystal lattice resulting in the active sites for the lithiation reaction.

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