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GEBZE TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DEVELOPMENT OF CATHODE MATERIALS FOR AQUEOUS ELECTROLYTE BATTERY SYSTEMS

SERKAN SEVİNÇ

A THESIS SUBMITTED FOR THE DEGREE OF

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FEN BİLİMLERİ ENSTİTÜSÜ

ÇEVREYE DUYARLI SULU ELEKTROLİT BATARYA SİSTEMLERİ İÇİN KATOT MALZEMESİ GELİŞTİRİLMESİ

SERKAN SEVİNÇ
YÜKSEK LİSANS TEZİ
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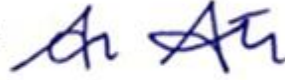
DANIŞMANI
PROF. DR. ALİ ATA

GEBZE
2016

GEBZE TEKNİK ÜNİVERSİTESİ	YÜKSEK LİSANS JÜRİ ONAY FORMU

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 27/06/2016 tarih ve 2016/43 sayılı kararıyla oluşturulan jüri tarafından 13/07/2016 tarihinde tez savunma sınavı yapılan Serkan SEVİNÇ'in tez çalışması Malzeme Bilimi ve Mühendisliği Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

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ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun

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SUMMARY

Demand for the renewable energy has been growing rapidly. Numereous numbers of new wind and solar installations are used over the past few years in order to meet the energy need and reduce global warming emissions. Main issue with those systems is their dependence on weather conditions. Therefore, produced energy must be stored which requires large scale energy storage systems. Although Li-ion batteries have potential to meet the demand, increasing cost of lithium due to the low resources as well as the use of flammable, toxic and expensive organic electrolytes prevent their manufacturing for large scale applications.

In this thesis in order to overcome these issues, safe, low-cost and clean battery systems production is aimed with the aqueous electrolyte Na-ion battery systems. High energy density and high capacity $NaFePO_4$ is used as cathode material. Since this material is not possible to synthesis by chemical methods, first of $LiFePO_4$ was synthesized by hydrothermal method and then $NaFePO_4$ was obtained by electrochemical displacement of Li-ions with Na-ions in sodium containing aqueous electrolyte. Afterwards working potential and electrochemical properties are determined. As anode material polysulfide is used due to the sulfur abundancy and its high capacity. Full cell experiments demonstrate a 0.7V cell together with 40 mAh/g capacity almost no fading over 100 cycles.

Key Words: Aqueous electrolyte, Na-ion, Li-ion, Energy storage.

ÖZET

Dünya genelinde artan enerji ihtiyacını karşılamak ve karbondioksit salınımını engellemek amacıyla yenilenebilir enerji üretim sistemlerine (rüzgâr, güneş) olan talep hızla artmaktadır. Fakat bu sistemlerden üretilen enerji hava durumuna göre değişiklik göstermektedir. Bu nedenle üretilen enerjinin depolanması için yüksek boyutlu enerji depolama sistemleri gereklidir. Li-ion bataryalar ihtiyacı karşılayabilecek potansiyelde olmasına rağmen artan lityum fiyatları ve kullanılan yanıcı organik elektrolitlerden kaynaklanan güvenlik sorunları yüksek boyutlarda üretimin önüne geçmektedir.

Bu tezde bu sorunu aşmak amacı ile çevreye duyarlı, daha güvenli ve ucuz olan sulu elektrolit batarya sistemlerinin geliştirilmesi amaçlanmıştır. Katot malzemesi olarak yüksek kapasite ve enerji yoğunluğuna sahip olan $NaFePO_4$ kullanılmıştır. Bu malzemenin kimyasal olarak sentezlenemediği için öncelikle $LiFePO_4$ hidrotermal yöntemle sentezlenmiş ve daha sonra bu malzemeden elektrokimyasal olarak lityumun yapıdan çıkartılıp yerine sodyumun yapıya girmesiyle $NaFePO_4$ katot malzemesi sentezlenmiş ve sulu elektrolit ortamında çalışma voltaj aralığı ve elektrokimyasal özellikleri incelenmiştir. Anot malzemesi olarak ise ucuz fiyatı ve yüksek kapasitesi nedeniyle sülfür kullanılmıştır. Sulu elektrolit ortamında yapılan tam hücre deneylerinde 100 çevrimin sonunda 0.7V tam hücre potansiyeli ile 40 mAh/g kapasite değerleri elde edilmiştir.

Anahtar Kelimeler: Sulu elektrolit, Na-ion, Li-ion, Enerji depolama.

ACKNOWLEDGEMENTS

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LIST of ABBREVIATIONS and ACRONYMS

Abbrevations and Acronmys	**Explanations**
°C	: Celsius
ARABs	: Aqueous electrolyte rechargeable alkali-metal ion batteries
CAE	: Compressed air energy storage (CAES)
DMC	: Dimethy carbonate
EC	: Ethylene carbonate
EG	: Ethylene glycol
FES	: Flywheel energy storage
EVs	: Hybrid electrical vehicles
ICP-MS	: Inductively coupled plasma mass spectrometry
LIB	: Lithium ion batteries
LiPF6	: Lithium Hexafluorophosphate
TEGDME	: Tetraethylene glycol dimethyl ether
Ni-MH	: Nickel-metal hydride batteries
NMP	: N-methylpyrrolidinone
PHS	: Pumped hydroelectric storage
PVDF	: Polyvinylidene fluoride
PC	: Polypropylene carbonate
RT	: Room-temperature
SEM	: Scanning electron microscopy
SIE	: Solid electrolyte interface
SCE	: Saturated calomel electrode
TES	: Thermal energy storage
TGA	: Thermogravimetric analysis
XRD	: X-ray diffraction
ZEBRA	: Zero Emission Batteries Research

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1. INTRODUCTION

Global warming and climate change issues have become the major concerns of humanity in 21st century. Use of fossil fuels that results in greenhouse gas emission is the main factor of these isssues. Currently 68% of world's electricity is produced from fossil fuel and 3% is from renewable energy sources such as solar and wind power. There has been a significant effort to develop renewable energy sources. Developed countries rapidly increasing the number of installed solar and wind power energy production systems. However, renewable energy resources are dependent on the time, weather, and location, while the electric energy consumption is also relatively fluctuant. Large-scale stationary energy storage systems (EES) become the key systems for balancing the energy output. Especially rechargeable batteries, have been considered as promising candidates for large-scale applications. Among rechargeable batteries aqueous electrolyte battery systems are able to meet safety, cost and toxicity concerns and could be new candidate for the large-scale stationary energy storage systems.

2. LITERATURE REVIEW

2.1. General Reasons for Energy Storage

Energy storage is a process of storing energy that can be released to use at a later stage. Energy storage devices convert the energy into electricity and return it back to the system. With the development of renewable energy production systems such as wind and solar cells and integration of those systems into smart grid electricity distribution networks, energy storage systems become crucial importance. As seen in Figure 2.1 [1] there is always fluctuations in demand and produced electricity. Therefore, effective energy storage systems are required in order to achieve following goals:

- Low carbon emission and clean energy future,
- Energy security and reliability,
- Efficient energy conversion and distribution,
- Reduce air pollution.
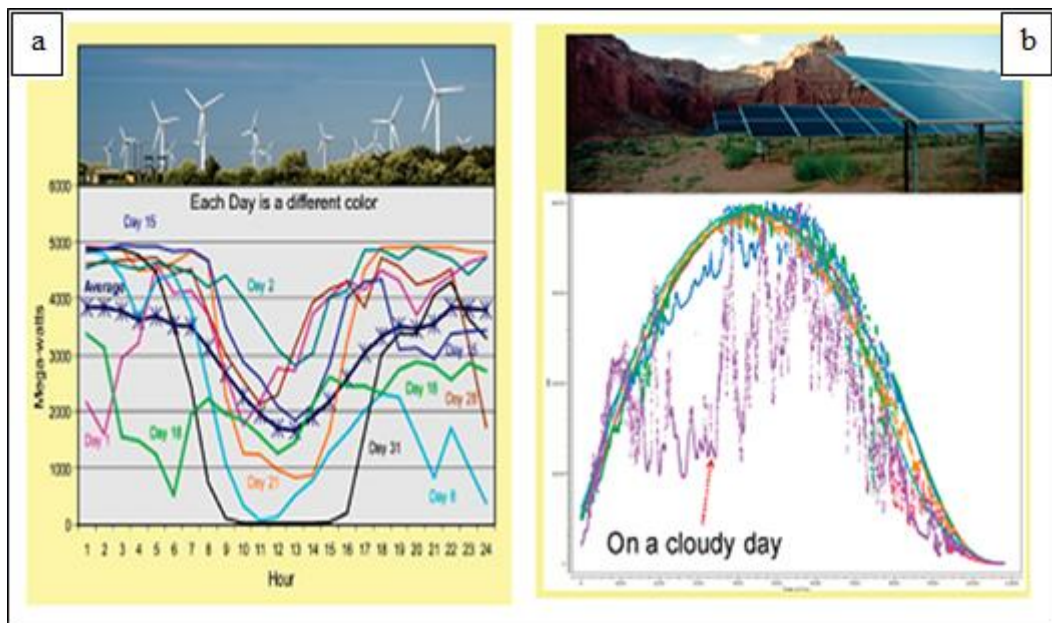
Figure 2.1: Daily profiles of a) wind power and b) solar cell systems .

2.2. Energy Storage Systems

This section aims to provide a brief description of most of the relevant energy storage technologies.

2.2.1. Pumped Hydroelectric Storage

Pumped hydroelectric storage (PHS) is the most used form of energy storage technology for storing large amounts of electrical energy. This technology enables to store hundreds to thousands of megawatts per installation. It has round trip efficiencies in the range of 70-85% [2-4]. High efficiency and simple engineering methods makes this system economically attractive way of storing large amount of energy.

A pumped hydroelectric energy storage system uses low-cost electricity (during off-peak hours), to pump water to higher level where water is stored as gravitational potential energy. Stored energy is converted back into electricity, upon releasing water that passes through a generator into a lower level reservoir. Flow down of water provides electricity when the electricity is at high-cost (e.g. during on-peak hours) as shown in Figure 2.2 [5].
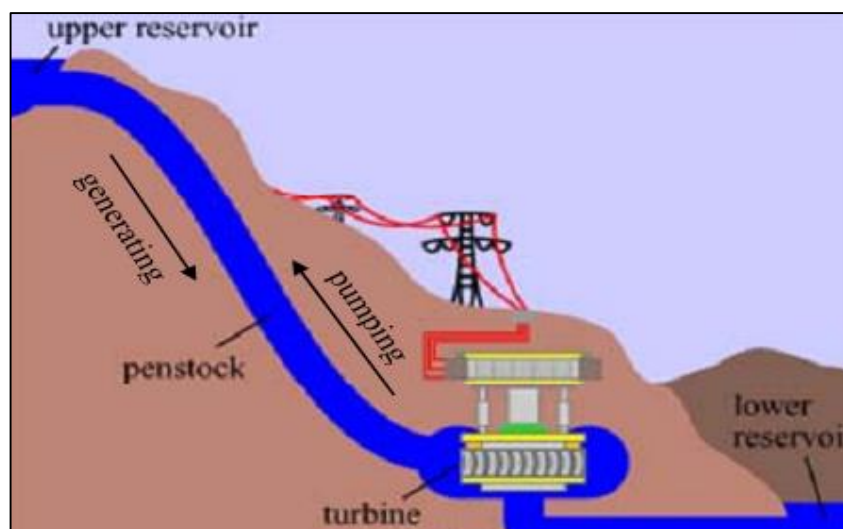
Figure 2.1: Pumped hydroelectric energy storage system.

Pumped hydroelectric energy storage system has also some drawbacks since it has low power and energy density. It requires very large areas and suitable geography and also very large facilities which makes difficult and costly construction systems. It is also limited by water availability which means that the system is not suitable for rainless areas. Damming rivers are also another critical issue that can cause flooding. Despite these drawbacks, pumped hydroelectric energy storage systems can operate much longer than other available technologies and does not suffer from capacity loss or decline of energy output as in the batteries or solar cells.

2.2.2. Compressed Air Energy Storage

Compressed air energy storage (CAES) is a relatively new energy management technology system. There are two commercially operating CAES plants in Germany and USA. These facilities use same operating systems. Working principle is based on diabatic process. Low cost, off-peak power is used to compress air into a underground storage vessel such as hard rock caverns, abandoned mines, and underwater bladders. During peak times of electricity, pressurized air is mixed with fuel such as hydrogen, natural gas, gasified biomass etc. and then combusted in a gas turbine to convert back to electricity [6].Schematic presentation of a compressed air energy storage system is shown in Figure 2.3 [7].
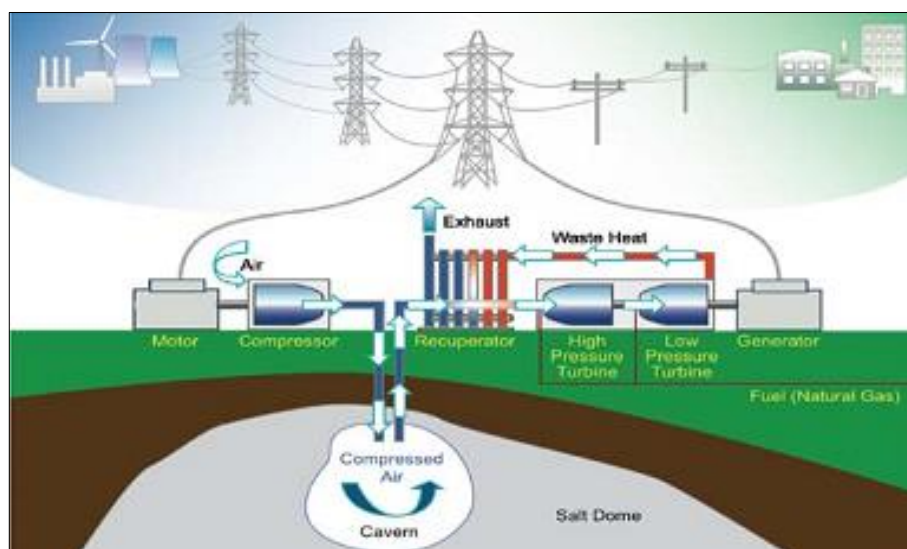
Figure 2.2: Compressed air energy storage system.

2.2.3. Flywheel Energy Storage

The working principle flywheel energy storage (FES) is based on storing electricity in the form of rotational kinetic energy. It uses a rotor and magnetic bearing placed in a vacuum chamber (Figure 2.4) [8] to convert kinetic energy to electricity. To charge the flywheel electrical energy is used to increase the rotational speed of the flywheel. To discharge, kinetic energy is converted back into electricity via a generator from the flywheel by allowing the flywheel is slowing down to power the motor-generator.

FES is suitable for applications which require high cycling, high power and small response times. FES key feature is their instantaneous response times therefore flywheels are used for the protection against temporary interruptions in the power supply. FES used for power applications range between 100 kW to 2 MW with discharge times ranging from 5 to 50 seconds. FES's round trip efficiency ranges between 70 and 80 percent and only loses 1 to 2 percent of the rated power output [9].

There are a few major drawbacks regarding flywheels. They usually require low friction magnetic bearing setups and spin in a vacuum enclosure which means high initial costs [10]. Noise pollution during operating of FES or mechanical breakdown creates possible danger to environment. Also cost per kWh is very high since they are used for short term applications. However, FES does not produce emission and pollution.
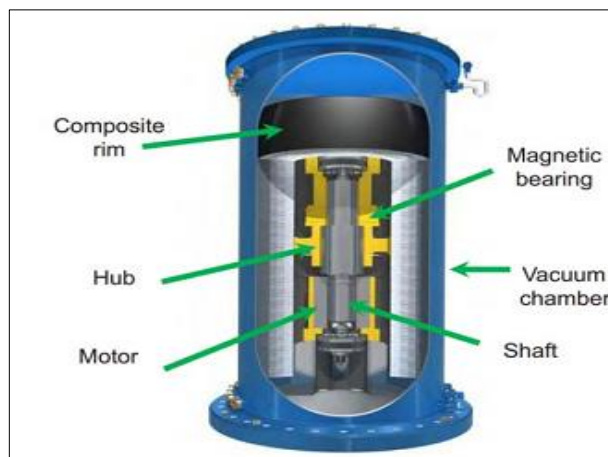
Figure 2.3: Flywheel energy storage system.

2.2.4. Thermal Energy Storage

Thermal energy storage (TES) is a type of energy storage system in the form of thermal energy. In principle TES (Figure 2.5) [11] system uses hotter or colder reservoir than ambient temperature. The logic is as follows; during the night, water is frozen into ice; during the day, the ice is used to cool air conditioning systems thereby reducing the need to draw power from the grid. Similarly, heat can be added to ceramic bricks or hot water heaters when the energy to do so is available. When energy is required, it can be reclaimed from the stored heat. This is much the same in principle as molten salt thermal storage. A simple, two-tank, direct molten salt energy storage system utilizes a receiver to reflect sunlight onto a heating chamber. Fluid from a cool tank is pumped to a heating chamber where it is brought to a very high temperature. It is then transferred to a tank containing heated fluid for storage. When heat energy needs to be recovered, it is used to create stream that powers a generator. There are other configurations, but the overall principle remains the same.

There are several types of thermal energy storage technologies. Sensible heat storage and latent heat storage are most used form of TES. Sensible heat storage stores energy by increasing or decreasing the temperature of medium without any phase change. Boiling of water is an example which phases change does not occur. On the contrary in latent heat storage systems heat causes a phase change and energy stores in the form of latent heat. For instance, ice energy storage is common way used to cool air in conditioning systems. During the night, water is frozen into ice or lower temperatures than ambient thereby reducing the need to draw power from the grid when the electricity demand is peak. Molten salt energy storage is another most used type in solar thermal power plants. In these systems salt is heated to a liquid state by reflecting the sunlight into a reservoir heating the reservoir to higher temperatures. When electricity is required the hot salt is pumped into a steam generator. The most efficient systems use sodium nitrate, potassium nitrate and calcium nitrate salt mixtures reaching annual efficiency of 99% [12].
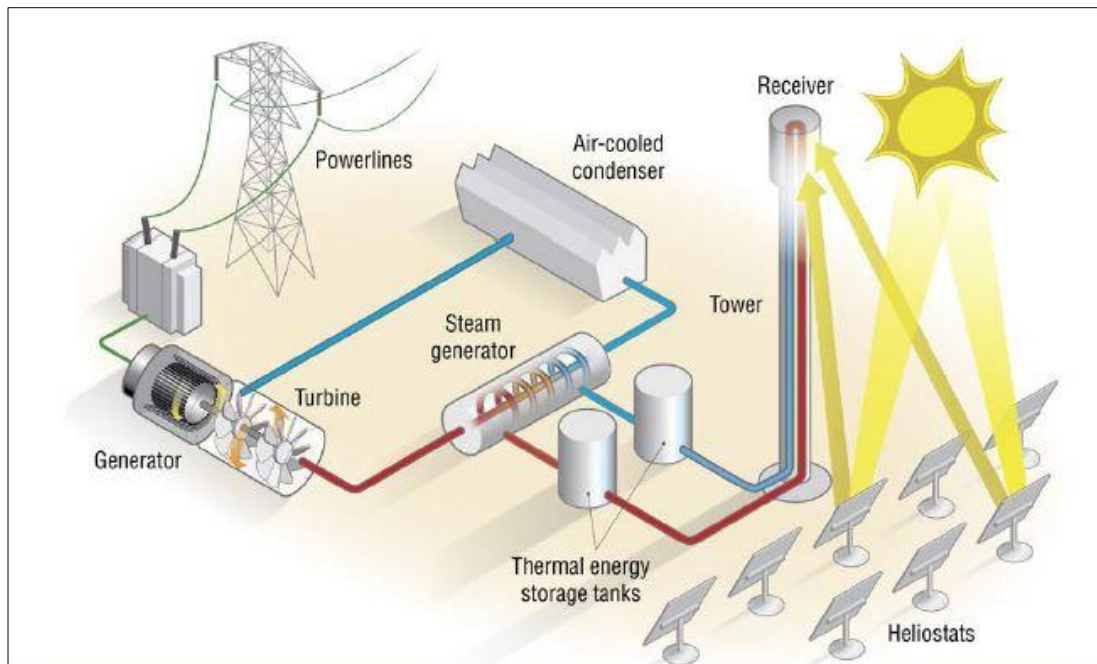
Figure 2.4: Thermal Energy Storage.

2.2.5. Electrochemical Capacitors

Electrochemical capacitors, which also called double layer capacitors or super-capacitors, use primarily high area porous carbon materials. Super capacitors (Figure 2.6) [13] store up to 100 times more energy per unit volume or mass than conventional capacitors which uses dielectric constant to separate two parallel plates where as in super capacitor a separator and a liquid electrolyte is used. Although energy density is 3–30 times lower than batteries power density is several orders of magnitude greater [14].

Even though super-capacitors suffer from high self-discharge rates compared to conventional batteries they do not suffer from charge-discharge rate limitations and can withstand millions of cycles due to their working mechanism which does not require ion intercalation unlike batteries. For these reasons they are mostly used for power factor correction and voltage support rather than energy storage [15].
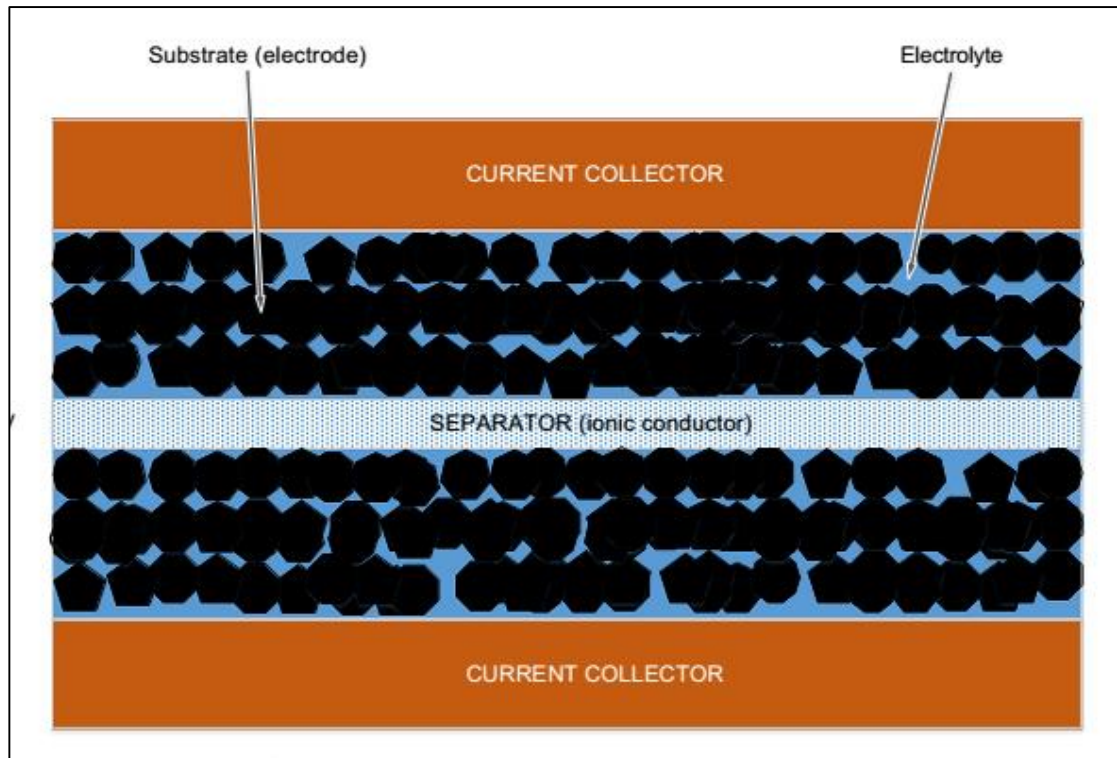
Figure 2.5: Symmetric supercapacitor schematic diagram.

2.2.6. Rechargable Batteries

Batteries store energy in the form of chemical energy which convert it back to electrical energy when required. They are consisted of cells which contain cathode electrode, anode electrode and electrolyte. There are two types of batteries primary (non-rechargeable) and secondary batteries (rechargeable). Primary batteries are non-rechargeable, chemical reactions are non-reversible. Secondary batteries are rechargeable, chemical reactions that take place during charge-discharge process are reversible. In 1800 Alessandro Volta built the first battery called voltaic pile. Volta used copper and zinc plates, immersed in salt solution separated by brine-soaked paper cloth. Voltaic pile generated 0.76V In 1836 by British chemist John Frederic Daniell invented a battery that is widely used for power source for electrical telegraph networks [16]. Daniell was trying to eliminate hydrogen bubbling observed in voltaic pile. His battery consisted of copper sulfate solution and copper pot which is filled with a copper sulfate solution, in which was immersed an unglazed earthenware container filled with sulfuric acid and a zinc electrode. Daniell cell generated about 1.0 volts [17].

There are several types of conventional batteries used in different applications. Lead-acid, nickel-metal hydride and lithium-ion are most used types.

2.2.6.1. Lead-Acid Batteries

Lead acid batteries are the most common electrochemical energy storage system. Lead acid batteries have more than 100 years of history. They are made of lead as anode, lead dioxide as cathode and sulfuric acid as electrolyte. It was first used in 1865 for commercial purpose in electrical vehicles. Although lead acid batteries offer low specific energy and low power, short cycle life and toxicity its widely used because of technical maturity and low cost [18].

Lead acid batteries first used by GM in 1996, in an electric vehicle EV 1 GM which used a 533 kg lead-acid battery with 70 miles of driving range. High weight and short driving range could not meet customer needs and discontinued mass production of EV 1.

Lead acid batteries have about 2 V nominal voltages and efficiency ranges between 75 and 85 percent [9]. There are some difficulties of lead acid batteries which include: sensitivity to temperature, self-discharge, sulfation, hydration, and degradation. Optimal operation is temperature is 25°C. If the temperature drops below -40°C, the electrolyte may freeze and if the temperature rises too high, the battery may overheat and cause an explosion [5].

2.2.6.2. Nickel-Metal Hydride

Nickel-metal hydride batteries (Ni-MH) are widely used for energy storage applications. It consists of hydrogen for the cathode and nickel hydroxide for the anode [19]. Ni-MH batteries have two to three times the capacity of an equivalent size Ni-Cd battery and can reach the energy density of a lithium ion battery. Nickel-metal hydride batteries became popular for the early hybrid electric vehicles because of their greater energy density, lighter weight, and smaller volume than lead acid batteries [20]. Research on Ni-MH batteries began at the Battelle-Geneva Research Center and invented in 1967. Ni-MH became commercially available in 1989. Components of Ni-MH battery is shown in Figure 2.7 [20].
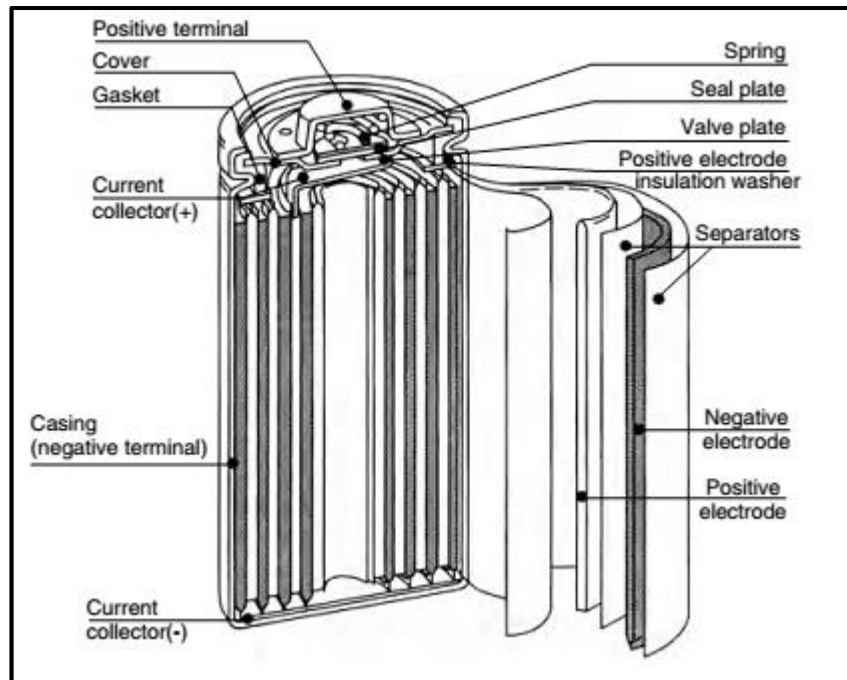
Figure 2.6: Components of Ni-MH battery.

NiMH batteries first used by Toyota's Prius electric car in 1997. Toyota recently announced that the company will switch back to lithium-ion batteries because of their higher energy densities and longer ranges [20, 21].

2.2.6.3. ZEBRA (Sodium-Nickel-Chloride)

Zero Emission Batteries Research Activity is abbreviated as ZEBRA. It uses nickel chloride and sodium for cathode and anode respectively. It is superior to nickel-metal hydride batteries and comparable to lithium-ion batteries. Their main weakness is the high operating temperature, the battery must maintain between 270 $^{\circ}$C and 350 $^{\circ}$C in order to keep their metal salt electrolyte in liquid [21].

2.2.6.4. Lithium-ion Batteries

Lithium-ion batteries are generally confused with lithium batteries. While lithium batteries use lithium metal as anode and metal oxide as cathode, lithium-ion batteries use graphite as anode (negative electrode), lithium containing transition-metal oxide as a cathode (positive electrode) material and a lithium salt containing

organic material as an electrolyte. It may also use polymers or ceramics as an electrolyte.

The first commercial lithium-ion battery was produced by Sony Corporation in June 1991 [22]. The battery consisted of lithium cobalt oxide as positive electrode materials and graphite as an anode material with an energy density around 180 Wh/kg almost 5 times higher than Lead-acid batteries.

Main advantage of lithium-ion batteries are safety issues over the lithium batteries since they use highly reactive metallic lithium as anode which is also prone to dendrite growth. Figure 2.8 illustrates the dendrite growth mechanism of a lithium battery [23]. Dendrite growth observed in lithium batteries, prevented in Li-ion batteries by replacing the lithium metal with a graphite. Although energy densities of Li-ion batteries are lower compared to lithium batteries they are safer, have higher stability and longer cycle life.
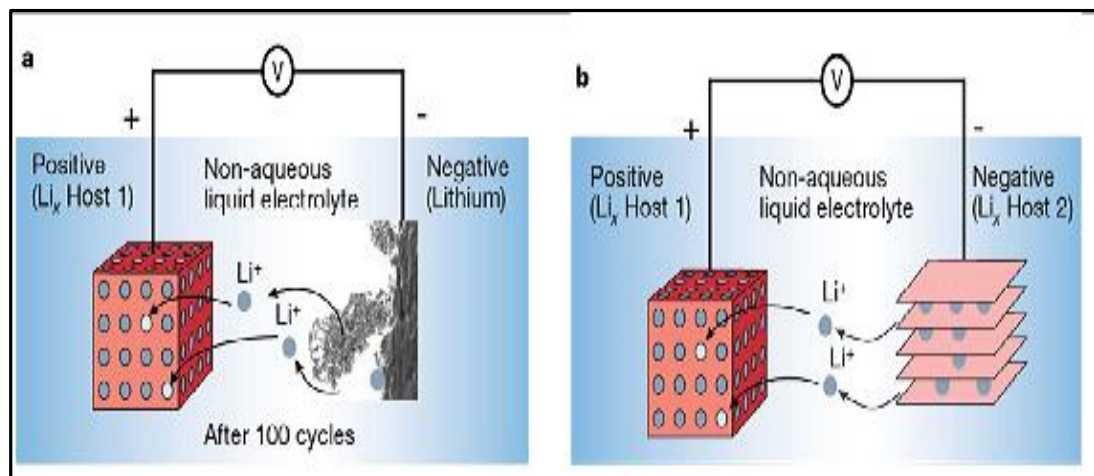
Figure 2.7: Schematic representation of a) Li and b) Li-ion batteries. Rechargeable Li-metal battery (the picture of the dendrite growth at the Li surface was obtained directly from in situ scanning electron microscopy measurements).

Figure 2.9 illustrates the operating principle of the lithium-ion battery [24]. Cell is constructed, in the discharged state. When it is charged, lithium ions move from the positive electrode through the electrolyte to anode and electrons flow from cathode to the anode through the external circuit. When the battery is discharged lithium ions move from anode to cathode side.
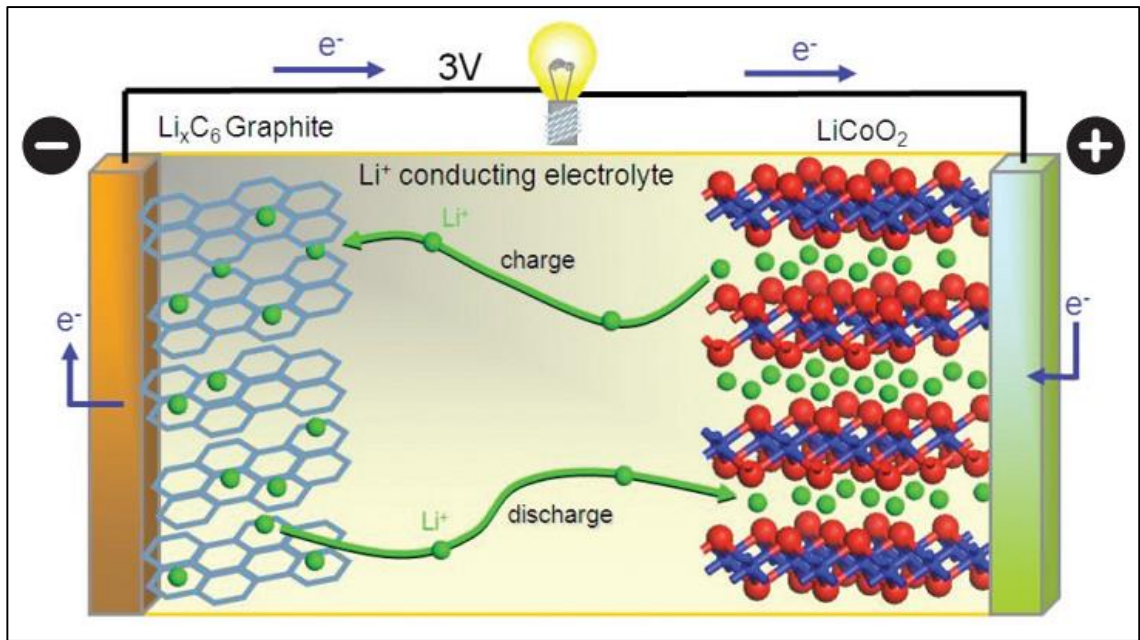
Figure 2.8: Lithium ion battery function and components.

Li-ion batteries (LIB) are generally used in consumer electronics due to their high energy density, low discharge rates, and long cycle life. LIB shows the highest volumetric and gravimetric energy density compared to other rechargeable batteries shown in Figure 2.10 [25] and Table 2.1 [26].
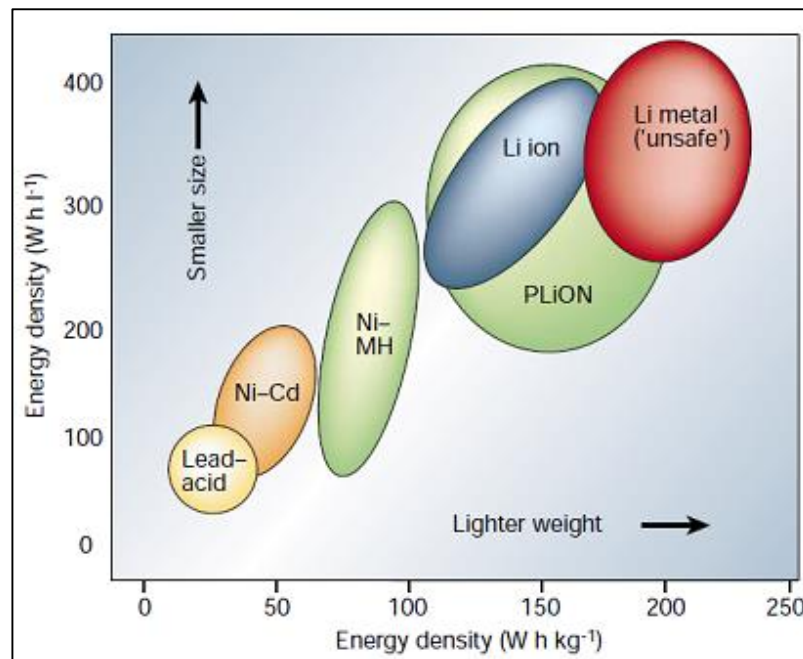
Figure 2.9: Comparison of different rechargeable battery technologies
in terms of volumetric and gravimetric energy densities.

Table: 2. 1: The performance parameters of various rechargeable batteries

Types of battery	Energy density (Wh/kg)	Cycle durability	Self-discharge (Per month)	Cell Voltage (V)	Charge time (h)
NiMH	30-80	500-1000	25%-30%	1.2	2-4
NiCD	40-60	1000-1500	10%-20%	1.25	1
Lead-acid	30-40	600-800	5%-20%	2.1	8-16
Li-ion	100-170	1200	5%-12%	3.5	1-3

Currently there are three types of cell constructions; prismatic, cylindrical and pouch cells (Figure 2.11 and 2.12) [24]. Prismatic cells generally use aluminum or steel cans. These metal cans allow heat radiation. Prismatic lithium cells have higher energy density since they can be packed more efficiently. They can be fabricated up to 100 Ah. Cylindrical cell is the most manufactured type. 18650 (18mm diameter, 650mm long) standard size cylindrical cells are mostly used on laptop batteries.
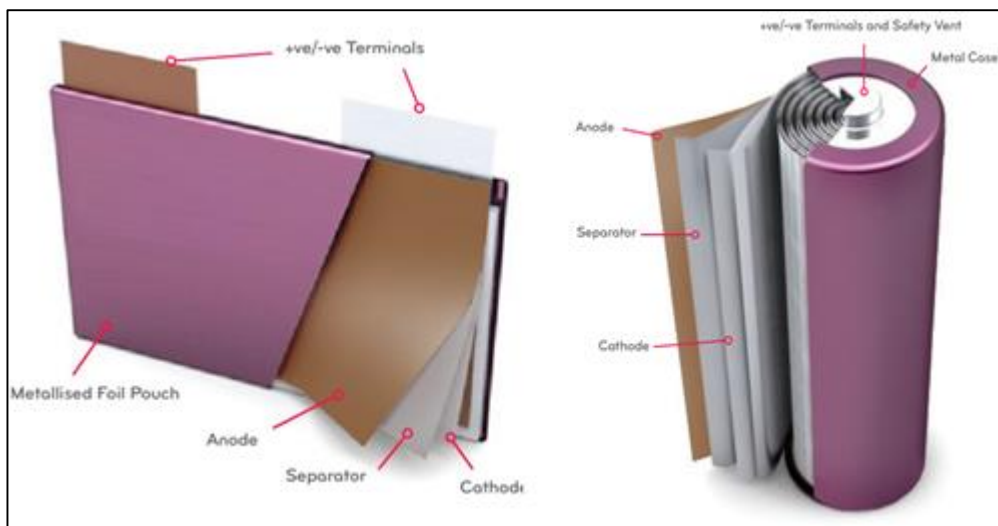
Figure 2.10: Schematic representation of prismatic cell (left)
and cylindrical cell (right).

The last type is Pouch cells that make the most efficient use of available space and they can reach up to 90 – 95% packing efficiency. They have lower weight compared to two other types therefore energy density is higher.
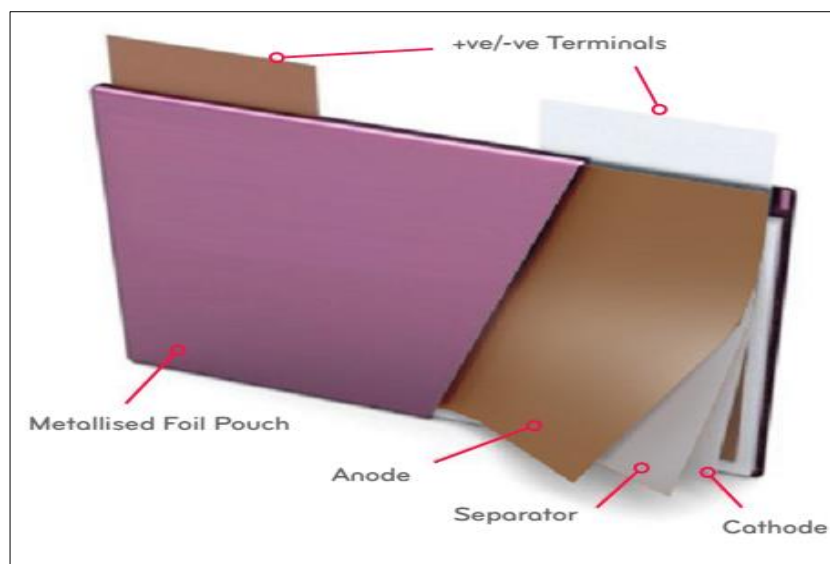
Figure 2.11: Schematic representation of pouch cell.

2.2.6.5. Aqueous Electrolyte Rechargeable Alkali-ion Batteries

Although rechargeable lithium-ion (Li-ion) batteries with organic electrolytes is the best the alternative for portable consumer electronic devices and high power applications such as electric vehicles and energy storage for renewable energy systems with its longer lifetime and high energy and power density, they still have some critical drawbacks [27-29].

Cost and safety are still important issues. Li-ion batteries use expensive and flammable organic electrolytes therefore Li-ion batteries can easily catch fire, which is a crucial importance for especially large scale energy storage applications. In order to overcome those problems associated with Li-ion batteries, researches have been trying new materials and solutions. In 1994 Dahn reported first aqueous battery system replacing the organic electrolyte with an aqueous electrolyte. This novel battery consisted of of $LiMn_2O_4$ as cathode,VO_2 as anode material and 5M $LiNO_3$ as electrolyte [30, 31]. Dahn tested this newly adopted cell configuration in a coin cell. The cell had promising result 1.5V output voltage and 55 W.h/kg which is competitive with both Pb-acid (about 30 Wh/kg) and Ni-Cd (about 50 Wh/kg) technologies. Since then aqueous electrolyte battery systems has gained great attraction due to low cost, safety and environmental friendliness.

Aqueous electrolyte rechargeable alkali-metal ion (Li$^+$, Na$^+$) batteries (ARABs) are promising candidates for large-scale applications. These batteries can eliminate the main challenges of conventional LIBs which use expensive electrolytes and salts, safety issues (flammable organic electrolytes), and strict manufacturing conditions. The charge-discharge rate limitations are also solved. Ionic conductivity of the aqueous electrolyte is several orders of magnitude greater than organic electrolytes [30, 32, 33].Conductivity and resistivity graphs are shown in Figure 2.13 a) [34] b) [35]. Advantages and disadvantages of aqueous electrolyte over organic electrolyte are also shown in Table 2.2.
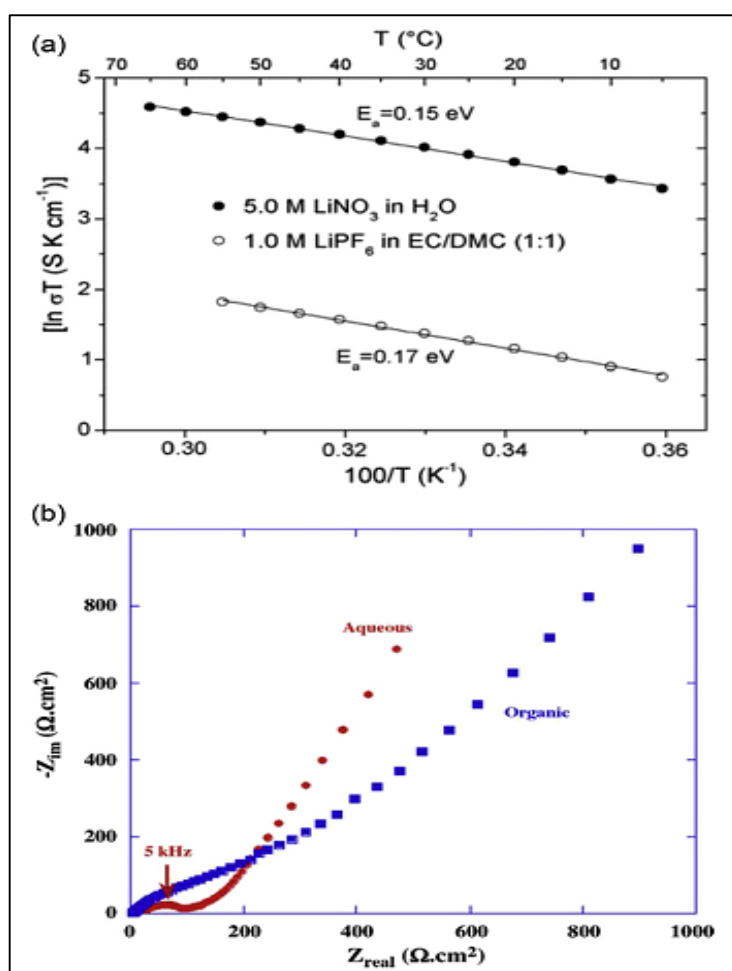
Figure 2.12: a) Arrhenius plot of 5 M LiNO$_3$ solution and 1 M LiPF$_6$ in EC/DMC (1:1) and b) electrochemical impedance spectroscopy response recorded of LiFePO$_4$ film in 1 M LiNO$_3$ solution and 1 M LiClO$_4$ EC/DMC.

Table 2.2: Advantages and disadvantages of aqueous electrolyte over organic electrolyte.

Advantages	Disadvantages
• Faster Kinetics • Absence of SEI Layer • Cheaper Electrolyte • Safe • Environmentally Friendly	• Instability of Materials • Side Reactions with O_2 • Low Voltage

Although ARABs are promising alternative to Li-ion batteries for large scale applications, there are a few positive and negative cathode materials because of thermodynamic stability of water which is limited to 1.23V. Beyond this voltage water electrolysis starts and oxygen and hydrogen evolution occurs shown in Figure 2.14 [35]. Voltage and capacity properties of
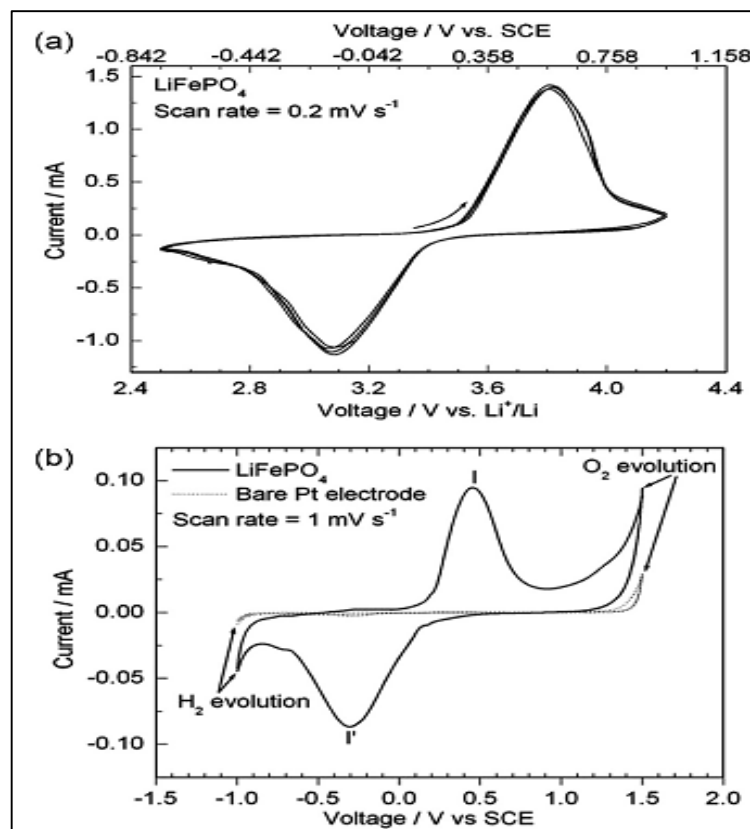
Figure 2.13: Cyclic voltammograms of $LiFePO_4$ electrode in a) 1 M $LiPF_6$-EC/DMC (1:1) non-aqueous electrolyte and b) 1 M Li_2SO_4 aqueous electrolyte.

- LiFePO$_4$ as positive electrode

After its discovery and commercialization by Sony Corp. in 1990 [5], lithium-ion batteries became the most important secondary battery. The cell is consisted of a graphite anode a cathode. LiCoO$_2$ and electrolyte lithium hexafluorophosphate dissolved in an organic electrolyte such as ethylene carbonate/dimethyl carbonate mixture embedded in a separator. Although LiCoO$_2$ batteries are widely used because of their high potential and high volume energy density, they have some limitations for large scale applications:

- Low specific capacity 140 mAh/g, only 0.5 of Li-ion can be extracted despite its high theoretical capacity 273 mAh/g,
- Oxygen evaluation may occur during overcharge which consequently increases the temperature and internal pressure causing explosion [25],
- Cobalt is not earth abundant material and it is toxic.

Due to above limitations several other transition metals are investigated instead of Co such as Nickel, Mg, Mn, Ti and Fe substitutes. However, these materials did now show promising results as an alternative to cobalt containing LiCoO$_2$ [36, 37].

Later on a large and growing body of literature has investigated phosphate compounds with a general formula Li$_x$M$_y$(PO$_4$)$_z$ (M =Mn, Ni Co, Fe). Among them them LiFePO$_4$ showed most promising results. In 1997 Padhi published the first investigation of Li intercalation into LiFePO$_4$ [38]. Because of several important features LiFePO$_4$ gained great attraction both from industry and scientific point due to following properties:

- High theoretical (170 mAh/g) and practical capacity over 150 mAh/g and relatively high voltage 3.45 vs Li/Li$^+$,
- Long cycle life,
- Environmental compatibility and abundancy of Fe.

In addition to these features, LiFePO$_4$ is also a chemically stable material so thermal runaway risk is very low, due to the strong P-O covalent bonds in (PO$_4$)$^{3-}$ polyanion which stabilize the Fe^{3+}/Fe^{2+} redox couple through the Fe-O-X inductive effect, then prevent O$_2$ release at high states of charge, making LiFePO$_4$ thermally

stable [39]. Also electrochemical potential (3.45 V) is lower than the oxidation potential of the organic electrolyte. $LiFePO_4$ has corner-shared FeO_6 octa-hedra and edge-shared LiO_6 octahedra running parallel to the b-axis and PO_4 groups which share one edge with a FeO_6 octahedron and two edges with LiO_6 [39, 40]. In charged and in discharged ($FePO_4$-$LiFePO_4$) states of $LiFePO_4$ have similar crystal structures. Volume change and density change are 6.8% and 2.6% respectively [40]. Due to similar crystal structure excellent reversibility are observed. Crystal structure of $LiFePO_4$ in charged and discharged state is shown in Figure 2.15 [38].
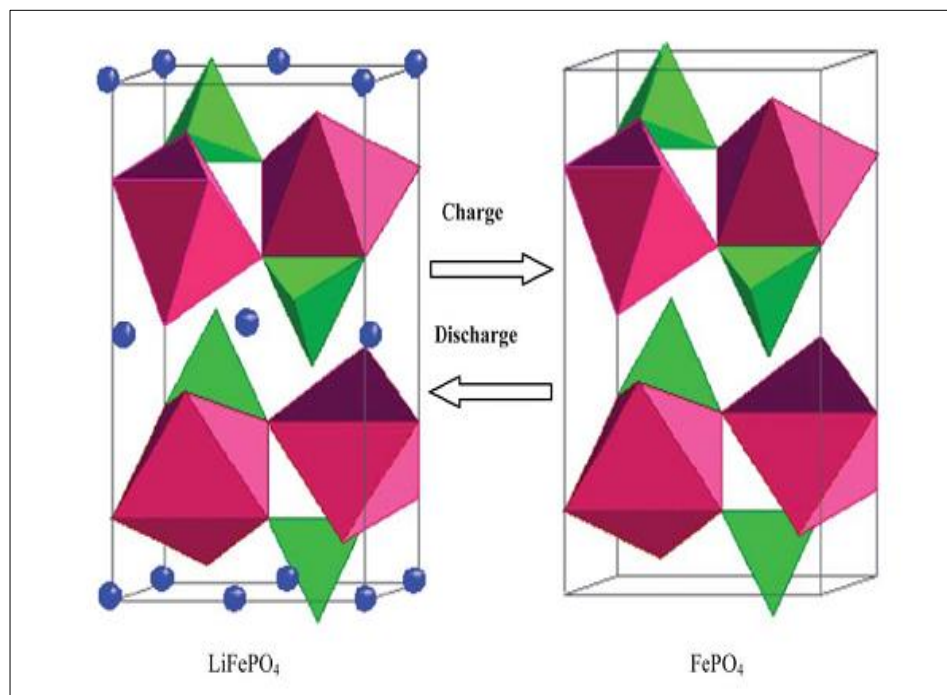
Figure 2.14: Crystal structures of a) $LiFePO_4$ and b) $FePO_4$.

Those features mentioned above has promoted the use of $LiFePO_4$ in large scale applications especially transportation applications in electrical and hybrid vehicles. One main drawback of $LiFePO_4$ is the low conductivity, about 10^{-9} to 10^{-10} S/cm [41], which is lower than the electronic conductivities of most other the phosphor olivine cathode materials. Ionic diffusivity of lithium ions is also limited, easiest pathway is [010] direction (Figure 2.16) [42].
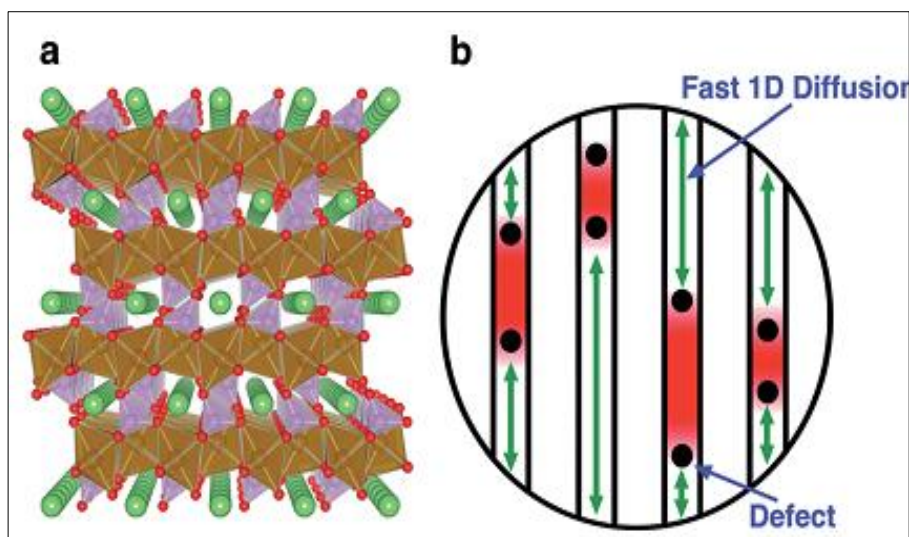
Figure 2.15: a) Crystal structure of LiFePO₄ illustrating 1 D Li+ diffusion channels oriented along the [010]. b) Schematic illustration of Li+ diffusion impeded by immobile point defects in 1D channels.

In order to overcome ion diffusion limitation, high surface area nano sized particles are synthesized which enable fast charge transfer through [010] channel [43-46]. In order to address low electronic conductivity uniform carbon coating or ion doping such as Mg^{+2} and Mn^{+2} should be made with nanosized particules [40, 47].

LiFePO₄ has been synthesized with different chemical methods including hydrothermal [48, 49], solvothermal [50-52], microwave [53, 54] and solid state [55, 56].For the synthesis of LiFePO₄ solvent selection, pH of the reaction medium, concentration, temperature, and source are important parameters. Solid state synthesis requires high temperature and it is difficult to control particle size. Microwave is a very fast synthesis method in 10 to 30 minutes compounds can be synthesized but for the mass production it is not feasible. In this thesis hydrothermal method showed the best electrochemical results which are easy to change morphology and particle size by changing the pH and concentration of solution.

LiFePO₄ is one of most commercially used positive cathode material feasibility of it working in aqueous environment and stability in water is investigated [57, 58]. Studies performed revealed that basic or acidic conditions accelerate aging of LiFePO₄. Although neutral condition is found to be optimum pH, it does only slow down the aging. As the immersion time increases Li_3PO_4 formation and increase in Fe(III) concentration observed. Dissolved oxygen has significant effect on capacity fading of LiFePO₄. Eliminating the dissolved oxygen and coating the material with

carbon greatly increases cycle life [57, 59]. There are numerous full cell application using LiFePO$_4$ as cathode material in aqueous electrolyte rechargeable batteries [60, 61].

- NaFePO$_4$ as positive electrode

The concern of this thesis is to find suitable positive and negative electrode materials for large scale energy storage applications. Since the lithium prices are increasing and it is not an abundant element, so we need to find alternative materials. The first idea is use to Na instead of Li which is highly abundant and shows similar electrochemical properties compared to Li. It is found that synthesis of olivine NaFePO$_4$ is not feasible in any chemical methods. Maricite phase is favored over olivine phase, which has no free channels for Na ion diffusion in the crystal structure [62, 63]. Feasibility of electrochemical replacement of Li by Na ions in LiFePO$_4$ was investigated in organic electrolytes [64-66].

The kinetic of the sodium insertion/deinsertion is found to be faster than the lithium one, which is assumed due to weaker Na-PO$_4$ bond than Li-PO$_4$ bond [67]. Casas-Cabanas also studied the cycling stability of a NaFePO$_4$/NaTi$_2$(PO$_4$)$_3$ aqueous full cellThe battery delivered 0.6 V and 70 mAh/g over 20 cycle at 1C rate which makes NaFePO$_4$ is a promising candidate for aqueous Na-ion cells [68].

- Polysulfides as negative electrode

Sulfur is an abundant, low cost material and it is mostly produced as a by product of removing sulfur-containing contaminants from natural gas and petroleum. Sulfur is used in conventional Na/S batteries. It has high energy density, long cycle life and high thermal stability [69, 70]. Its operating temperature is over 300 ^{o}C in which sulfur (m.p. 118 ^{o}C) and sodium (m.p. 98 ^{o}C) are in liquid state. Beta-alumina solid electrolyte (β-Al$_2$O$_3$) is used as a separator. Final discharge product is Na$_2$S$_3$ with a 558 mAh/g theoretical capacity and 760 Wh/kg theoretical energy density [69]. Although Na/S batteries are commercially available for large scale systems, due to high operating temperature generated electricity is also used to heat up the system which leads to lower efficiency. Moreover, sulfur and polysulfides are corrosive and reacts with metallic sodium in case of a failure in β-Al$_2$O$_3$ solid electrolyte and may cause explosion. Room-temperature (RT) Na/S batteries with tetraethylene glycol

dimethyl ether (TEGDME) as an electrolyte is used to overcome disadvantages of solid electrolyte. Assuming Na_2S is the final product the sulfur cathode has a theoretical specific capacity of 1672 mAh/g and the theoretical energy density of 1230 Wh/kg/ which is much higher than high temperature Na/S battery. However room temperature Na/S batteries have several drawbacks such as insulating nature of sulfur and formation of non-conductive and non-soluble products (Na_2S) upon cycling [71]. In order to eliminate the formation of Na_2S, dissolved polysulfide (catholyte) rather than sulfur impregnated composites has been used resulting in superior performance compared with RT Na/S batteries. Although RT Na/S batteries have promising results formation of SEI layer, highly reactive metallic Na and expensive organic electrolytes prevents its commercialization due to cost and safety issues. Aqueous rechargeable batteries (ARB) could meet those criteria. ARB has many advantages over organic electrolyte battery which is mentioned above (Aqueous Electrolyte Rechargeable Alkali-ion Batteries).

As negative electrode dissolved polysulphides, whose potential is in the range of electrochemical stability of water (-0.5 V vs SHE) can also be used as in aqueous electrolyte Na-ion batteries. Although there is no work reported about the use of polysulfides in aqueous electrolyte Na-ion batteries, there are several research papers published about aqueous electrolyte Li-ion batteries. The idea of using of dissolved polysulfide in aqueous electrolyte was first studied by Licht et al in batteries and in photoelectrochemical solar cells [72-74]. Recently, Visco et al. patented lithium-sulphur batteries functioning in the aqueous electrolyte system [75]. However, use of highly expensive Li conductive membrane and limited cut-off voltage due to instability of water and resulted in lower capacity and prevented its possible applications. Demir-Cakan et al. proposed a new type of full cell configuration. Instead of high cost ceramic membrane, Li-ion conductive polymer was used as a membrane and transition metal oxide ($LiMn_2O_4$) as cathode instead of metallic lithium and dissolved polysulphides rather than solid sulfur/carbon composite as anode was used. The cell performed a 1.5 V output voltage with 110 mAh/g capacity over 100 cycles at high current density, which could compete with other conventional aqueous electrolyte systems such as NiMH or Pd–acid rechargeable batteries [76, 77].

3.EXPERIMENTAL PART

3.1. Synthesis of Cathode Materials

3.1.1. Synthesis of LiFePO4

FeSO$_4$.7H$_2$O, LiOH and H$_3$PO$_4$ were used for the synthesis of LiFePO$_4$ nanoparticles. Iron sulphate FeSO$_4$.7H$_2$O, 99.8%), lithium hydroxide (LiOH, 99.9%) and orthophosphoric acid (H$_3$PO$_4$ 85wt. %) were used without further purification as received from Sigma-Aldrich. LiFePO$_4$ is synthesized in three ways as follows:

3.1.1.1. Hydrothermal synthesis

LiFePO$_4$ cathode material was synthesized by hydrothermal method with H$_2$O and DMSO mixture (the volume ratio of glycerol and water is 1:1) for the synthesis FeSO$_4$, LiOH and H$_3$PO$_4$ (85%) in stoichiometric amounts of 1:3:1 were dissolved in deionized water/DMSO mixture separately. Then FeSO$_4$ and H$_3$PO$_4$ solution mixed followed by addition of LiOH with vigorous magnetic stirring for 30 min. This dark green viscous suspension was transferred into a Teflon® lined autoclave (Parr Instrument Company, 25 mL vessel size) and heated at 180°C for 12 h. Then gray-green precipitates were obtained and washed with water and acetone several times and dried at 70°C for 3h. Then the sample was mixed with 20 wt. % sucrose and the temperature was ramped to 700°C with a rate of 10°C /min. The heat treatment was performed under reducing atmosphere (5% H$_2$+ 95% Ar).

3.1.1.2. Solvothermal synthesis

Same synthesis procedure was applied on this method except Ethylene glycol was used as solvent instead of water/DMSO mixture. The idea of using EG is to prevent oxidation of Fe^{+2} to Fe^{+3} and as nucleation growth agent.

3.1.1.3 Microwave-assisted synthesis

In this method microwave synthesis reactor Anton-paar Monowave™ was used in order to synthesize LiFePO$_4$ nanoparticles. The microwave reactor could handle 6-20 ml reactant solution, to which 800 W microwave power could be delivered. Its working temperature ranges from room temperature to 200°C with control precision of ±1°C and the heating rate can reach over 100°C per minute. Microwave reactor can work up to 300 °C and 30 bars. Reactor was controlled by a computer program, so the reproducible heating profile and pressure can be implemented.

3.1.2. Synthesis of NaFePO$_4$

NaFePO$_4$ synthesis is accomplished in two different ways by chemical oxidation of LiFePO$_4$ and electrochemical displacement of Li$^+$ ions with Na$^+$. Solvothermal or hydrothermal methods were not applied. These synthesis approaches form maricite phase of NaFePO$_4$ which does not have electrochemical activity in contrast with electrochemically active olivine phase.

3.1.2.1. Chemical synthesis of NaFePO$_4$

Fully desodiated FePO$_4$, were prepared in Argon filled glovebox using stoichiometric amounts of NO$_2$BF$_4$ (95 %, Aldrich) in acetonitrile solvent (anhydrous, 99.8 %, Aldrich) according to the following reaction:

$$NaFePO_4 + NO_2BF_4 \rightarrow FePO_4 + NaBF_4 + NO_2 \qquad (2.1)$$
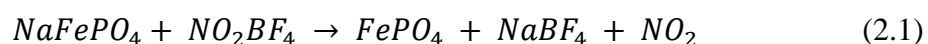
NO$_2$BF$_4$ is a strong oxidizing agent equivalent to a 4.8 V potential versus Na+ / Na. The solution was maintained at 60°C for 24 h. Final products of the desodiated phases were obtained by washing with acetonitrile using a centrifuge and dried in vacuum oven 2h at 80°C. Then obtained product is converted to NaFePO$_4$ by electrochemical oxidation performed in aqueous solution of 1M NaNO$_3$ for the

aqueous electrolyte battery and in EC:PC (50/50) 1 M $NaClO_4$ as the electrolyte for the organic electrolyte system.

3.1.2.2. Electrochemical synthesis of NaFePO₄

Fully sodiated NaFePO₄ were prepared directly electrochemical displacement of Li+ in LiFePO₄ with Na + in aqueous solution of 1M $NaNO_3$ for the aqueous electrolyte battery and in EC: PC (50/50) 1 M $NaClO_4$ as the electrolyte for the organic electrolyte system.

3.2. Synthesis of Anode Materials

3.2.1. Synthesis of K₂Sₓ and Na₂Sₓ

For the preparation of polysulphides, metallic sodium, sulphur and ethylene glycol diethyl ether were used without further purification as received from Sigma-Aldrich. K_2S_x is also bought form Sigma Aldrich All the reagents kept in glovebox and synthesis also performed in Ar filled glovebox. Reactions were made according to stoichiometric ratios of -sodium versus sulphur.

For example, in order to synthesize 1.7 g of Na_2S_3, 0.55 gram of metallic sodium which was cut into very small pieces and 1.15 gram of sulphur powder and 8 gram of ethylene glycol diethyl ether were mixed in a 50 mL vial, respectively. This mixture was heated at 50^oC by stirring for 2.5 h on a magnetic stirrer. Thereafter, the mixture was reheated gradually from 50^oC to 150^oC and kept for one day at same temperature without stirring. The next day, the solvent was transferred to a big beaker with a pasteur pipette and finally the mixture was dried at 150^oC to obtain the solid Na_2S_3 powder.

3.3. Electrochemical Methods

3.3.1. Electrode Preparation

3.3.1.1. Half Cell Electrode Preparation

The electrochemical characterization of the organic electrolyte batteries was carried out using Swagelok type cell. For the organic electrolyte half-cell configuration $LiFePO_4$ powders were mixed with Ketjen-black carbon (in a weight ratio of 80: 20). A mixture of 0.2 g of the active material and 0.02 g of Ketjen-black was ground in an agate mortar. Cathode was redried at 100 °C under vacuum for 3h and transferred to an argon filled glove box for storage before assembling the cells. The typical cathode loading was 7 - 10 mg powder.

Aqueous electrolyte half-cell performances were tested in a homemade system. Cathode was prepared by casting a slurry of $LiFePO_4$ Ketjen-black and polyvinylidene fluoride (80:10:10 wt.%) in N-methyl-2-pyrrolidinone. The solution in NMP was mixed overnight to form a uniform slurry mixture with suitable viscosity. The slurry was casted onto thin sheets of graphite current collector with the thickness 1mm and $2cm^2$ and dried at 80 °C in a vacuum oven overnight. The typical cathode loading was 3-5 mg powder. A three-electrode electrochemical cell was employed for cyclic voltammetry and half-cell galvanostatic charge-discharge tests. Saturated calomel electrode (SCE) and graphite sheet were used as reference and counter electrodes, respectively.

3.3.1.2. Full Cell

Cathode was prepared by casting slurry of $LiFePO_4$ as mentioned above except it is casted on $1cm^2$ graphite current collector. Anode active material was prepared by dissolving adequate amount of polysulfide either in lithium or sodium salts. Galvanostat/potentiostat VMP3. All the electrochemical measurements were conducted at room temperature.

K$_2$S$_X$ and Na$_2$S$_2$ solutions were prepared by dissolving 120mg of K$_2$S$_X$ in 0.25M Na$_2$SO$_4$ and 60mg Na$_2$S$_2$ in 0.25M Na$_2$SO$_4$.

3.3.2. Cell Construction

3.3.2.1. Half Cell

The organic electrolyte electrochemical cells (Swagelok type cells) were assembled using the lithium foil as anode. A porous Celgard film was used as separator. 1M LiPF$_6$ (lithium hexafluorophosphate) dissolved in a mixed solvent of ethylene carbonate (EC) and polypropylene carbonate (PC) (1:1 in weight) was used as an electrolyte for the lithium battery tests and Na foil and NaClO$_4$ (sodium perchlorate) were used for sodium battery tests. Cell assembly was carried out in a glove box filled with high purity argon gas, in which the water and oxygen concentrations were less than 1 ppm. The Swagelok cell component stacking sequence is shown [55] in Figure 2.4 and Figure 2.5 shows the flow chart for lithium ion coin cell fabrication.

3.3.2.2. Full Cell

For the full cell configuration, experiments were carried out using two-electrode Swagelok-type cells. Cathode was around 2-4 mg on graphite current collector, the electrolyte consisted of a solution of 2M of sodium (Na$_2$SO$_4$-NaNO$_3$) or lithium (LiSO$_4$-LiNO$_3$) salts dissolved in water and anode is composed of adequate amount of polysulfides dissolved in 0.25M sodium or lithium salts. Nafion membrane is used as an ion selective separator.

3.4. Electrochemical characterization

Electrochemical measurements were used to characterize the performance of the electrodes in a lithium-ion and sodium-ion battery systems. Cyclic voltammetry was used in order determine working potentials of cathode and anode active materials The

capacity and cycling performance of the materials were investigated by galvanostatic charge-discharge measurement at various current densities. Half-cell performances were measured versus Li/Li+ for the lithium batteries and versus Na/Na+ for sodium-ion batteries.

4. RESULTS and DISCUSSION

4.1. Electrochemical and Morphological Characterization

For the synthesis of $LiFePO_4$, three methods are used; solvotermal, hydrothermal and microwave assisted synthesis routes. Among those methods, hydrothermal synthesis procedure showed the best results which are consistent with literature. Delacourt et al. showed that $LiFePO_4$ nanoparticles could be synthesized in water/DMSO as solvent with less than 200 nm particles size with a narrow size distribution [78].

Narrow particle size distribution is a key parameter for uniform carbon coating and homogenous current distribution in electrode which will decrease Li^+ diffusion path length and eventually result in better battery performance. All the electrochemical and morphological results are based on optimized hydrothermal synthesis of $LiFePO_4$ nanoparticles.

The phase purity of the $LiFePO_4$ nanoparticles was analyzed by X-ray powder diffraction. XRD pattern of $LiFePO_4$ in Figure 4.1 shows no impurities. Generally hydrothermal route results in some impurities mainly Fe_2O_3 due to oxidation of iron. In order to prevent that $FeSO_4.7H_2O$, which is used as iron source, dissolved in solvent mixture without heating and also argon was purged to remove dissolved oxygen.
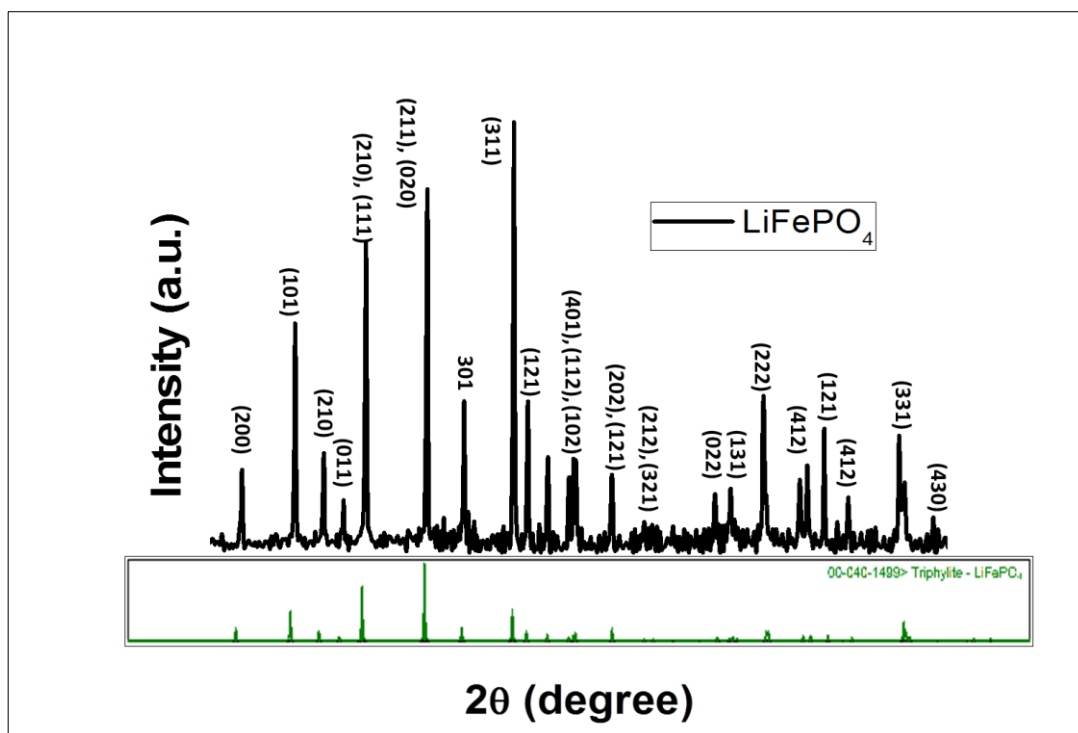
Figure 4.1: XRD pattern of carbon coated LiFePO₄/C nanoparticles.
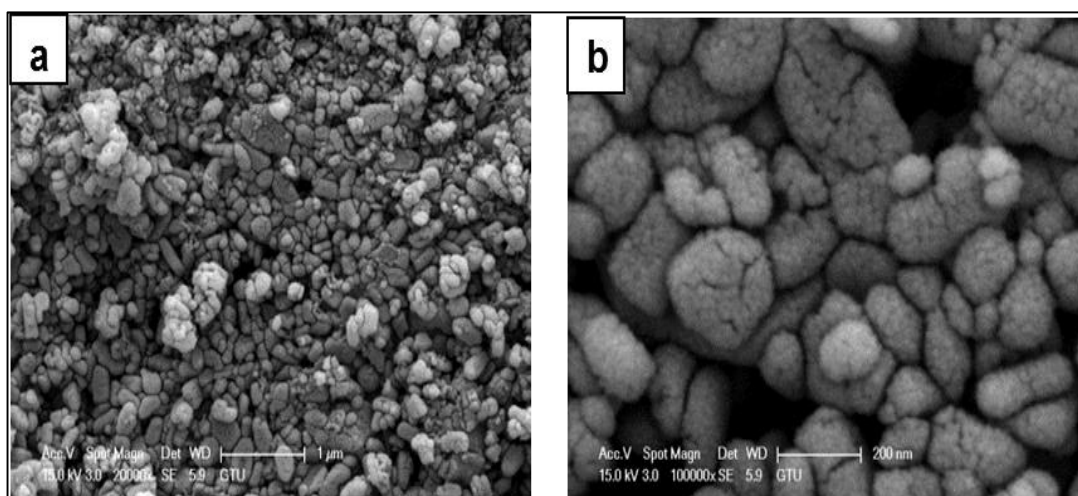
Figure 4.2: SEM images of LiFePO₄ nanoparticles in different magnifications at a) 20000x, b)100000x.

SEM images (Figure 4.3) show that the LiFePO₄ nanoparticles were synthesized with uniform size distribution under 200 nm. Also there is no agglomeration is observed. Hard agglomerated particles would result in bad cycling performance. Figure 4.3 shows the voltage profiles during galvanostatic charge and discharge of LiFePO₄/C at 34 mA/g (0.2 C) rate for 20 cycles. Charge-discharge

profile seen in Figure 4.3 depicts the low polarization which is due to small particle size and uniform carbon coating. The cycle performance of LiFePO$_4$/C composites at a current density of 34 mA/g (0.2 C) and 170 mA/g (1 C) is shown in Figure 4.4. No capacity fading is observed over the charge/discharge cycles, demonstrating an excellent cycling performance for LiFePO$_4$/C composites. LiFePO$_4$/C nanoparticles show around 155mAh/g and 140mAh/g capacity at 0.2C and 1C rates subsequently.
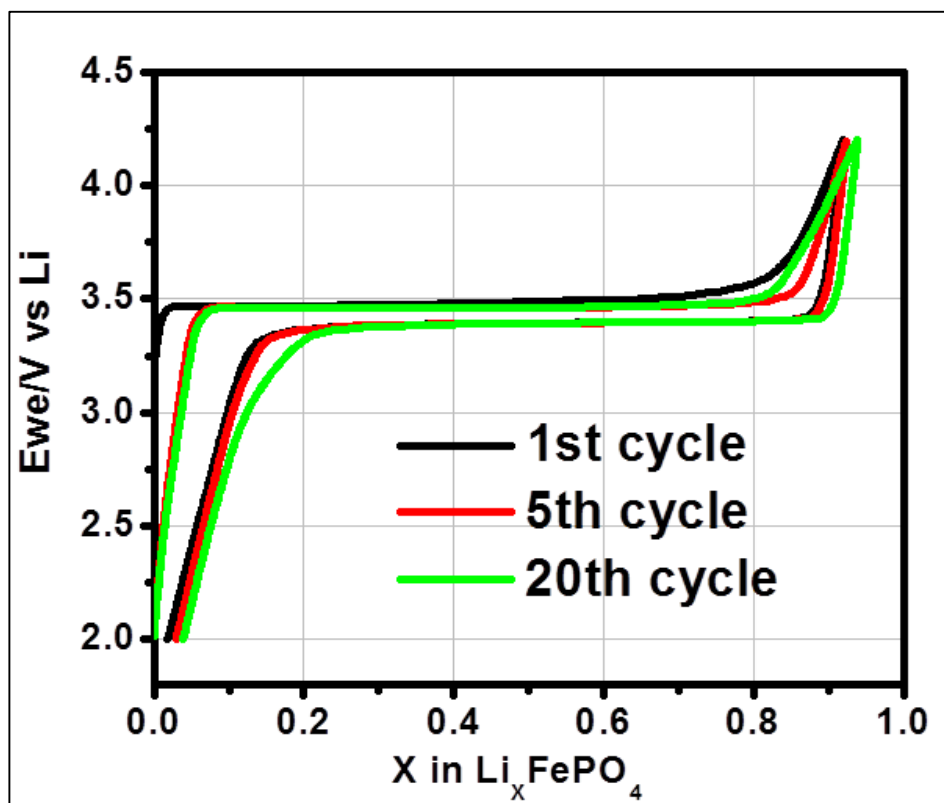
Figure 4.4: Charge-discharge profile of LiFePO$_4$/C at C/5 rate in 1M LiPF$_6$ dissolved in EC:PC (1:1 in weight).
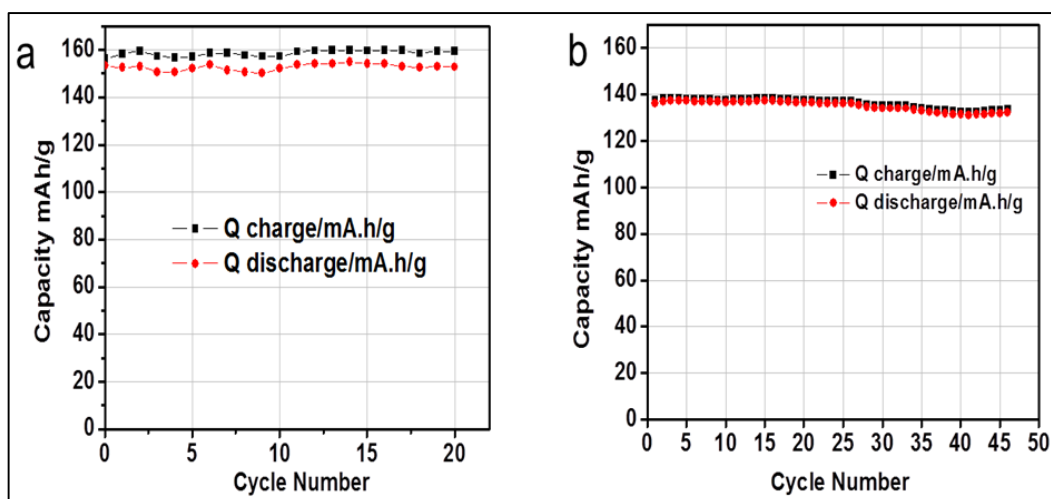
Figure 4.5: Cycling performance of LiFePO$_4$/C in 1M LiPF$_6$ dissolved in EC:PC (1:1 in weight) a) at C/5 and b) at C/1.

Hydrothermal synthesized LiFePO$_4$/C composite nanoparticles showed excellent cycling performances at different rates in organic electrolyte. Then electrochemical performances of LiFePO$_4$/C particles in aqueous electrolyte performed. First of all working potential of the material in 1 M LiNO$_3$ solution is determined. It is found to be -0.4V-0.8V vs SCE. Cyclic voltammetry and galvanostatic charge-discharge tests were performed at pH 7 shown in Figure 4.5. High capacity fading is observed in aqueous electrolyte compared to organic electrolyte, because the capacity fading of LiFePO$_4$ in aqueous is affected both from chemical instability and electrochemical instability of LiFePO$_4$.

In the literature it is shown that the capacity fading is due to side reactions with dissolved oxygen, OH$^-$ and H$_2$O [57, 58]. Thus, basic or acidic conditions are detrimental to battery performance. It is also shown that depending on immersion time active materials are dissolved in water.
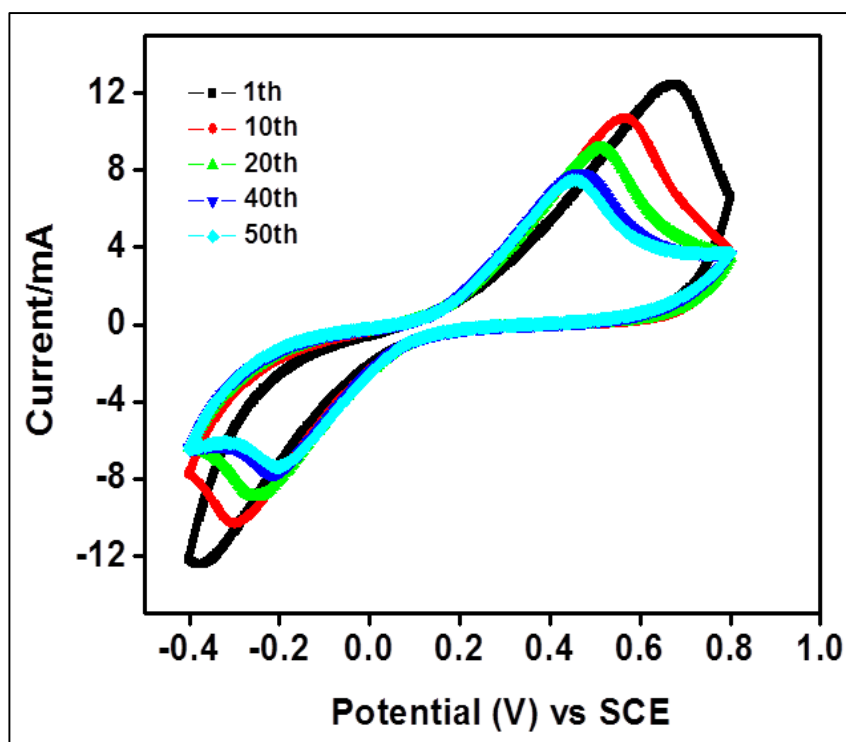
Figure 4.6: CVs profiles of LiFePO$_4$ for 50 cycles, taken at a scan rate of 5 mV/s in 1M LiNO$_3$ solution at pH 7.

Figure 4.7: a) Charge-discharge profile and b) galvanostatic cycling performance of LiFePO$_4$/C in 1M LiNO$_3$ aqueous solution at C/1 rate.

4.2. The Impact of Carbon Coating

As it is mentioned above when LiFePO$_4$ is exposed to dissolved oxygen, side reactions occur. Possible reactions involved are shown below in the presence of dissolved O$_2$ and H$_2$O.

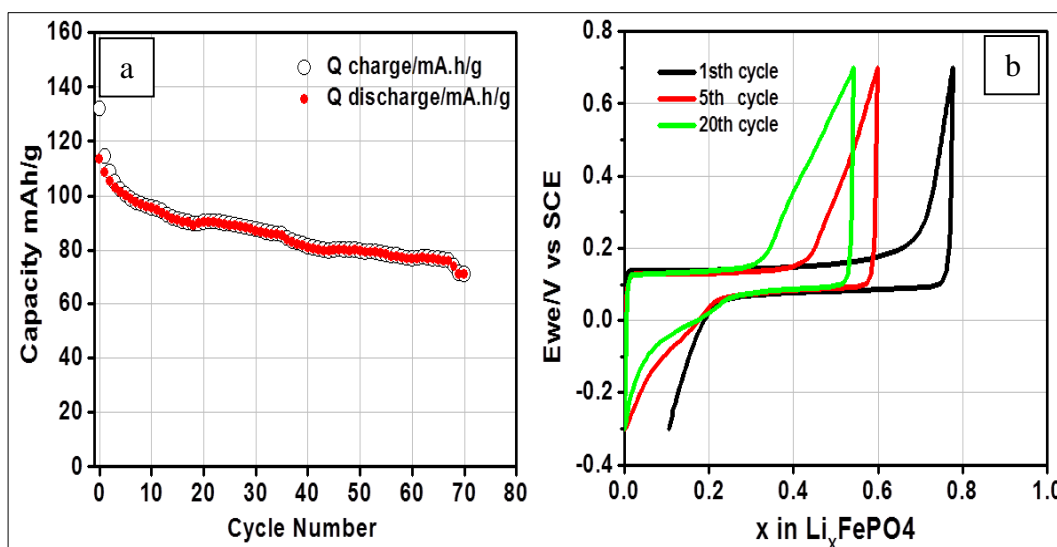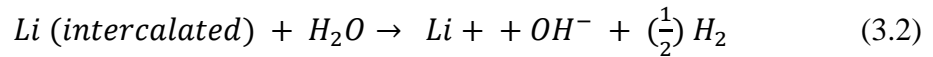$$Li\ (intercalated)\ +\ \left(\tfrac{1}{4}\right) O_2\ +\ \left(\tfrac{1}{2}\right) H_2 O\ \rightarrow\ Li +\ +\ OH^- \qquad (3.1)$$

$$Li\ (intercalated)\ +\ H_2 O \rightarrow\ Li +\ +\ OH^-\ +\ \left(\tfrac{1}{2}\right) H_2 \qquad (3.2)$$
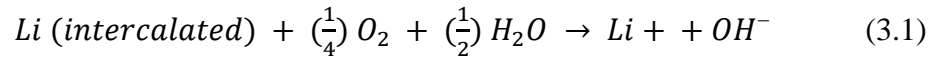
The calculated potential of the lithium intercalated compound V(x) in equilibrium with H$_2$O at a particular pH is shown as:

$$V(x)\ =\ 4.268\ -\ 0.059\ pH\ vs\ (Li/Li+)/V \qquad \text{Eq. (1)}$$

Equilibrium potential of lithium intercalated compound in H$_2$O as a function of pH value were plotted in Figure 7 in ref [58]. According to this data equilibrium potential of lithium intercalated compound in H$_2$O at pH 7 is 3.85 V which is slightly higher than intercalation potential of LiFePO$_4$ that is about 3.45 V. It is therefore likely that LiFePO$_4$ would theoretically be chemically oxidized by the O$_2$ instead of undergoing the electrochemical redox process. It can thus be suggested that some of the capacity loss of LiFePO$_4$ at pH 7 is because of the chemical instability of the electrode. It is also found that partial oxidation products of O$_2$ are H$_2$O$_2$ and OH$^-$. Possible reaction mechanisms are suggested as below:

$$Fe(II) +\ H_2 O_2\ \rightarrow\ Fe(III) +\ OH^- + OH^\bullet \qquad (3.3)$$

$$Fe(II)\ +\ OH^\bullet\ \rightarrow\ Fe(III)\ +\ OH^- \qquad (3.4)$$
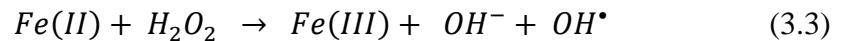
The experimental evidence on LiFePO$_4$ electrochemical performance in aqueous electrolyte is found that dissolved O$_2$ greatly affects the capacity fading while the active material does not have carbon coating shown in Figure 4.7.
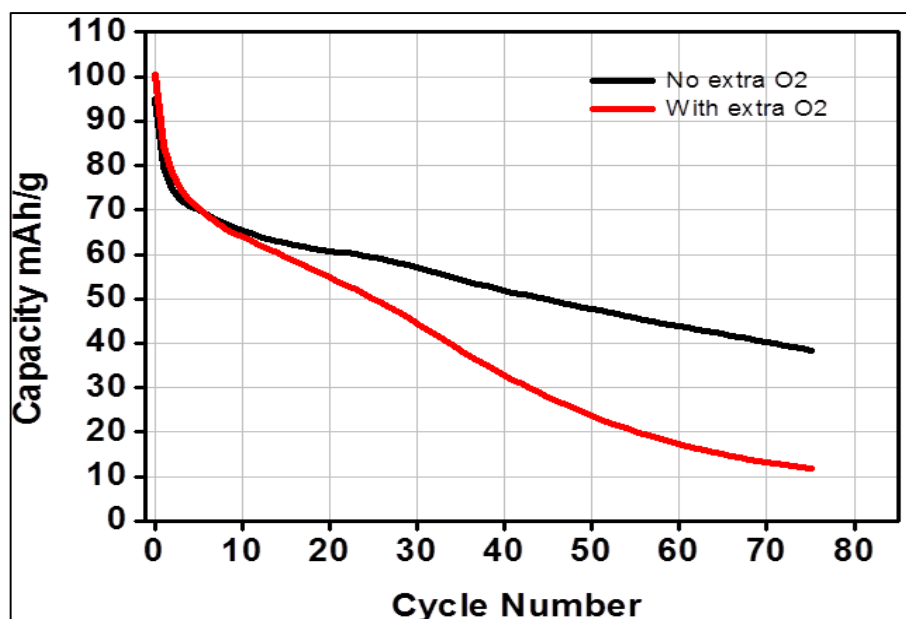
Figure 4.8: Galvanostatic cycling performance of pure LiFePO$_4$ in 1M LiNO$_3$ aqueous solution at C/1 rate. 2h oxygen was purged for the red line cell.

While carbon coating is used to increase the electronic conductivity of LiFePO$_4$ in organic electrolyte it the empirical findings in this study provide that carbon coating not only increase the electronic conductivity but also blocks the attack of oxygen and OH$^-$ ion by carbon layer therefore decreased capacity fading. Figure 4.8 demonstrates the effect of carbon coating.
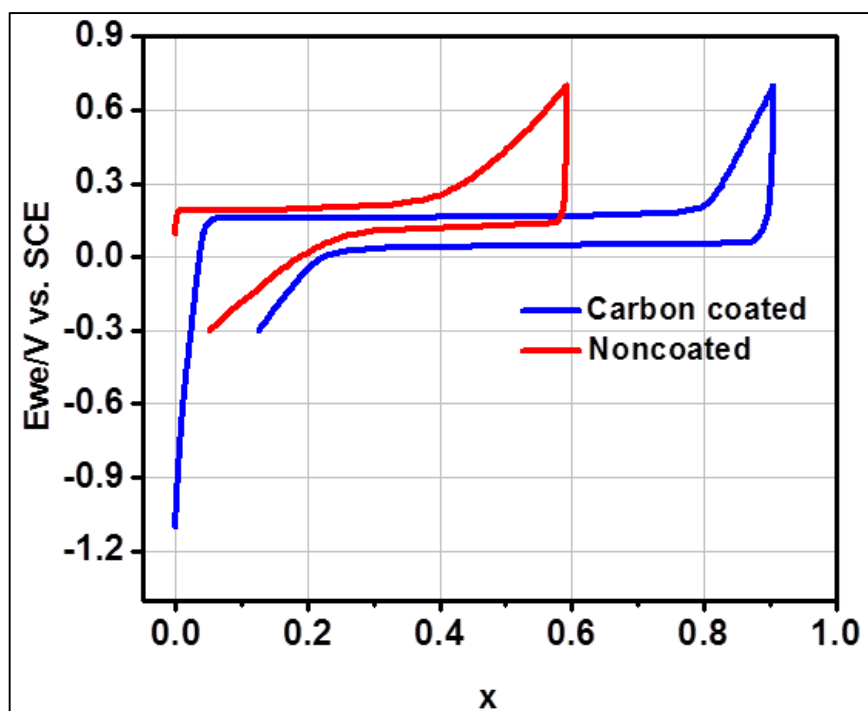
Figure 4.9: First charge-discharge profile of carbon coated and uncoated
LiFePO$_4$ in 1M LiNO$_3$.

Although the evidence from this study suggests that carbon coating does provide an effective way for preventing the capacity fading, it is not a solution itself. In order to further decrease capacity fading, the idea of cathode electrode coating which is composed of LiFePO$_4$/C, PVDF and Ketjen Black (80:10:10) was suggested. Therefore, 50 mg of cathode slurries were casted on two graphite plates then one is coated with Nafion by using print screen while the other did not have nafion coating. After that two graphite plates placed in 1 M LiNO$_3$ solution and ICP measurements performed. Table 4.1 shows the comparison of dissolved Fe^{+2} ions concentration of Nafion coated and uncoated sample as a function of immersion time without any pH modification.

Table 4. 1: Time dependent dissolved Fe^{+2} ions concentration of coated and noncoated samples at neutral pH

Time	Uncoated sample (ppm)	Coated sample (ppm)
1 day	44.8	38.02
3 days	140.65	55.32
5 days	189.6	70.40
10 days	265.55	105.75

ICP results revealed that nafion coating blocks the attack of O^2 and OH^- ion. It is apparent from Table 4.1 ICP-MS results are consistent with galvanostatic charge-discharge studies (Figure 4.9) and suggest that active material dissolution is decreased but not completely prevented. Therefore, further research should be done to optimize the coating thickness and coating method which would results in better capacity retention.

The most striking result to emerge from the Figure 4.9 is that until 20th cycle uncoated sample shows slightly higher capacity although capacity retention is higher. A possible explanation for this might be that nafion pores prevents the Li^+ intercalation but by the time pores get bigger as the intercalation proceeds.
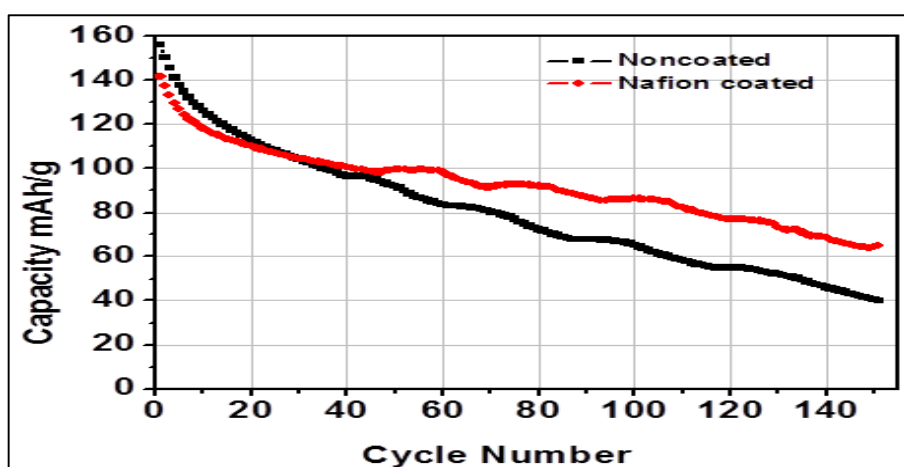

Figure 4.10: Galvanostatic cycling performance of nafion coated and uncoated LiFePO$_4$/C in 1M LiNO$_3$ aqueous solution at C/1 rate.

Until now electrochemical and morphological characterization results of LiFePO$_4$ are shown. Hereafter electrochemical results of NaFePO$_4$ will be discussed. Chemical synthesis synthesis (hydrothermal, solvothermal etc.) resulted in electrochemically non-active maricite phase of NaFePO$_4$ and also chemical oxidation of LiFePO$_4$/C disturbs the uniform carbon coating resulting in bad electrochemical performance As mentioned in the experimental part NaFePO$_4$ is synthesized by electrochemical displacement method

Contrary to LiFePO$_4$ where Li$^+$ extraction occurs in symmetrical biphasic mechanism, Na extraction occurs in two phases. Na$_{0.7}$FePO$_4$ behaves as intermediate phase. Two phase extraction of Na ions is shown in cyclic voltammetry data in Figure 4.10. From that figure complete conversion of LiFePO$_4$ to NaFePO$_4$ is observed in the first cycle. In the following cycles Li extraction peak (black) is not observed proving that no Li-ions are left in the structure. In situ XRD studies are also performed (Figure 4.11-4.12) demonstrating that conversion of LiFeP$_{O4}$ to NaFePO$_4$ is accomplished.

The requirement for an intermediate phase is due to the large cell volume mismatch between NaFePO$_4$ and FePO$_4$ (17.58% in volume). While LiFePO$_4$ transformation into FePO$_4$ occurs without intermediate phase because cell volume mismatch is only (6.9% in volume). Hence there is no additional phase is observed.

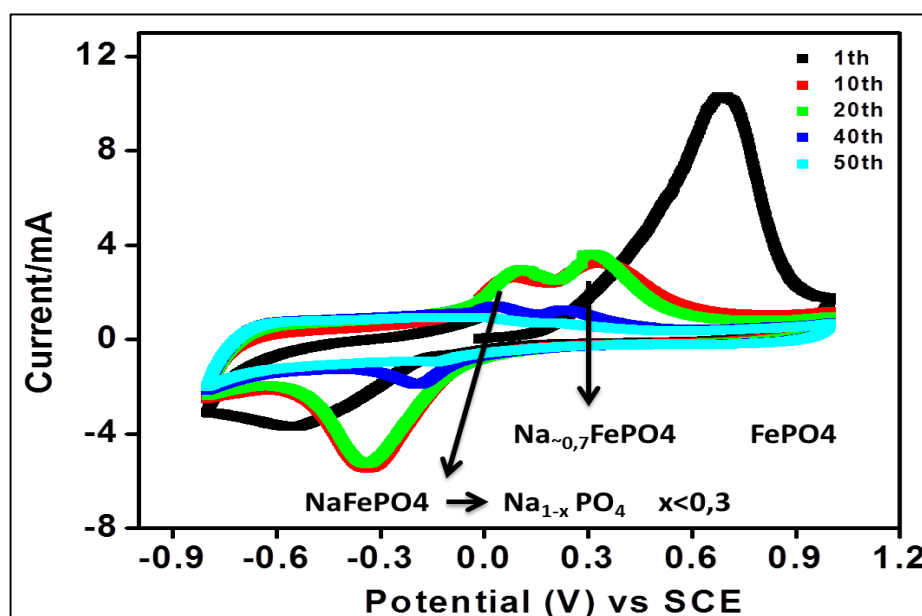Figure 4.11: The cyclic voltammograms of LiFePO$_4$/C in 1M NaNO$_3$ aqueous solution recorded at 5mV/s.
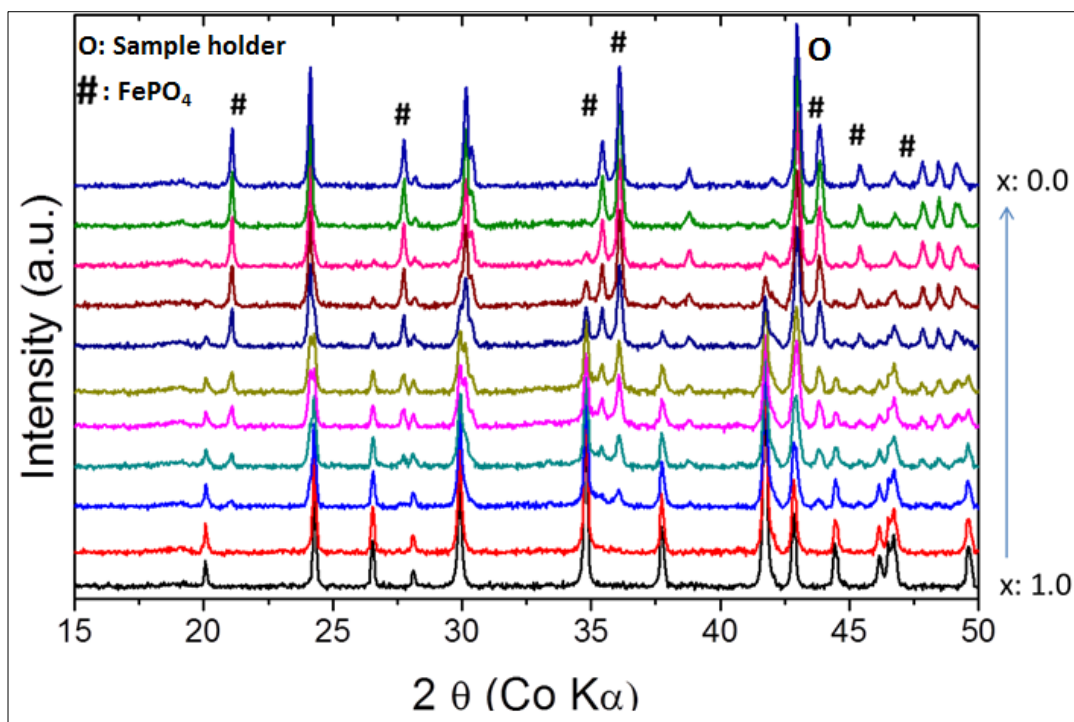
Figure 4.12: In situ XRD data of LiFePO$_4$ to FePO$_4$ conversion.
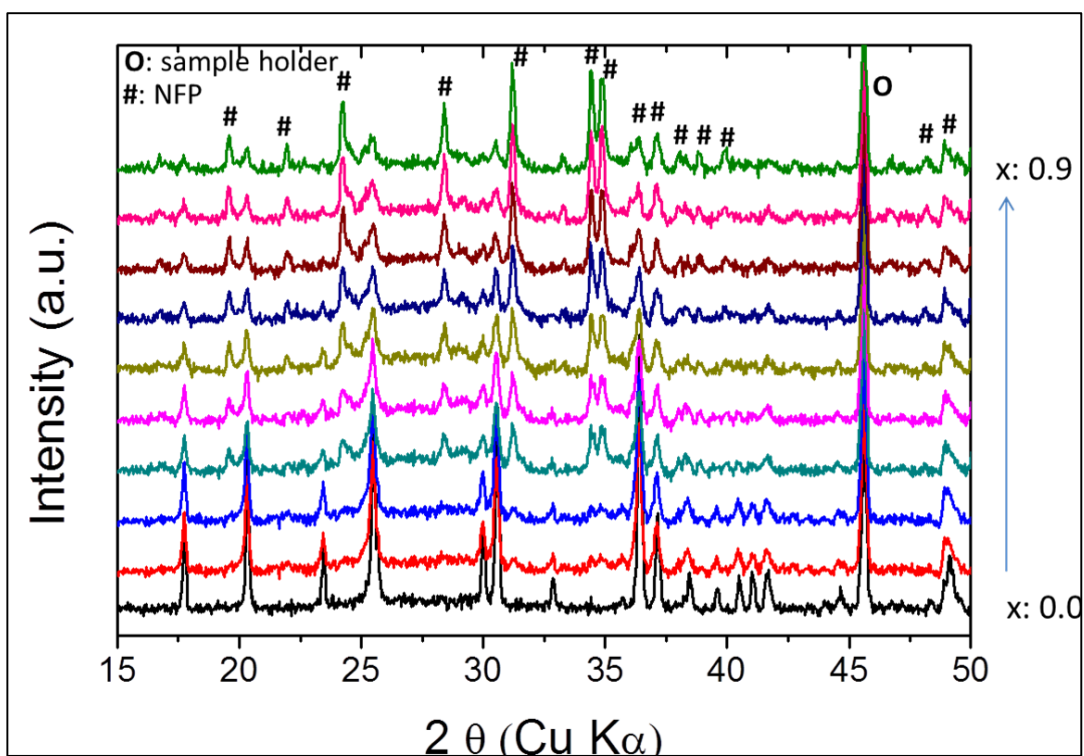
Figure 4.13: In situ XRD data of FePO$_4$ to NaFePO$_4$ conversion.

Working potential of NaFePO$_4$ is found to be -0.8V / 1V vs SCE. Thereafter galvanostatic charge-discharge experiments performed. Figure 4.13 a) shows the

voltage profiles during galvanostatic charge and discharge of NaFePO$_4$/C at 154 mA/g (1 C) rate for 20 cycles. Charge-discharge profile seen in Figure. 4.13 a) shows high polarization which is due to occurrence of two different phases during Na$^+$ extraction. The cycle performance of NaFePO$_4$/C composites at a current density of 154 mA/g (1C) is shown in Figure 4.13 b). Capacity fading is observed over the charge/discharge cycles, although in the first cycle Li$^+$ is almost fully extracted. NaFePO$_4$/C nanoparticles show around 45 mAh/g capacity at 1C rate over 100 cycles.
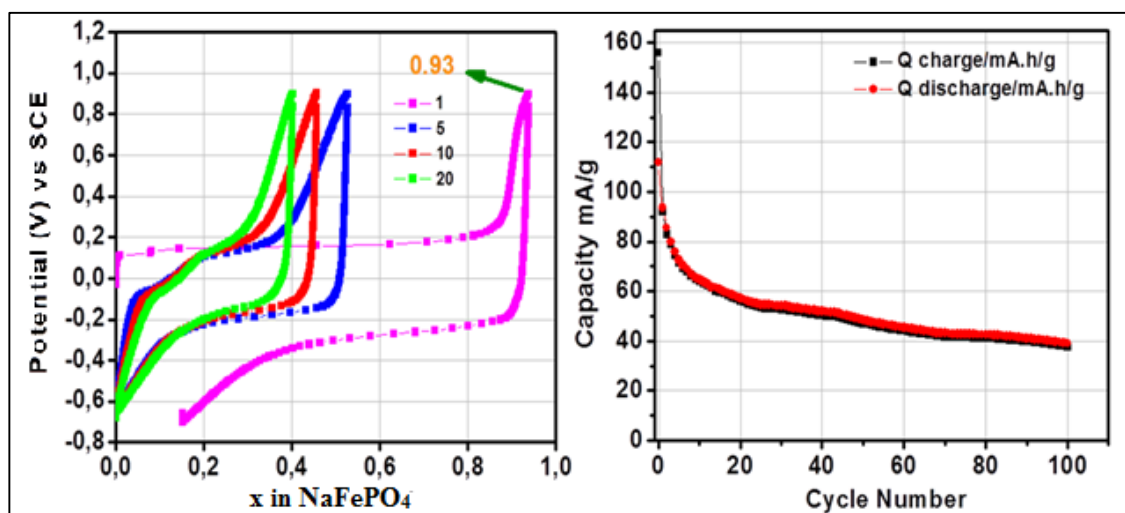
Figure 4.14: a) Charge-discharge profile and b) galvanostatic cycling performance of NaFePO$_4$ in 1M NaNO$_3$ aqueous solution at C/1 rate.

As mentioned above in the Nafion coating on LiFePO$_4$ shows lower capacity fading. Same experimental produce is also made for NaFePO$_4$. Figure. 4.14 shows the effect of nafion coating on the cycle performance of NaFePO$_4$. At the end of 50 cycles it is seen that uncoated sample has a capacity of about 40 mAh/g, while coated sample has about 70 mAh/g of capacity.
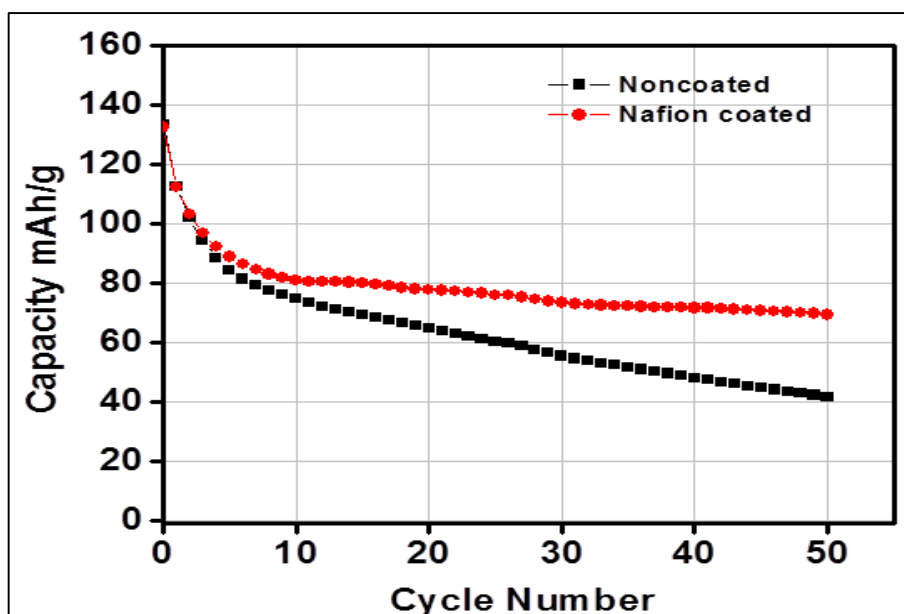
Figure 4.15: Galvanostatic cycling performance of nafion coated and uncoated LiFePO$_4$/C in 1M NaNO$_3$ aqueous solution at C/1 rate.

4.3. Electrochemistry of Polysulfide Compounds

After performing the electrochemical studies of LiFePO$_4$ and NaFePO$_4$ positive electrode materials, electrochemical properties of polysulfide compounds are found.
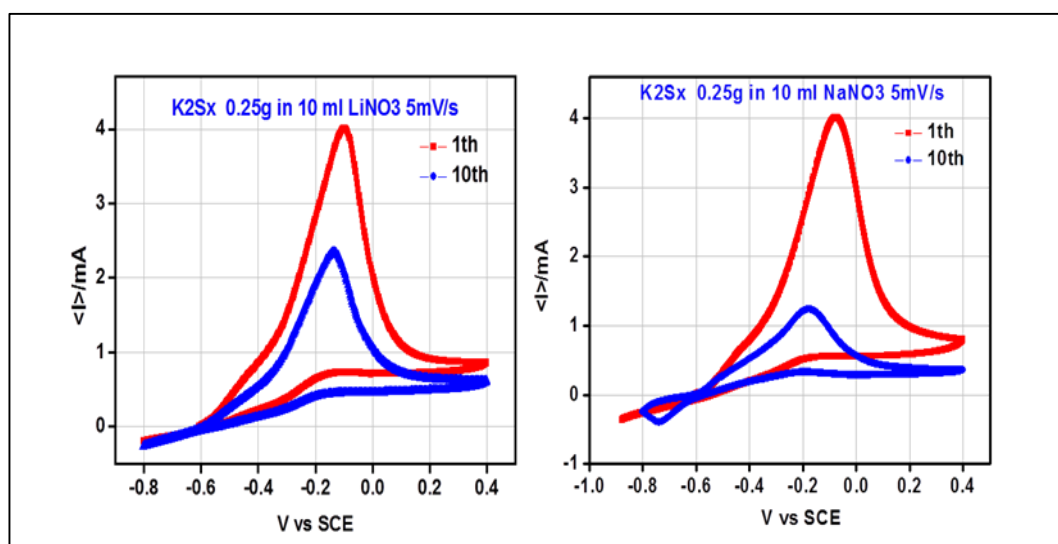
Figure 4.16: Cyclic voltammograms of dissolved polysulfide at a scan rate of 5 mV/s over 1.0–0.3 V vs. SCE.
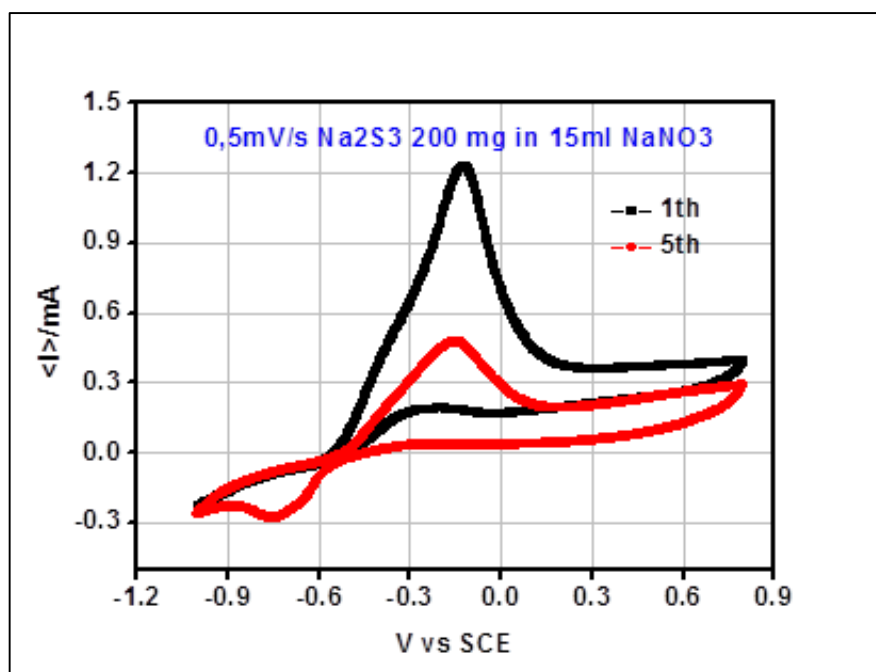
Figure 4.17: Cyclic voltammograms of dissolved polysulfide at a scan rate of 5 mV/s over -1.0 / 0.8 V vs. SCE

CV of the dissolved polysulphides, K_2S_X in both 1 M $LiNO_3$ and 1 M $NaNO_3$ aqueous solutions at a scan rate of 5 mV/s is shown in Figure 4.15 and in 4.16 CV of dissolved Na_2S_3 is in 1 M $NaNO_3$ is shown.
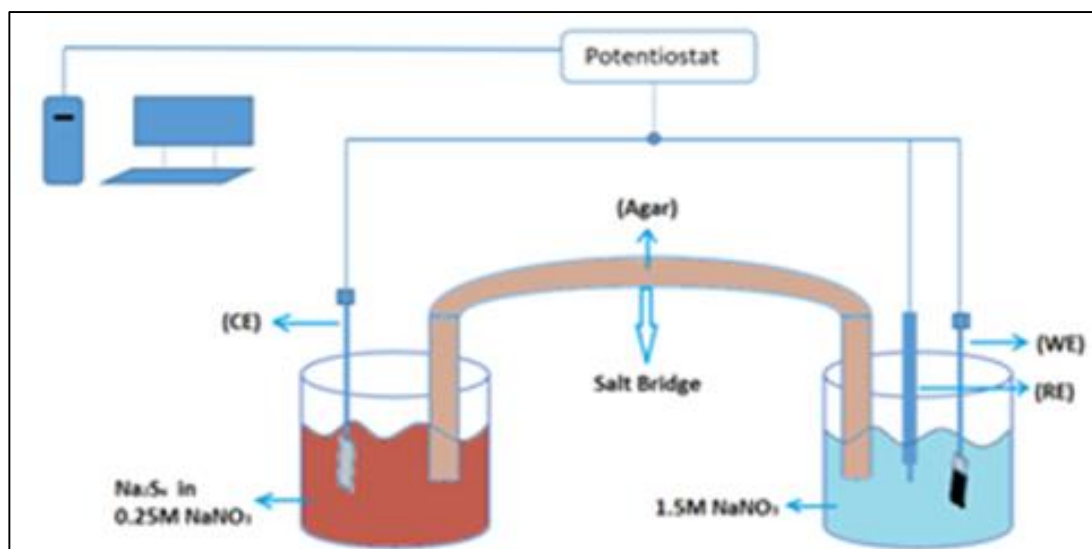
Figure 4.18: Schematic representation of a galvanic cell design used for the experiments in which $LiFePO_4$ is used as WE and dissolved polysulfide as CE.
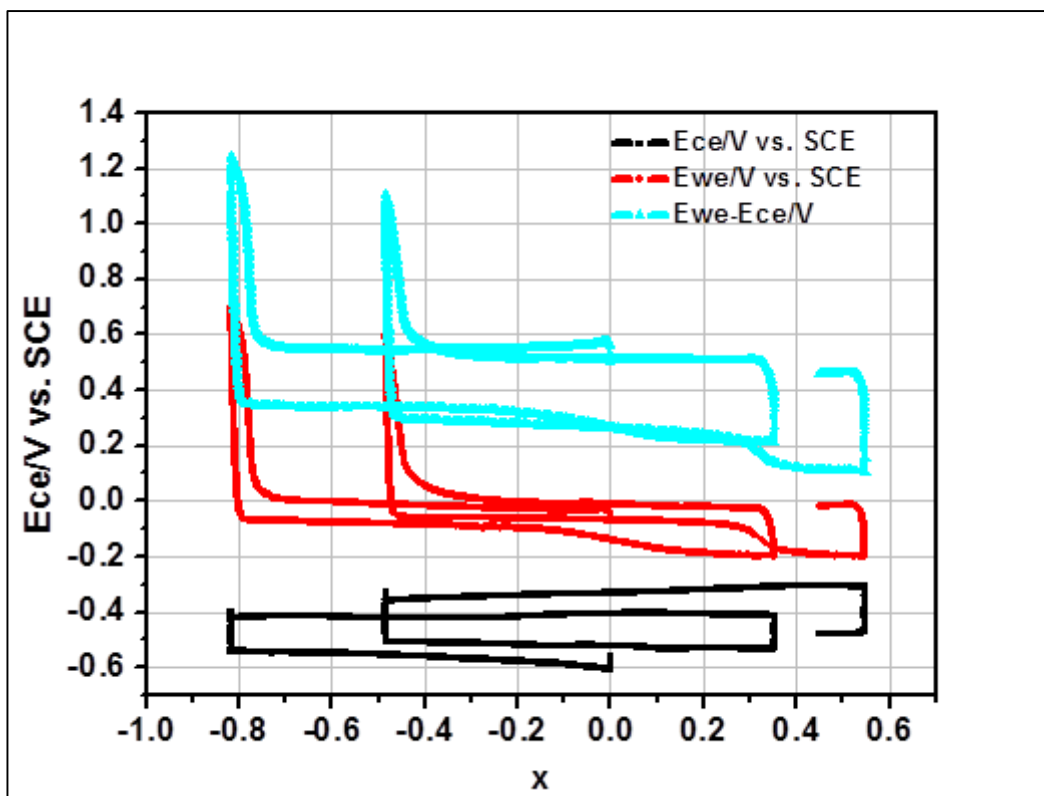
Figure 4.19: Half-cell galvanostatic performance of LiFePO$_4$ (red), dissolved polysulfide (black) and full cell light blue at a current density of C/50.

The results obtained from the preliminary analysis of the full cell shows that working potential of LiFePO$_4$/Na$_2$S$_3$ is between 0 to 1 V. Therefore, electrochemical tests of the full cell were made in that voltage range.
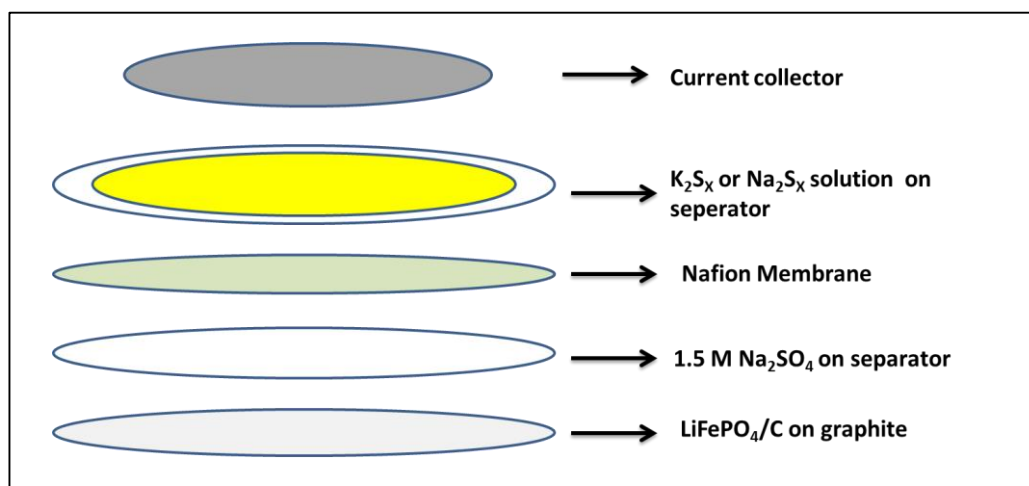
Figure 4.20: Schematic representation of Swagelok type full cell.

Briefly for the full cell experiments LiFePO$_4$ slurry used as positive electrolyte, a separator is placed on it and 1.5 M - 1 ml Na$_2$SO$_4$ solution used as electrolyte. Then 25.4mm-thick NAFION® Membrane NR-211 is placed. The idea of using Nafion membrane is to prevent leakage of the polysulphides. Anot side is prepared from polysulfide solution dissolved in 0.25M Na$_2$SO$_4$sodium. Before assembling full cell configuration, membrane leakage and polysulphide diffusion tests were performed. Leakage of the polysufides is detrimental to battery performance. Therefore, it is important to have equal amount of ion concentration on bothsides (anode and cathode).
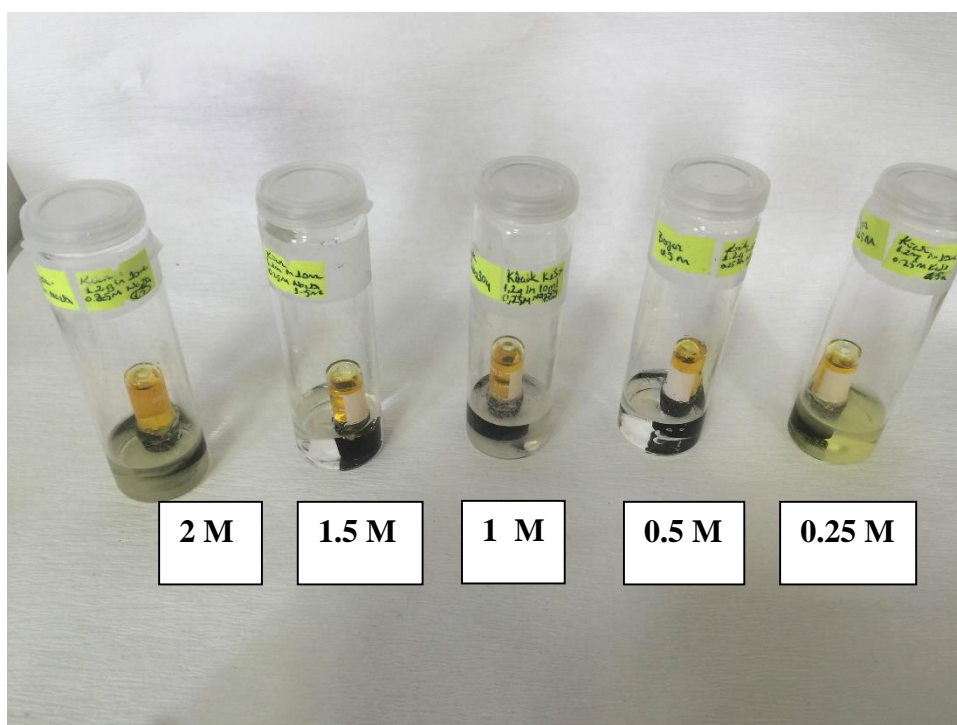
Figure 4.21: Experimental setup nafion membrane polysulphide leakage test with different salt concentrations after variable resting times.

In the small vials 0.25 M polysulphide dissolved in Na$_2$SO$_4$ salt and nafion membrane placed on the top of the lid. On the other side different concentration Na$_2$SO$_4$ solution are used. After several days, it was observed that with 1.5M and 0.5M salt solutions ion concentration can be equalize, hence diffusion of polysufide can be prevented. In the electrochemical experiments 1.5 M salt solution is used since the ionic conductivity is higher than 0.5M salt solution.

In Figure 4.21 and 4.22 cycling performance of full cell batteries at 1 C rate are shown. It is apparent from the graphs that both polysulfides (Na_2S_2-Na_2S_3) shows about 40 mAh/g capacity around 0.7V without any capacity fading over 100 cycles.
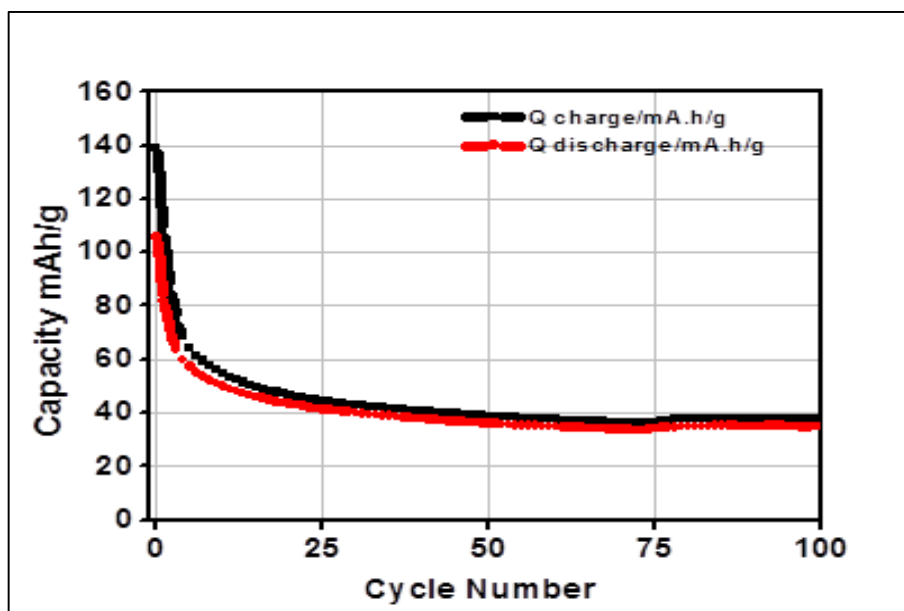
Figure 4.22: Cycling performance of the aqueous electrolyte $LiFePO_4$– Na_2S_2 polysulphide cells at a 1 C current density. Capacity values refer to $LiFePO_4$, whose theoretical capacity is 170 mAh/g.
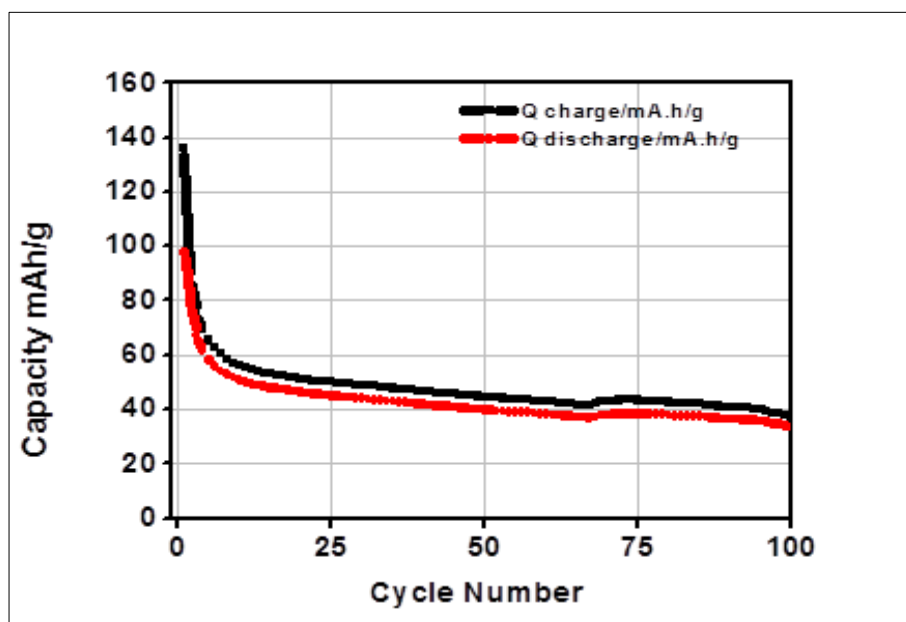
Figure 4.23: Cycling performance of the aqueous electrolyte $LiFePO_4$– Na_2S_3 polysulphide cells at a 1 C current density.

5. CONCLUSION

In summary, in this dissertation first of all $LiFePO_4$ nanoparticles with less than 200 nm is synthesized by using H_2O and DMSO mixture as solvent. Electrochemical performances in both organic and aqueous electrolyte solution are performed. In organic electrolyte $LiFePO_4$/C nanoparticles showed excellent results about 155mAh/g and 140mAh/g capacity at 0.2C and 1C rates, respectively. In contrast to organic electrolyte in aqueous electrolyte showed faster capacity fading due to the side reactions with O_2 and OH^- and dissolved active material. In order to prevent fast capacity fading, cathode material coated with Nafion membrane and it is found to prevent dissolution of active material that is confirmed both with ICP and electrochemical experiments.

Secondly $NaFePO_4$ is synthesized by aqueous electrochemical displacement from $LiFePO_4$. At the end of 50 cycles $NaFePO_4$ has a capacity of about 40 mAh/g. Nafion coating also increased capacity retention reaching to 70 mAh/g after 50 cycles.

Lastly electrochemical properties of polysulfides such as K_2S_X and Na_2S_X are investigated as anode materials. Cyclic voltammetry and galvanostatic charge-discharge experiments performed. Then full cell experiments are done combining $NaFePO_4$ as positive electrode and Na_2S_X (X= 2, 3) as negative electrode. Those full cells show about 40 mAh/g capacity around 0.7V over 100 cycles.

The results of this investigation show that with high solubility and cheapness polysufides are promising anode materials for rechargeable sodium-ion batteries for large-scale energy storage applications. It is possible to manufacture high energy density sodium ion batteries that consist of earth abundant elements. Further research might explore the increasing the working voltage of the battery by combining with other electrode materials.

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BIOGRAPHY

Serkan Sevinç was born, in Istanbul, Turkey. He graduated from Kagıthane Anotolian Higschool. He received a B.S. degree from Department of Chemistry of Fatih University and and M. S. degree from the Department of Materials Science and Engineering of Gebze Technical University in 2016. He is currently a Ph.D. candidate in the same department. His research activity is focused on developing novel cathode materials for aqueous electrolyte Na-ion batteries.