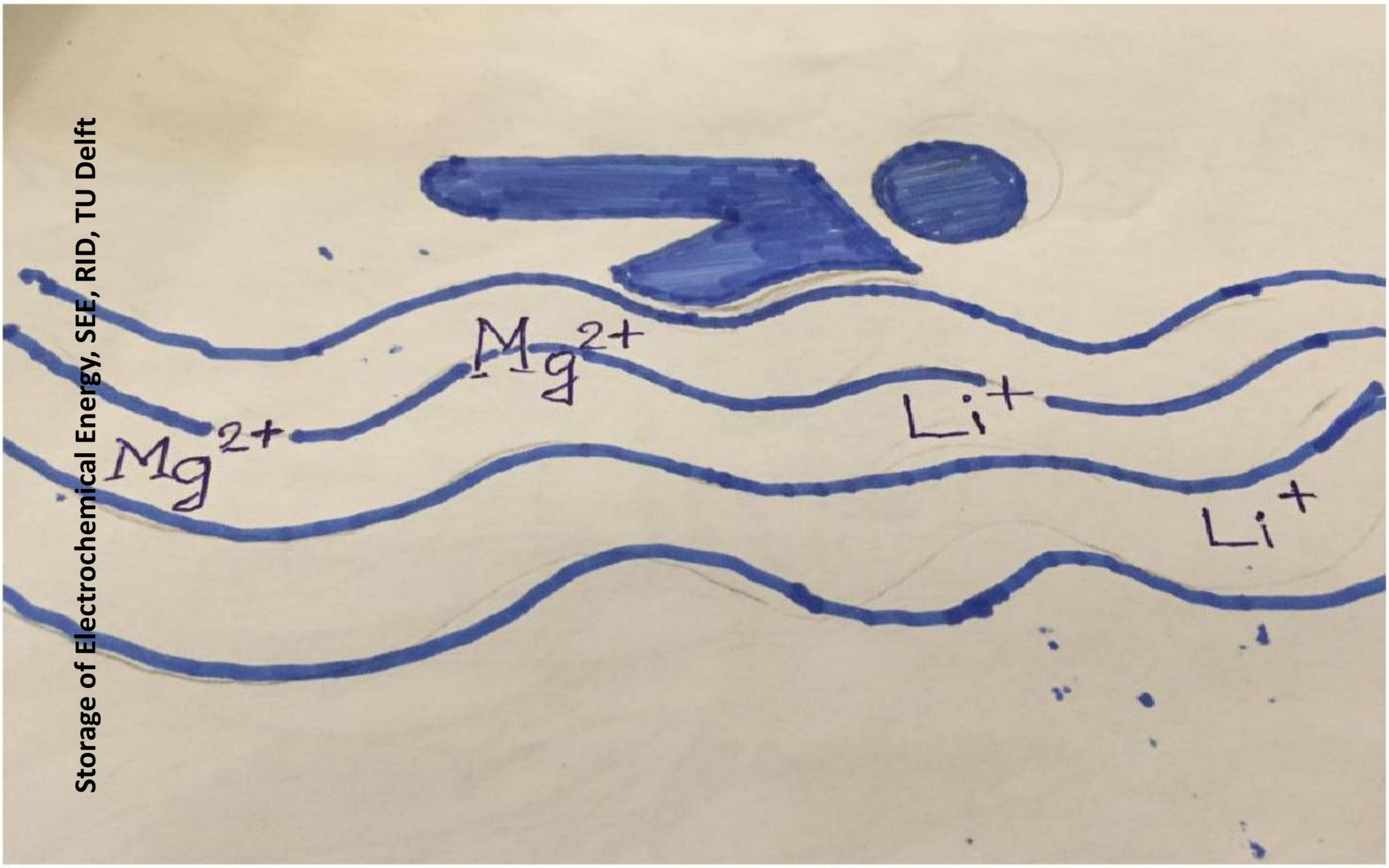
Perylene as Cathode for Magnesium Batteries

A feasibility study

Bhavya Shetty



Storage of Electrochemical Energy, SEE, RID, TU Delft

TU Delft

Perylene as Cathode for Magnesium Batteries

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by

Bhavya Shetty

in partial fulfillment of the requirements for the Master of Science in

Sustainable Energy Technology

at Delft University of Technology,
to be defended publicly on Wednesday August 14, 2019 at 9:30 AM.

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This thesis is confidential and cannot be made public until August 15, 2019.

TUDelft Delft University of Technology

Acknowledgement

First and foremost, I sincerely thank Dr. Erik Kelder for his supervision during this period and Dr. Wolter Jager for agreeing to share the organic material for battery testing. I would also like to thank Frans, SEE's dearest and most favorite resource without whom this project would have come to a standstill. The laughs, the chats, the whistles, the advices; Frans, you truly are the best. A big shout out to Remco, who, in spite of not being my direct supervisor has helped me in ways I cannot even imagine!

Rense, I am going to miss our lunch breaks, and Mina, thanks for being there at every instant. Thanks to Anjali, Mindy and my fellow master folks for keeping up with my raging moments. Radha, even though you have been missing in action, thanks for the wonderful times in Korvezeestraat/EWI!

Thanks Michiel Zaayer for being the best professor I have ever come across in the TU, you are filled with warmth and goodness, you have restored my faith in humanity! Continue spreading your awesomeness!

Last but not the least, I love my parents and my little pup bobo, who motivates me to be happy each day irrespective of what's in store. She's my life!

Bhavya Shetty
Delft, August 2019

Abstract

The transition to renewable energy creates a mismatch between energy production and consumption. Batteries are a good way to store energy and solve this mismatch. Batteries store renewable energy and supply to the grid when necessary. In order to make a successful transition towards renewable energy, the search for high capacity, low cost battery systems are on the rise.

Magnesium ion batteries (MIB) have attracted much attention from battery researchers around the globe. Magnesium is divalent in nature and offer a higher theoretical capacity than that of lithium. However, the magnesium research is still in the niche stage and the search continues for better electrolyte systems and for high voltage cathode materials. Currently, extensive research is being done in employing organic materials for battery cathode materials. Organic materials are made from naturally occurring compounds and are easy to dispose since they have no metals. Perylene diimide is an organic material gaining importance as cathode material in metal ion batteries.

The goal of the project is to determine the voltage window of perylene in lithium and magnesium battery systems. Cyclic Voltammetry (CV) is employed to measure the electrochemical activity of the cell. The output of the CV is a scan of the current versus the voltage. During the operation of the cell, duck shaped peaks are observed which correspond to the reduction/oxidation activity of the cathode and the anode respectively. The current corresponding to the peaks is used to determine the cathodic and anodic current of the cell. Once the voltage and the current are known, the area under the peaks is calculated to determine the charge/discharge capacity of the cell.

Since no prior research was done on magnesium, the most common cathode material (inorganic), chevrel phase molybdenum sulphide is synthesized and tested. Research with the perylene as cathode material is started with lithium because lithium is being studied extensively in the research group. Tests with both the monomer and the polymer has been conducted against lithium and magnesium battery systems. The lithium cell employing perylene is optimized as much as possible and is shown to be electrochemically active. The lithium cell shows a redox voltage of 2.5V vs Li/Li^+. In the magnesium system, perylene is active as small peaks are observed at 1.5V and 1.7V vs Mg/Mg^{2+}. However, the cell fails to operate after the first charge. This is most likely due to the electrolyte forming a passive film on the surface of the anode. It is recommended to disassemble the magnesium cell after the first discharge cycle to observe the magnesiation on the cathode and the passive film formation on the anode.

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Introduction

This chapter addresses the current energy scenario on a global scale, the necessities of storage technology along with the methodology, the research question, and the scope of the project.

1.1. Role of fossil fuels and current energy trends

The 3 main types of fossil fuel which provide energy are coal, crude oil, and natural gas. Combustion of fossil fuels produces large amounts of carbon dioxide (CO_2) gas, which is one of the greenhouse gases (GHG) that contribute to global warming. Fossil fuels are not sustainable on the long run because of the negative impacts they have on the environment and also because their availability is limited. Most of the world's crude oil comes from USA, Russia, and Middle Eastern countries. Amongst Middle Eastern countries, Saudi Arabia has the maximum crude oil production. The price of crude oil is mainly dependent on the supply and demand on the global scale, and on the political stability of the countries, amongst other factors. When the supply is high and the demand is low, the price of the crude oil is low, and vice-versa. Fossil fuels are expected to decline in the coming years and the contribution of fossil fuels to the total primary energy demand is expected to be about 59% by 2040 compared to the current share of 80% [7]. Two-thirds of the total GHG is constituted by CO_2 emissions resulting from burning fossil fuels. 1000 g of CO_2 is emitted for every kWh of electricity that is generated from coal combustion [2]. Transition to renewable energy sources is the need of the hour to limit the increase in global surface temperature to below 2°C. Renewable energy sources (RES) can help fight climate change and currently contribute about 14% to the total energy demand. It is important to increase energy production from RES in order to make a successful transition from dependency on fossil fuels [8]. As fossil fuel sources are depleting, it is important that we shift our focus to utilize renewable energy sources on the large scale.

The five main types of RES include solar energy, wind energy, biomass, geothermal energy, and hydroelectric power. Energy production from RES (especially solar and wind farms) is making significant progress in many countries. However there is not enough focus either by government or by opinion makers to make the general public aware of power production from RES. The limitation of infrastructure prevents the public to move from fossil fuels to renewable energy. Developing countries look at the short term view in using conventional fuels in terms of economics. This is because the government supports it by subsidizing fossil fuels. Even to this day, for a significant portion of the population, access to energy is still considered as a luxury. Due to this, they do not think in terms of the sustainability of the energy resource used. Hence, there is a need to focus on renewable energy production on a larger scale.

The targets for energy production from renewable sources set by countries is being increased due to the increasing number of renewable energy plants installed. In 2014, the European Union set a target contribution of 27% to the total electricity production by 2030 and in June 2018, it set a higher target contribution of 32% by 2030 [1]. The Ministry of New and Renewable Energy (MNRE) of India has set a target of 175 GW by the year 2022. Wind power in India currently has a capacity of 60 GW and solar power has a capacity of 100 GW. The MNRE increased the target capacity of RES to 227 GW by 2027 [1]. China, being the largest energy producer and consumer in the world has also employed RES to improve the air quality, because as of now, the air quality in mainstream cities is highly polluted. China accounts for the world's largest installed solar capacity (94 GW) in the world. The country hopes to achieve a target contribution of 20% from RES by 2030

[1].

Zero-emission vehicles (ZEV) are gaining popularity in several countries. In the state of California, the Government has passed a mandate that by 2025, there should be over 1.5 million ZEV's on the road. In California, as of 2018, few hydrogen fuel stations for fuel cell electric vehicles (FCEV's) were already present [9]. By 2020, The Government of Japan aims to have 160 hydrogen fuel stations and 40,000 FCEV's and 800,000 FCEV's on the roads by 2030 [9]. The hydrogen at hydrogen fuel station comes from natural gas reformation. Producing hydrogen from solar power would be ideal, but this technology is not in use yet. In Germany, a French company, Alstom, is working on trains that runs on fuel cells and can travel for one 1000 km at a maximum speed of 140 km/h [9]. In 2017, the national railway operator of The Netherlands, Nederlandse Spoorwegen (NS), runs entirely on wind energy. The trains utilize 1.4 terawatt hours (TWh) and this energy is provided by Eneco [10]. Figure 1.1 shows the share of renewable energy sources in the current energy scenario. Power sector accounts for 58% and this constitutes of electric vehicles (EV) for the most part.

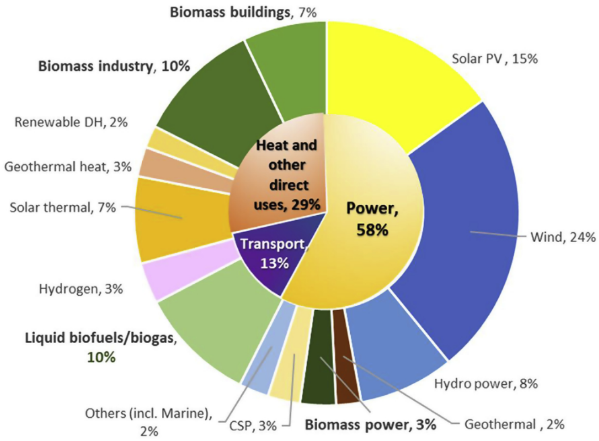

Figure 1.1: Share of RES [1]

1.2. Necessity for storage technologies

Mismatch between energy production and energy consumption calls for the need for energy storage. Any form of renewable energy will not be able to generate power throughout the year at all times. Storage system is necessary for power supply when the main electricity grid is shut down. Energy storage is the crux of any form of energy. With growing population, it is becoming increasingly hard to keep up with the current energy demands. Storage technologies currently in use are mechanical storage, electrochemical storage, electromagnetic storage, and thermal storage. Since electrochemical energy storage (EES) is the focus of this project, it will be discussed in detail. For short-term energy storage, batteries have proves to be quite reliable. For long term storage, batteries are not ideal because of the high costs associated with them and their ability to self-discharge. The main purpose of battery energy storage system (BESS) is to reduce the cost of electricity. When the price is high, stored energy can be used and when the cost is low, energy can be stored. The major setback of an electrochemical storage system is the high cost associated with the technology.

Figure 1.2 shows the wind power profiles measured on a daily basis in Tehachapi, California. It can be seen that power production peaks at night and during the day it is in megawatts (MW) or it is sometimes zero. The demand during the night time is low, and the power produced can be stored for use in the day time. Similarly, solar power is maximum during the day if the sky is clear, and it is low on cloudy days and zero in the night.

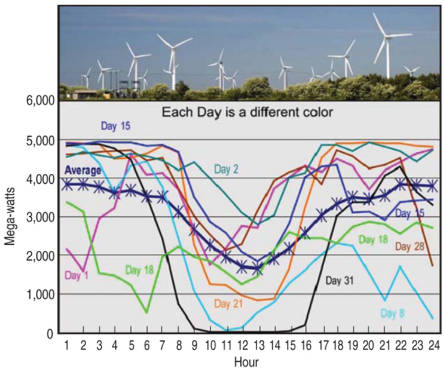

Figure 1.2: Wind power profiles in Tehachapi, California [2]

Stored energy from renewable sources can be used on days when insufficient power is produced and the demand is high. EES is employed in 2 ways, namely, off-grid energy storage and on-grid energy storage. In off-grid storage, the renewable energy system is not connected to the grid. For example, a stand-alone PV system does not provide any electricity to the grid, hence the name stand-alone which implies it is independent from the grid. On-grid storage systems are connected to the electrical grid. During high renewable energy production, depending on whether the demand is high or low, the surplus energy is stored. Also, the electrical grid powers the storage system during low production time (charging). When energy production from RES is low and the demand is high, the storage system gives back power to the grid (discharging). The charge and discharge cycle is illustrated in figure 1.3.

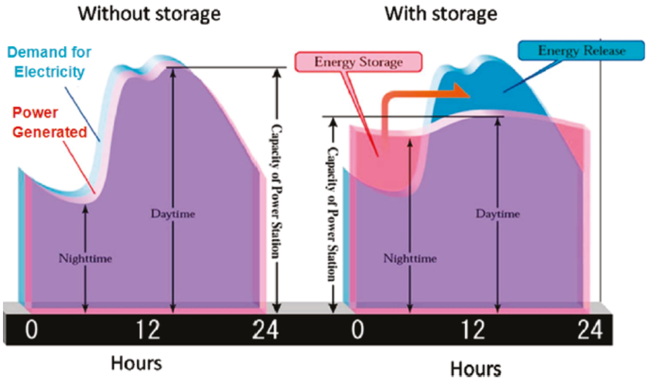

Figure 1.3: Balancing energy supply and energy demand [2]

There are 3 main types of EES systems; namely, flow batteries, fuel cell systems, and batteries:

- Flow batteries are rechargeable and the energy is stored in the electrolyte solution, which is usually made of metallic salts.
- Fuel cell is an electrochemical cell which converts chemical energy from a fuel to electrical energy.
-

Batteries are a form of electrical storage system which stores electrical energy in the form of chemical energy.

The different kinds of rechargeable batteries are briefly explained in section 2.3. Batteries can be classified as primary batteries (non-rechargeable) and secondary batteries (rechargeable). In a primary battery, when the battery has been exhausted, it cannot be recharged, i.e., it is meant for a single use only. Secondary batteries are charged by connecting it to an external power source and is discharged when the battery powers an external load. Since, these batteries are rechargeable, they are used extensively in electric vehicles, portable electronic devices, grid connected, and off-grid storage systems. This report will discuss secondary batteries in detail as they are in high demand in the current battery market.

When a battery discharges, oxidation occurs at the anode, causing it to release electrons which flow through an external circuit and recombine at the cathode, which undergoes reduction. When a battery charges, the electrons are forced to move in a opposite direction by applying an external voltage. During the charging process, the electrical energy is converted to chemical energy which is stored by the battery. The driving force causing the battery to discharge is the chemical potential gradient between the cathode and the anode [11]. This causes the electrons to flow and current is generated to counterbalance the ionic current produced inside the cell. The electrical current produced by the cell equals the ionic current produced inside the cell [11]. A battery usually consists of the cathode, separator, electrolyte and the anode. Anode and cathode is where the oxidation and reduction reactions take place respectively. The function of the separator is to selectively allow only the flow of ions across the electrodes. The separator also plays a crucial role in preventing electrical contact between the electrodes. The electrolyte is usually a salt dissolved in a solvent and its primary function is to conduct only ions across the electrodes.

1.3. Availability of lithium and magnesium

1.3.1. Lithium

The availability of lithium is distributed around the globe. It is found in large concentration in two main sources, i.e., in silicate minerals (40%) and in brines rich with minerals (50%) [12]. Up until the 1980, lithium was mainly mined from mineral-rich brines. Lithium production from brines rich in minerals was way cheaper than lithium extraction from minerals. Because the cost of lithium production from the brines was cheap, safety rules were not taken into account and this proved to be an environmental hazard. Since then, several brines units were shut down. The demand for lithium has increased drastically, thanks to lithium ion batteries and theier application in EV's. The lithium ion battery market is expected to grow to 180 billion euros by 2024 [12]. Due to the increasing demand in lithium ion batteries, lithium is extracted from both brines and mineral deposits. In 2009, lithium extracted from minerals and brines accounted for 13% and 87% respectively [12]. Chile, Bolivia, and USA contain about 57% of the total lithium reserve in the world [12]. Silicate mineral field in Afghanistan and Ireland are currently being considered for large-scale lithium extraction. One of the environmental impacts of lithium mines is acid mine damage (AMD) [12]. AMD happens when old mines are not covered properly and it eventually comes in contact with groundwater. This is highly toxic as it contains copper and lead which can stay in the food chain for centuries to come. One of the cons of mining lithium is that a lot of freshwater is required and this is a scarce resource in a few locations.

Currently, less than 1% of the lithium is recycled [12]. Since the metal is found in abundance, there is no driving force to encourage lithium recycling. Lithium waste is also not big enough for lithium recycling to take off as an industry. Due to the increasing number of portable electronic devices employing lithium ion batteries, proper disposal is a must, otherwise they can make their way into the food cycle and get accumulated in the human system for a long time.

1.3.2. Magnesium

More than 20% magnesium is found inside the crystal structure of more than 80 crystals [3]. From figure 1.4, it can be seen that dolomite, magnesite, olivine, and brucite are the commonly used raw materials for magnesium production because they have a higher magnesium content than the rest of the materials.

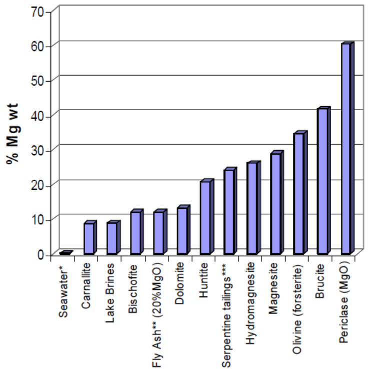

Figure 1.4: Raw materials for Mg production [3]

Dolomite [$CaMg(CO_3)_2$] and Magnesite [$Mg(CO_3)$] are the commonly used ores to extract magnesium [3].

Dolomite is found everywhere on the globe. Most of the magnesium extracted in China comes from dolomite ores. Although magnesite has more magnesium compared to dolomite, large magnesite ores are not found yet. 12 billion tonnes of magnesite is found in the world with majority of it in China, Turkey, Canada, and India [3]. China is currently leading in magnesium production. Many small plants had to be shut down in China because they failed to meet the minimum safety standards.

Although mining is not preferred because of its environmental hazards, it is necessary to create a balance in the global economy. Mining creates employment opportunities and contributes to the growing economy.

1.4. Scope of the study

Magnesium battery systems are being extensively researched because of the following reasons:

- The main raw material, magnesium is abundantly available in the earth's crust.
- It has a higher volumetric energy density compared to lithium.
- No dendrite formation like lithium-ion batteries.
- Forms less toxic compounds when compared to lithium.

The research is still in the niche stage and with the current rate of discoveries, magnesium is expected to make its way into the battery market in the far future. This is because magnesium-ion batteries are not competitive with lithium batteries. Extensive research is being carried out in the field of lithium-ion, lithium-sulphur, lithium-air, and lithium-polymer batteries. Organic electrode is also a subject of interest for use in every kind of battery. Other types of batteries are being explored to overcome the limitations faced by lithium-ion batteries. This project solely focuses on the fabrication and testing of lithium ion and magnesium ion batteries. The organic cathode used in this research is provided by the Organic Materials and Interfaces (OMI) group of TU Delft, under the supervision of Dr. W.F. Jager. Perylene will be extensively tested in both lithium and magnesium based battery systems.

The goal of the thesis is to determine if perylene is a suitable material for use in magnesium batteries. The carboxylic acid derivative of perylene has been tested in the past in sodium ion and lithium ion batteries and positive results were obtained. Even though the project focuses on magnesium batteries, perylene is first tested in lithium ion batteries to get a head start on the experimental work (since lithium-ion batteries are extensively studied across the world). Cyclic Voltammetry (CV) measurements are done on the cells. CV is done to determine the voltage window of the active material (since the material is not been tested before in literature). The voltage window set during the CV measurements is determined using a trial and error method. Going to very high voltages causes electrolyte decomposition at the surface of the electrodes, therefore, killing the cell. Both the polymer and the monomer of perylene has been provided by the OMI group. The polymer and the monomer is tested against lithium and magnesium cells and their results are discussed extensively in chapter 4.

Although a significant part of the project focuses on the redox activity of the polymer based cathode, the standard cathode material for magnesium batteries is also synthesized and tested. The standard cathode material for magnesium batteries which has been deemed successful in literature is molybdenum sulfide (Mo_6S_8). The synthesis and testing of $Cu_2Mo_6S_8$ in magnesium batteries is described in detail in chapter 3. Although molybdenum sulphide has been tested in various metal-ion battery systems in literature, molybdenum is also one of the most expensive metals in the world. To make magnesium batteries commercially viable, it is important to use cheap, low cost, and environmental friendly electrode materials. Hence, polymer based cathode material is explored.

1.5. Research Goal

The goal of the project is to answer the following research question:

Is perylene electrochemically active in a magnesium battery?

To fabricate and evaluate the performance of a magnesium battery system, the following battery components are employed:

- *Pure magnesium* as the *anode*
- Organic compound *perylene* as the *cathode*
- *Magnesium all-phenyl complex (APC) dissolved in tetrahydrofuran (THF) solvent* as the *electrolyte*

The research question can further be divided into sub-questions which aid in answering the main research question:

- Is perylene electrochemically active in a lithium battery?
- Is there any difference in the redox activity exhibited by the polymer and the monomer in both lithium and magnesium systems?
- Is perylene stable in a magnesium cell employing the magnesium-APC electrolyte?
- What can the poor capacity of the perylene based magnesium system be attributed to?
- Does the electrolyte decompose on the surface of the anode? If yes, how does it affect the performance of the battery?

Understanding the working of the battery and analyzing the different factors that influence the same help in answering the main research question.

1.6. Methodology

- **Phase 1: Literature Review**

  Work conducted by researchers in the past is studied to get an idea on the project. This includes the state-of-the-art technology concerning magnesium batteries, the pros and cons of the same as discussed by the relevant authors. Literature on organic materials in batteries is also studied to understand the working of perylene and the attachment and detachment of lithium and magnesium ions from the structure of perylene.

- **Phase 2: Experimental work**

  The first step in experimental work was to get acquainted with the laboratory, personnel, and safety rules. The battery was carefully fabricated using the cathode cast made out of perylene, the separator sheets, the standard available electrolyte and pure metal as the anode. Various tests were conducted by adding and/or removing components to determine if the capacity observed was indeed due to perylene or due to other additives.

- **Phase 3: Results, conclusions and documentation**

  The results obtained at each stage was analyzed and maximum effort was done to improve the performance of the battery. The results obtained and the overall experience of the projects served as a basis for the conclusion of the report. Recommendations are given based on the bottlenecks encountered during the project.

1.7. Report Structure

The structure of the report is as follows:

- Chapter 1 talks about the transition to renewable energy sources, the need for stroage technologies, EES, a brief introduction to the topic, the research questions and sub-questions, and the methodology followed to carry out this project.
- Chapter 2 discusses the basic terminologies associated with batteries, current state of the art technologies associated with magnesium batteries. The organic compound, perylene, is also introduced and relevant literature pertaining to using perylene as an active material in batteries is discussed.
- Chapter 3 discusses the synthesis and testing of the standard cathode material for magnesium batteries.

- Chapter 4 talks about the cathode preparation, the different methods adopted in making the cathode, the cell fabrication, cell testing, and the results of perylene against lithium and magnesium is discussed.
- Chapter 5 will answer the main research question by answering the research sub-questions in a logical sequence. The bottlenecks encountered during the project is mentioned and further recommendations on how to possibly overcome these problems for future researchers in this area is also touched upon.

2

Literature Review

This chapter discusses findings from literature that is relevant to this project. The working principle and the terminologies associated with batteries is covered for a better understanding of the latter part of the report. The timeline of magnesium batteries and their limitations is discussed. Perylene is introduced and their use as high capacity cathode material is covered.

2.1. Working Principle of a Battery

Batteries consist of a positive electrode, a negative electrode, a separator, an electrolyte and an external circuit which circulates the current carrying electrons. The function of the electrolyte is to facilitate the flow of ions from the positive electrode to the negative electrode and vice-versa. The primary functions of the separator is to prevent physical contact between the electrodes and to selectively conduct ions and not electrons, making them semi-permeable in nature. Figure 2.1 shows a lithium ion battery employing graphite as the anode active material and lithium cobalt oxide ($LiCoO_2$) as the cathode active material.

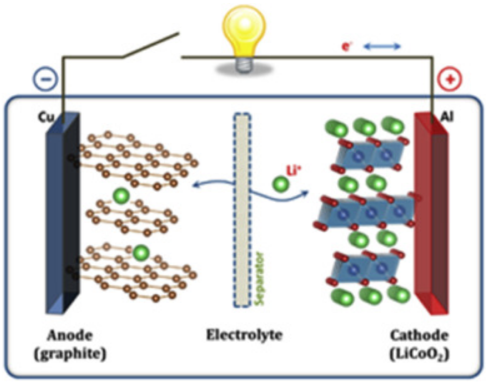

Figure 2.1: Lithium ion battery [4]

During charging, the ions remove themselves from the crystal structure of the cathode and travel to the anode via the ion conducting electrolyte. The electrons move to the anode via the external circuit. During discharge, the ions move to the cathode via the semi-permeable separator. During the charge process, the metal ion goes back to the anode and the electrons go back to the anode via the external circuit.

Conventional batteries use non-aqueous liquid electrolytes but according to recent findings, focus is now being shifted to solid electrolytes. Solid electrolytes have a higher cycle life. They also do not have the problem of electrolyte loss due to leakage and are lighter than batteries employing liquid electrolytes, making them easy and safe to transport. The major problem associated with solid electrolytes is the high resistance to the flow of ions in comparison to liquid electrolytes.

2.2. Battery Nomenclature

Since the rest of the report will explore batteries in technical terms, the basic terminologies associated with batteries is be briefly explained [13]. They are as follows:

- Anode: Negative terminal of the battery. Generally made up of conductive copper or aluminum and coated carbon or allotropes of carbon for better conductivity.
- Cathode: Positive terminal of the battery. They are made up of magnesium and copper and in lithium-ion systems, they are coated with lithium compounds.
- Beginning of Life (BoL): The capacity and power of the battery at the beginning of its lifetime.
- C-rate: C-rate refers to the charge/discharge rate of the battery. Lower the C-rate, higher is the discharge time of the battery and vice-versa. For example, a battery with C-rate of 2C will be discharged in 60 min/2C= 30 min another battery with C-rate of 0.5C will be discharged in 60 min/0.5C= 120 min.
- Capacity: Capacity refers to the quantity of energy in the system. It is measured in Amperes (A) or Ampere-hour (Ah).
- Capacity fading: When the amount of charge delivered by the battery decreases after each use, it is known as capacity fading.
- Cycle: The discharge and charge process of a battery is known as the cycle. When the battery discharges completely and then charges, it is known to have completed one cycle.
- Current: Flow of electrons through the external circuit produces current, which is measured in Amperes, denoted as A.
- Depth of Discharge (DoD): The amount of energy that has been discharged from the battery. For example, 70% DOD means that 70% of the charge has been utilized and 30% of charge is left in the battery. To increase the cycle life of the battery, the DoD is reduced.
- Electrodes: Electrodes refers to the anode and the cathode.
- Electrolyte: The main function of the electrolyte is to facilitate movement of ions to and fro the electrodes and to selectively let only ions through the semi-permeable membrane (and not electrons). The electrolyte is usually liquid, but more research is being conducted on solid electrolytes because they are safer and lighter in weight compared to liquid electrolytes.
- End of Life (EoL): When the battery can no longer provide the required energy and power, EoL is said to have reached.
- Open-circuit voltage (OCV): The voltage difference between the electrodes under no-load conditions.
- Energy: Amount of energy that is stored in the battery, measured in kilowatt hour, denoted as kWh.
- Energy density: Amount of energy stored in the battery relative to its weight (kg) or volume (L). Gravimetric energy density is the energy density with respect to the unit mass, it is measured in kWh/kg. Volumetric energy density is the energy density with respect to the unit volume, it is measured in kWh/L.
- Battery energy storage system (BESS): BESS includes the entire battery, the battery cells, the mechanical and the electrical components.
- Power density: Power density is the power delivered per unit mass of the battery. It is measured in kW/kg or in kW/L.
- Primary battery: Non-rechargeable batteries are primary batteries.
- Secondary battery: Rechargeable batteries are secondary batteries.
- Separator: Separates the electrodes from one another.

- Short-circuit: Short-circuiting of the battery occurs when the anode and cathode are connected and excessive current flows through the battery causing safety hazards.
- State of Charge (SoC): Gives a measure on the charge that is left in the battery after discharge. For example, SoS of 100% implies that the battery is full charged.
- State of Health (SoH): SoH measures the performance of the battery in comparison to the values obtained during BoL. SoH gives information on the number of cycles the battery can provide until it reaches EoL.

2.3. Electrochemical Energy Storage

This section gives a basic introduction to the different kinds of batteries available on a global scale. The types of batteries currently used and their key advantages and limitations are given below [14]:

- Nickel-cadmium batteries (NiCd):

  Pros: Low cost

  Cons: Experiences memory effect. When the battery is charged repeatedly without being completely discharged, the battery does not get charged to its full capacity, hence storing less energy. Other cons include high toxicity of cadmium and high initial cost.

  Feasible for use in renewable energy systems: No

- Nickel-hydrogen batteries:

  Pros: Tolerant to overcharging, good cycle life

  Cons: High initial cost, unfavourable cell conditions, and low volumetric energy density

  Applications: Space applications, example: spacecrafts

  Feasible for use in renewable energy systems: No

- Nickel-metal hydride batteries (Ni-MH)

  Pros: Environmentally benign

  Cons: Experiences memory effect, low cycle life, unfavourable cell conditions

  Applications: Portable electronics, medical devices, and automobiles

  Feasible for use in renewable energy systems: Not yet, but its being studied extensively for application in distributed renewable energy systems.

- Nickel-zinc batteries (Ni-Zn)

  Pros: More environmental friendly compared to Ni-Cd batteries, has higher volumetric energy density and power density compared to Ni-Cd batteries

  Cons: Self-discharge rate is high, zinc dendrites are formed across the electrodes causing safety hazards

  Feasible for use in renewable energy systems: Not yet, but it has the potential to replace Ni-Cd and lead-acid batteries due to the increased volumetric energy density and power density.

- Lead-acid batteries

  Pros: Low cost, can be moved around easily

  Cons: Low shelf life, decreased cycle life, and depth-of-discharge is low

  Feasible for use in renewable energy systems: Yes. In spite of its limitations, they are used in stand-alone photovoltaic (PV) systems. By replacing the anode with carbon, the corrosion at the cathode is reduces, improving the cycle life of the battery.

- Sodium-sulphur batteries (NaS)

  Pros: High battery efficiency, low cost of starting materials, good cycle life, and high energy density

  Cons: High operating temperatures of the cell

  Feasible for use in renewable energy systems: Not yet. For stand-alone renewable energy systems, Na-S batteries are not used due to their high operating temperature. For large-scale applications, Na-S batteries are competent with Li-ion batteries.

- Sodium-nickel chloride batteries ($Na\text{-}NiCl_2$): $Na\text{-}NiCl_2$ batteries were first made by Zeolite Battery Research Africa Project (ZEBRA) group in South Africa. Hence, they are also called as ZEBRA battery.

  Pros: Long cycle life, good battery efficiency, and rate of self-discharge is low

  Cons: Electrolyte is a molten sodium salt and high temperatures are required to keep the solution molten at all times. Fires have been reported in the past due to the reaction of molten sodium with water.

  Feasible for use in renewable energy systems: Yes, they can be used for large-scale storage systems.

- Lithium ion batteries (Li-ion): Li-ion batteries are the most popular kind of batteries on the commercial scale. They are used in various applications such as, portable electronics and EV's. Most breakthrough inventions are in Li-ion batteries, due to their high energy density and their low rate of self-discharge.

  Pros: high energy density, low rate of self-discharge, low cost

  Cons: Formation of dendrites in the anode of the battery leading to loss of active material and decreased battery capacity.

  Feasible for use in renewable energy systems: Yes and it is already in use in stand-alone PV systems.

- Flow batteries: Flow batteries is a form of electrical energy storage which falls between a regular battery and a fuel cell. The electrolyte is composed of metallic salts. The anode and the cathode are dissolved in the electrolyte and are separated by a membrane. Exchange of ions between the electrodes generates electricity.

  Pros: The energy density of the battery is dependent on the volume of the electrolyte used. More volume of electrolyte, more the capacity. The electrolyte can be used repeatedly and it lasts for over a decade.

  Cons: Complex system architecture, so the starting materials of the battery is of relatively higher cost. The battery is bigger and heavier in size, and they are not suited for small-scale or mobile applications.

  Feasible for use in renewable energy systems: Yes, but only for large-scale energy storage. Japan is the leading manufacturer of flow batteries of capacity of several megawatts for storage of solar energy.

2.3.1. Flow batteries

Flow batteries is a form of electrical energy storage which falls between a regular battery and a fuel cell. The energy is stored in the electrolyte, which is composed of metallic salts and it is stored in external tanks [11]. During discharging, the chemical energy stored in the electrolyte is converted to electrical energy. The electrolyte solution is pumped through the electrodes which are separated by a semi-permeable membrane [11]. Exchange of ions between the electrodes generates electricity. Since the electrolyte is stored in external tanks, the system is scalable. The energy density of the battery is dependent on the quantity of the electrolyte used. Hence, higher energy density is achieved if the volume of the electrolyte used is high. The electrolyte can be used repeatedly and it lasts for over a decade. The battery has quite a complex system architecture, so the starting materials of the battery is of relatively higher cost. The battery is also big and heavy in size, limiting their application to large-scale storage system.

2.3.2. Fuel Cell Systems

Fuel cell is an electrochemical cell which combines hydrogen and oxygen as fuel to produce electricity. Applications of fuel cells are categorized based on their temperature of operation (low, medium, and high temperature fuel cells). The fuels are stored in separate tanks and are utilized only upon demand. There are many types of fuel cells but in this section proton exchange membrane fuel cells (PEMFC) will be briefly discussed. The reactions taking place in a PEMFC:

$$\textbf{Anode}: H_2 \text{ -> } 2H^+ + 2e^-$$
$$\textbf{Cathode}: 0.5O_2 + 2e^- \text{ -> } O2^-$$

Currently, hydrogen fuel comes from natural gas reformation. Hydrogen can also be produced by electrolysis, where water is split into hydrogen and oxygen. Electrolysis for fuel cell applications is a highly energy demanding process and the energy consumed can be used to charge a battery. Nonetheless, energy from RES can be used to produce hydrogen during off-peak hours. The major setbacks of hydrogen fuel cells include the source of hydrogen production and the large-scale transportation of hydrogen. Existing infrastructure for natural gas cannot be used for transportation of hydrogen without modifications because the latter is more reactive and is more prone to leakage. Even with zero carbon emission, the costs and problems associated with fuel cells overshadow the advantages, making it incompetent compared to other EES systems.

2.3.3. Battolyser

Battolyser is a combination of battery and electrolyser invented by Dr. Fokko Mulder at Delft University of Technology. It is a combination of nickel-iron battery and an electrolyser. During charging, the battery produces NiOOH and reduced Fe which acts a catalyst for the electrolysis of water. The produced H_2 fuel can be used in fuel cells and can be useful to industries for the production of ammonia. During peak-hours, power is supplied back to the grid and in off-peak hours, the energy stored in the battery can be used for the electrolysis of water. The overall efficiency of the system is 90%.

2.4. Rechargeable Magnesium Batteries

Magnesium ion batteries are cheaper, safer and more sustainable compared to Li-ion, Ni-Cd, and Pb-acid batteries. Because of the +2 charge on magnesium, each magnesium ion can combine with $2e^-$ whereas Lithium being a monovalent metal, combines with $1e^-$. For grid-connected systems, since magnesium is abundant in nature, magnesium batteries can be a viable option.

Non-rechargeable magnesium batteries are commercially available but rechargeable magnesium batteries do not stand close to lithium ion batteries on the commercial scale yet. Commonly used organic electrolytes for magnesium batteries have ppm levels of water. Pure magnesium anode reacts with the water to form a layer of magnesium oxide on the surface. The layer of MgO formed is passivating and it inhibits the movement of Mg^{2+} ions across the electrodes [15]. Decomposition of the electrolyte on the surface of the anode can also negatively impact the performance of the battery. When employing chloride containing electrolytes, the chloride dissociates into Cl^- ions, which also hinders the movement of Mg^{2+} ions [15].

Overcharging and overdischarging are common problems in large battery systems as observed recently in lithium ion batteries. However, this is not fully studied in Mg battery systems and its implications are not recorded in literature [16]. Commonly employed organic magnesium electrolytes, are highly corrosive to battery parts, such as, springs, caps, cans, and current collectors. Magnesium organohalo-aluminate in THF solution is corrosive to copper, aluminium, and stainless steel current collectors at high voltages [16].

2.5. Cyclic Voltammetry

Cyclic voltammetry is an electrochemical measurement which is used to determine the redox activity of a species. The voltage range of the active material can be determined from CV, as the potential range at which the peaks are observed is the voltage range for that active material.

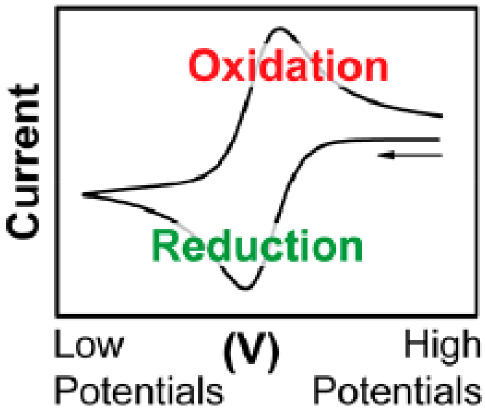

Figure 2.2: Typical CV curve [5]

The resulting curve looks like the one shown in figure 2.2 and is called voltammogram or cyclic voltammogram [5]. The Y-axis corresponds to the current and the X-axis corresponds to the voltage. While doing a CV scan, the scan rate plays a very important role in determining the capacity of the cell. Suppose the scan rate is 1mVs^{-}1, then it means that the speed at which the voltage is varied is at 1mVs^{-}1. CV scans have a forward scan and a reverse scan. During these scans, duck shaped peaks are observed. The duck shaped peaks correspond to the redox activity of the active material. Depending on whether the cell is charged or discharged first, cathodic peak(s) and anodic peak(s) can be seen. In the cyclic voltammetry results, show in 4, since it is a fully charged cell, the cell is discharged first. During the discharge process the ions and the electrons move from the anode to the cathode. The anode loses electrons in the process. When the cell is discharged first, there is bulk movement of ions across the separator to the cathode. A peak is observed then and this is called the cathodic peak, and the current at this peak is called the cathodic current. This peak is due to the combination of metal ions at the cathode. During the charge process, the electrons flow through the external circuit to the anode and the the metal ions travel to the anode via the separator. The peak observed due to this is called the anodic peak and the corresponding current is called the anodic current.

During the discharge process, there is a bulk diffusion of ions from the anode to the cathode. The diffusion layer grows bigger at the surface of the electrode and slows down the bulk movement of ions from the anode to the cathode. Scan rate of the CV determines the capacity of the cell. At a higher scan rate, the size of the diffusion layer decreases, hence there is faster movement of ions from the anode to the cathode. But also when the scan rate is high, the ions may fail to intercalate into the active material and will stay at the surface. This results in a low capacity.

Working electrode (WE) is the electrode at which the main reaction of interest occurs. The active material for the working electrode should be inert in the voltage range at which the cell is measured. Flow of electrons between the working electrode and the counter electrode determines the current. The surface area of the counter electrode must be higher than that of the working electrode. This is because the kinetics of the reactions at the counter electrode does not slow down the reaction at the working electrode [5]. At the start of the CV scan, almost zero current flows and this is called capacitive current because it behaves like a capacitor [5]. The potential measured across the electrodes when there is no current flow is called the open circuit potential (OCP). The value of OCP must be higher than the voltage at which the metal ion is accepted.

2.6. Conclusion

Based on the work carried out and the data gathered, there is a huge potential for magnesium batteries due to its inherent safety considerations and cheap availability. Much is to be done in selecting the right battery components for further research.

3

Chevrel Phase

Since no previous research has been done in the field of magnesium batteries in the SEE group, a reference material was needed to get the research started. From literature, it was determined that the most promising cathode so far for magnesium batteries is the chevrel phase molybdenum sulphide.

Chevrel phase comprise of molybdenum chalcogenides with the molecular formula $M_xMo_6T_8$. The presence of sulphur makes them useful in desulfurization of compounds, and since they are synthesized under high temperatures, they are resistant to high temperatures, thus extending their application as catalysts [17]. Resistance to temperature Chalcogenides represent elements from group 16 of the periodic table. This includes oxygen, sulphur, selenium, tellurium, and polonium. The M in $M_xMo_6T_8$, it can be monovalent, divalent, or trivalent. Depending on the size of the ion, x varies anywhere between 0 and 4 [18]. X is a chalcogen and can be either sulphur or selenide.

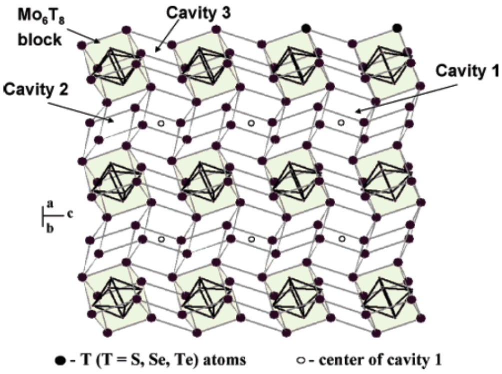

Figure 3.1: Cavities present in the $M_xMo_6T_8$ crystal structure
[18]

The Mo_6T_8 blocks are stacked together providing a three dimensional channel for magnesium insertion and extraction. From figure 3.1, it can be seen that there are 3 types of cavities formed in between the Mo_6T_8 blocks present in the crystal structure of the chevrel phase. Cavities 1 and 2 are occupied by cations because they are far away from the molybdenum atoms. The repulsion forces due to Mo atoms is strong in cavity 3 [18]. The insertion of Mg into the crystal structure of the chevrel phase takes place in two steps, resulting in the formation of two new phases, as indicated by the following equations [18]:

$$Mo_6S_8 + Mg^{2+} + 2e^- \longrightarrow MgMo_6S_8 \tag{3.1}$$

$$MgMo_6S_8 + Mg^{2+} + 2e^- \longrightarrow Mg_2Mo_6S_8 \tag{3.2}$$

The anodic, cathodic, and overall reaction taking place in magnesium ion battery employing $Cu_xMo_6S_8$ as cathode are shown in equation 3.4, equation 3.3, and equation 3.5 and the synthesis is explained in section 3.1.

$$2Mg \longrightarrow 2Mg^{2+} + 4e^- \tag{3.3}$$

$$Cu_xMo_6S_8 + 2Mg^{2+} + 4e^- \longrightarrow Cu_xMg_2Mo_6S_8 \tag{3.4}$$

$$Cu_xMo_6S_8 + 2Mg \longrightarrow Cu_xMg_2Mo_6S_8 \tag{3.5}$$

Temperature plays a major role in the diffusion of Mg ions into the chevrel phase. When T in $M_xMo_6T_8$ is selenide, Mg intercalation and de-intercalation happens at ambient temperature (25°C) [18]. But, when the chalcogen used is sulphur, complete intercalation happens at ambient temperature, but during de-intercalation, 25% of the magnesium ions cannot be removed from the Mo_6S_8 crystal structure. Complete removal of magnesium ions from the Mo_6S_8 crystal structure needs to take place at higher temperatures (60°C) [18].

3.1. Synthesis of $Cu_xMo_6S_8$

The synthesis of the chevrel phase is a solid state reaction taking place under high temperatures. The precursors are first ball milled followed by high temperature thermal treatment under an inert atmosphere according to the following equation [19]:

$$2CuT + 3Mo + 3MoT_2 \longrightarrow Cu_xMo_6T_8 \tag{3.6}$$

Synthesis is followed as per literature [19]. High energy mechanical milling was employed to synthesize the chevrel phase. The precursors used for the synthesis was molybdenum sulfide (MoS_2), molybdenum powder (Mo), and copper sulfide. Mo (1.2 g, 99.9% Sigma-Aldrich), MoS_2 (1.9 g, 99.9% Sigma-Aldrich), and CuS (0.79 g, 99.9% Sigma-Aldrich) were weighed out and coarsely mixed in a pestle and mortar. The precursor was then transferred to a zirconium oxide ball mill grinding jar (ball:powder ratio of 10:1). The ball to powder ratio (BPR) is an important factor in ball milling because it determines the effectiveness of the milling process. More the number of balls and lesser the amount of powder results in a more effective milling process. Using more balls results in more collisions per unit time and by using less powder, the velocity of a single ball is higher. Diameter of balls used was 10 mm. The precursors were ball milled under ambient conditions at 480 rpm for a period of 4 hours. An X-Ray Diffraction (XRD) scan was conducted after the ball milling process to see if any intermediate phase of the chevrel phase was formed.

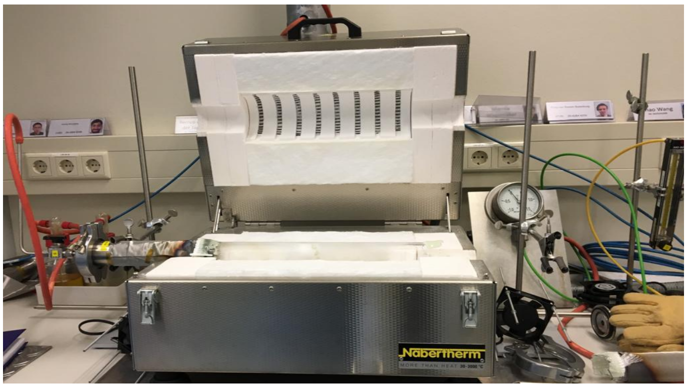

Figure 3.2: Tube furnace employed for thermal treatment

The ball milling procedure was followed by high temperature thermal treatment. The precursor powder was made into pellets of diameter 13 mm by applying a pressure of 1 tonne. It was made into pellets to have better interaction between the particles, which would result in the homogeneous formation of $Cu_2Mo_6S_8$. The pellets were put in a boat crucible and transferred to the tube furnace where it was heated at a 1000°C under an argon atmosphere for a period of 5 hours. The temperature setting of the furnace was set to cool down to 20°C in a period of 1 hour. Pellets after the thermal treatment are shown in figure 3.3. The pellets were ground using a pestle and mortar and an XRD scan was conducted to determine if $Cu_2Mo_6S_8$ was formed.

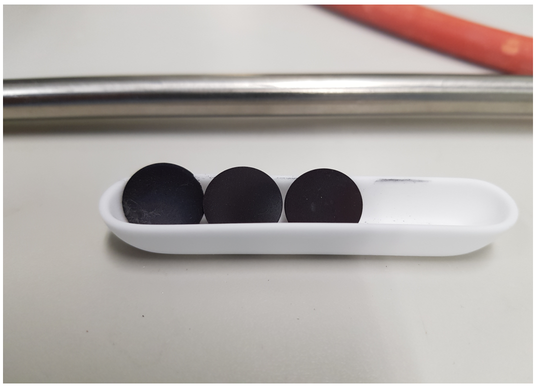

Figure 3.3: Pellets after thermal treatment

Peaks corresponding to the formation of molybdenum oxide can also be seen. After the thermal treatment, the tube furnace was found to be broken. The glass could have cracked either during the process due to the high temperature of 1000°C or after the heat treatment, because it was cooled at a rapid cooling rate from a 1000°C to 20°C in a period of 1 hour. Since the timing of the glass breakage is unclear, it is not known if the MoO_2 was formed before or after the thermal treatment. Since the XRD scan confirmed the presence of the chevrel phase $Cu_2Mo_6S_8$, the next step was to remove most of the copper out of the structure, so that magnesium insertion could take place. From literature, it was noted that to extract most of the copper out of the structure from the crystal structure, it was required to leach the powder in hydrochloric acid accompanied by constant bubbling using pure oxygen for a period of 7 hours [17]. Pure oxygen was used because it reacts with the H from HCl and forms water and the reaction proceeds faster. This method was practically not feasible since pure oxygen was a scarce resource at the research group and it is also dangerous to work with pure oxygen. The $Cu_2Mo_6S_8$ was leached in 6N hydrochloric acid and air was bubbled through the mixture to speed up the process. The leaching reaction is shown below [17].

$$Cu_2Mo_6S_8(s) + 8HCl(aq) + O_2 \longrightarrow Mo_6S_8(s) + 2H_2O + 2[CuCl_4]^{2-}(aq) + 4H^+(aq) \tag{3.7}$$

Removal of copper from the structure of the synthesized chevrel phase is necessary to achieve full Mg^{2+} intercalation and de-intercalation. All of the copper cannot be extracted as some of it is required to maintain the stability of the crystal structure. Since it was the first attempt at trying to extract the copper out of the chevrel phase, repeated XRD scans were done after short intervals of bubbling to notice if the peaks corresponded to that of literature. In total, the $Cu_2Mo_6S_8$ was leached for a period of 26 hours. The leached solution was washed with a mixture of ethanol and water three times to reduce the concentration of hydrochloric acid. A mixture of water and ethanol was chosen because the $Cu_2Mo_6S_8$ particles settled faster at the bottom of the beaker when ethanol was added, making it easier to wash the particles. When the particles could not be separated from the water and ethanol mixture manually, it was evaporated, leaving behind a black powder. The powder was dried thoroughly in a vacuum oven at 80° and stored in a glass vial for future uses.

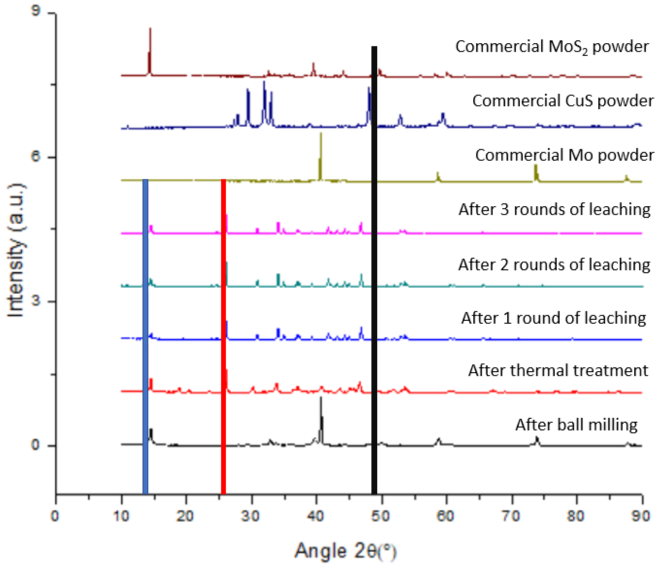

Figure 3.4: XRD scan of the chevrel phase at every step of the synthesis

XRD scans were done after every stage to observe the phases formed. The first scan was done after ball-milling. From figure 3.4, it can be seen that there is no chevrel phase formation after ball-milling, the peaks correspond to that of the precursors (MoS_2, CuS, and Mo). The blue bar corresponds to the formation of $Cu_2Mo_6S_8$. The blue bar passing through the peak in the first scan (denoted by the black pattern), can be mistaken for the formation of $Cu_2Mo_6S_8$, but the peak corresponds to that of MoS_2 and not that of $Cu_2Mo_6S_8$. The red bar corresponds to the formation of MoO_2. This was probably formed during the synthesis or after the synthesis, due to the broken glass tube (refer to figure 3.2). The black bar passing through all the patterns corresponds to the MoS_2, which means that not all of the precursor was entirely used up in the reaction process.

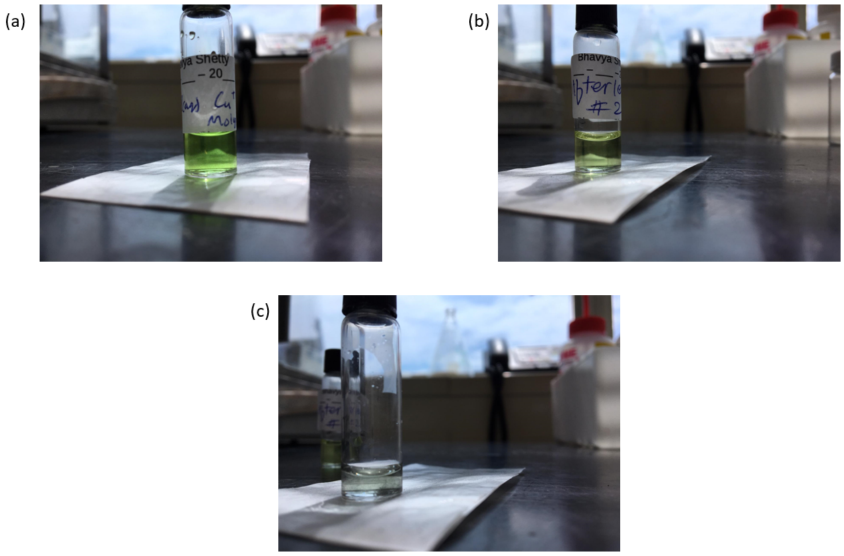

Figure 3.5: (a) After 2 hours of leaching (b) after 14 hours of leaching and (c) after 26 hours of leaching

Figure 3.5 show the colour of the HCl solution after three rounds of leaching respectively. The green colour in solution in figure 3.5 (a) is due to the low concentration of Cu^+ ions in the solution. As the leaching time progresses, the solution becomes a light blue colour to almost colourless as shown in figure 3.5 (b) indicating the presence of high concentration of Cu^+ ions in the solution. Although XRD scans were done to confirm the presence of $Cu_2Mo_6S_8$, the amount of copper left in the sample could not be determined from XRD alone.

Element	Number of moles	Weight %
Copper	0.003	0.212
Molybdenum	0.670	64.30
Sulphur	0.773	24.80

Table 3.1: Results from ICP-OES analysis

Inductively coupled plasma - optical emission spectrometry (ICP-OES) was done to determine the exact amount of copper left in the sample after the third round of leaching. Inductively coupled plasma (a source of plasma) is used to excite the electrons and atoms, and as a result of the excitation, they emit electromagnetic radiations at corresponding wavelengths [20]. The result of the ICP-OES analysis is shown in table 3.1. Hence, the overall structure is $Cu_{0.03}Mo_{6.7}S_{7.7}$.

3.2. Cathode Preparation

For the cathode preparation, stoichiometric quantities of Polyvinylidene Fluoride (PVDF) (10 wt.%) was added to 1.2 ml N-Methyl-2-Pyrrolidone (NMP) and was stirred for about 10 minutes until all of the PVDF was dissolved in the NMP. Stoichiometric quantities of carbon black (20 wt.%) and $Cu_{0.03}Mo_6S_8$ (70 wt.%) were weighed first and then ground together in a pestle and mortar until the mixture looked homogeneous. The carbon black and $Cu_{0.03}Mo_6S_8$ mixture was then added to the PVDF and NMP mixture and the resulting mixture was stirred continuously for 4 hours. The slurry was then cast on copper foil and aluminum foil using a doctor blade of thickness 200μm (refer to figure 3.6). Prior to casting, the copper foil was cleaned using oxalic acid to remove the layer of copper oxide. After casting, the coating is dried in a conventional oven at 65°C. Electrode discs of diameter 12.7mm are cut out and are dried overnight in the vacuum oven at 80°C. After drying them overnight, the electrode discs were weighed, and the mass of active material present was noted down. The electrode discs were then transferred to the glovebox where the cells were made. The reason magnesium cells were made in the glovebox was because the solvent of the electrolyte is tetrahydrofuran (THF) and THF is toxic to human health, flammable, and unstable in air.

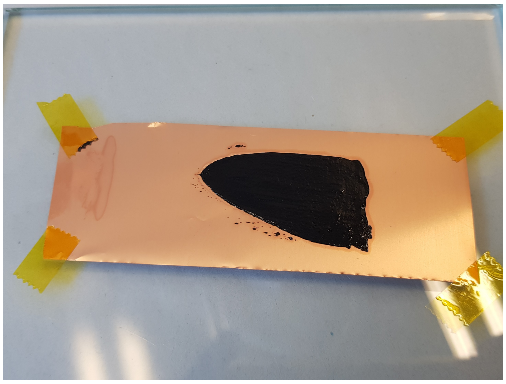

Figure 3.6: NMP based coating cast on copper electrode

Figure 3.7: Lab cell parts

To construct magnesium cells, lab cells were used since lab cells were easier to open up and reuse electrode materials (refer to figure 3.7). The availability of magnesium was a problem in the research group, hence, by using lab cells, the magnesium discs could be reused and circulated amongst other people involved in magnesium research. The magnesium discs of 16mm diameter were provided by the workshop in the RID, and since only limited number of discs were provided, they had to be reused. Coin cells could be de-crimped but that was not preferred. After conducting electrochemical measurements, the cell was opened, the magnesium was cleaned with alcohol and sanded to remove traces of the previous experiment. In magnesium cells, glass fiber separator of 19mm diameter was used. The electrolyte used in magnesium batteries is the magnesium all phenyl complex (Mg APC) dissolved in THF solvent.

3.3. Battery Testing

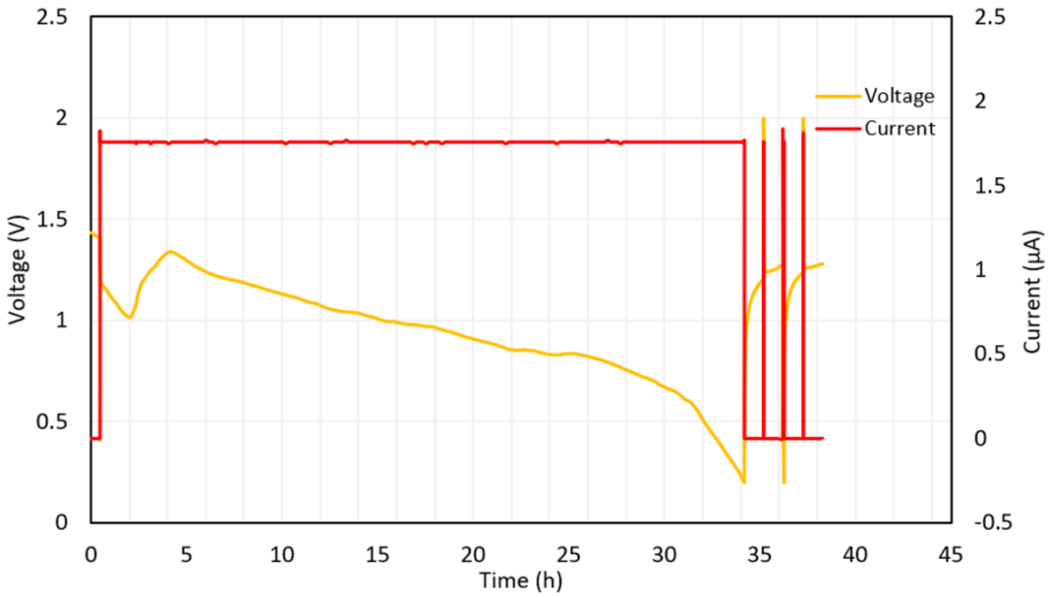

Figure 3.8: Discharge curve of $Cu_{0.003}Mo_6S_8$ versus Magnesium

Figure 3.8 shows the charge discharge curve of the chevrel phase cathode versus pure magnesium anode. Since it is a fully charged cell, the cell discharges from 1.3V until 0.2V. The discharge voltage observed at 1.4V corresponds to that in literature [19]. After discharge to 0.2V, the cell tries to charge but from figure 3.8, it looks like a higher voltage is required for magnesium extraction. This could be due to:

- the expansion of the crystal structure of the chevrel phase
- loss of contact due to dissolution of PVDF in THF (refer to section 4.4)

3.4. Conclusion

The chevrel phase was successfully synthesized. Most of the copper was extracted by leaching the $Cu_2Mo_6S_8$ in HCl and by bubbling air through the mixture to speed up the process. ICP-OES analysis shows the negligible amount of copper that is left in the crystal structure. However, during the battery testing, the battery could be discharged but could not be charged. The system has not been optimized further because the main focus of the study was to test perylene as cathode in lithium and magnesium ion batteries. Since perylene was available, further tests were carried on to test the redox activity of the organic material.

4

Organic Cathode

The organic material was synthesized by Pierre Ranque and Chantal Schenker under the supervision of Dr. W.F. Jager from the OMI group, Department of Chemical Engineering, TU Delft. Tests have been carried out with the polymer and the monomer in lithium and magnesium battery systems.

4.1. Polymer for Battery Storage

Organic materials are made of elements that are found naturally. They can be made in a very sustainable way under low temperature conditions (below 200°C. They can also be disposed easily since they have no metals. Organic materials have poor conductivity intrinsically, hence a lot of carbon (conductive additive) is required [21]. Carbonyl compounds are bring studied extensively for use in lithium, sodium, and magnesium ion batteries. Each carbonyl group under goes reduction and oxidation process during discharge and charge process's respectively.

In case of monovalent systems, each carbonyl group can undergo reversible one electron reduction process. Polyimides have four carbonyl groups, and only two carbonyl groups can be used for ion and electron storage. The first cycle is reversible but the second cycle is irreversible because the lithiated cathode reacts with the electrolyte, forming unwanted by-products and the ring of the polymer opens [22]. Polyimides which have a perylene core have theoretical capacities around 140mAh/g and are insoluble in organic liquid electrolytes [21].

When the battery discharges, the lithium ions move from the anode to the cathode through the semi-permeable separator and attach themselves to the carbonyl groups opposite to each other (see figure 4.1). The electrons flow through the external circuit and combine with the lithium ions at the cathode. Ideally, 4 lithium ions could attach themselves to the 4 carbonyl groups present in perylene diimide. Due to overcrowding, the ions will struggle to stay in place. Equation 4.1 shows the reaction taking place at the anode.

$$2Li \rightleftharpoons 2Li^+ + 2e^- \tag{4.1}$$

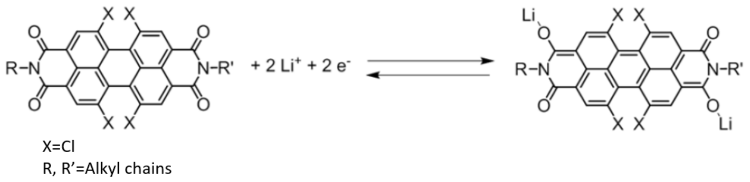

Figure 4.1: Reaction taking place at the cathode [6]

In the case of magnesium, 2 magnesium ions will attach themsleves to the carbonyl groups opposite to each other. Since magnesium is a divalent metal, each magnesium ion combines with two electrons, thereby, giving twice the capacity as that offered by lithium. Equation 4.2 shows the reaction taking place at the anode.

$$2Mg \rightleftharpoons 2Mg^{2+} + 4e^{-} \tag{4.2}$$

The theoretical capacities offered by the monomer and the polymer in lithium and magnesium battery systems are shown in table 4.1.

Active material	Metal	Capacity (mAh/g)
Monomer	Li	83.58
	Mg	167.16
Polymer	Li	92.83
	Mg	185.67

Table 4.1: Theoretical capacities offered by the monomer and the polymer in Li and Mg ion batteries

4.2. Cathode preparation

The cathode was prepared by three means; namely, NMP based coating, chlorobenzene based coating and PTFE based coating. Two approaches were taken to prepare the coating because after making a few NMP based coatings, it was realized that perylene does not dissolve in NMP and the resultant slurry formed may not be a homogeneous mixture after all. For a more homogeneous slurry, it was decided to dissolve perylene in a solvent and then add additive(s) to improve its conductivity. After preparing and testing the cells against lithium and magnesium, further bottlenecks were encountered, which is explained in section 4.2.3.

The method of preparation described in section 4.2.1, section 4.2.2 has the polymer as the cathode active material. PTFE based coating was done with the monomer. Monomer based cathode is also prepared the same way as the cathode material.

4.2.1. NMP based coating

To prepare the NMP based coating, stoichiometric quantities of Polyvinylidene Fluoride (PVDF) (10 wt.%) was added to the NMP and was stirred for about 10 minutes until all of the PVDF was dissolved in the NMP. Stoichiometric quantities of carbon black (40 wt.%) and the polymer (50 wt.%) were weighed first and then ground together in a pestle and mortar until the mixture looked homogeneous. The carbon black and polymer mixture was then added to the PVDF and NMP mixture and the resulting mixture was stirred continuously for 67 hours. The viscosity of the slurry is supposed to be somewhere in between the drip consistency and that of gel. The slurry was a bit too viscous, hence the excess NMP was evaporated until the right viscosity was obtained. The slurry was then cast on a copper substrate using a doctor blade of thickness 150μm. Prior to casting, the copper foil was cleaned using oxalic acid to remove the layer of copper oxide. After casting, the coating is dried in a conventional oven at 65°C. Electrode discs of diameter 12.7mm are cut out and are dried overnight in the vacuum oven at 80°C. After drying them overnight, the electrode discs were weighed, and the mass of active material present was noted down. The electrode discs were then transferred to the glovebox where the cells were made.

The comaprison between an NMP based coating and a chlorobenzene coating is shown in figure A.4 in appendix A. Since the active material does not dissolve in NMP, it can be seen that the NMP based coating does not have any capacity. The conclusion from this experiment is that dissolving the polymer/monomer is important as it is distributed homogeneously and promotes uniform distribution of electrons and ions.

4.2.2. Chlorobenzene based coating

As mentioned in section 4.2, chlorobenzene based coatings were prepared since perylene did not dissolve in NMP. The polymer has been tested previously by Pierre Ranque for use in lithium ion batteries and chlorobenzene was used as the solvent to dissolve the polymer [6]. Hence, no further research was done on the choice of the solvent and chlorobenzene was used to dissolve the polymer.

To prepare the chlorobenzene coating, the following composition was followed; polymer, carbon black and PVDF in a mass ratio of 50:10:10. Pre-determined amount of polymer was weighed out and transferred to a glass vial. Chlorobenzene was added to the vial containing the polymer drop wise, just until all of the polymer was dissolved in the solvent. Carbon black and PVDF was weighed out and ground coarsely in a pestle and mortar, until the mixture looked homogeneous. The carbon black and PVDF mixture was added to the polymer solution and was stirred continuously for 96 hours to get a homogeneous mixture. Since the addition of chlorobenzene does not make the solution viscous, like that of a NMP based slurry, making the cast with a doctor blade was not feasible. Evaporating the chlorobenzene would result in a reduced volume of the solvent but the solution would still be runny. Porous carbon sheets were used as the substrate. Carbon sheets were cut into electrode sheets of a diameter of 12.7mm. One to two drops of the coating was dripped onto the carbon discs and they were dried in a conventional oven at 65°C. Once the chlorobenzene was evaporated, the electrode discs were dried overnight in the vacuum oven at 80°C. The electrode discs were then weighed and the mass of active material was noted down. The electrode discs were then transferred to the glovebox for cell fabrication.

4.2.3. Polymer PTFE based coating for Mg batteries

Monomer/carbon nanofibers/PTFE in the ratio of 50/40/10. The polymer and the carbon nanofibers is first ground thoroughly using a pestle and mortar until the mixture looks homogeneous. Stoichiometric amount of PTFE is weighed out and added to the polymer carbon nanofibers. Isopropyl alcohol is added dropwise to make a slurry. Isopropyl alcohol is added accordingly until a mass of clay type consistency is formed. Once most of the material from the pestle and mortar comes together, it is taken off with a help of a spatula and stuck on a weighing paper. Prior to using the rolls, they are cleaned with alcohol to remove remnants of the previous experiment. Few drops of alcohol is added to the mass and it is rolled using the roller (thickness 25 micrometer). It is rolled at a higher thickness first and then gradually reduced to 25 micrometers, if the film is still stable. It is rolled for a few times until the film looks ready. It is then dried in a vacuum oven at 60 degree Celsius overnight. Since it is a standalone coating, the mass of the active material was quite high, i.e., 15.7mg. The cell was fabricated and then tested.

The results of the CV scan done at 0.1mV/s are shown in figure A.4 in appendix A. One of the possible explanation is that there is a film formed between the binder and the monomer which prevents the monomer from accepting ions. PTFE based coating was done to determine if there would be a higher capacity when compared to no binder chlorobenzene based coatings.

4.3. Cell fabrication

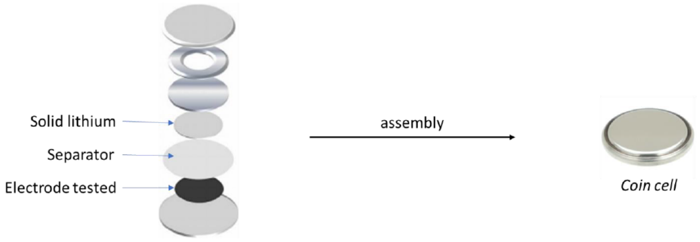

Figure 4.2: Coin cell parts shown in the way they are assembled [6]

The coin cells (CR2032) were fabricated in the glovebox under an argon atmosphere. Coin cell consists of the can, spacer disc, springs, and the cap (refer to figure 4.2). Lithium half cells were constructed using coin cells. The can formed the base of the coin cell within which the electrode disc of diameter 12.7mm was put coating side up. In lithium cells, two kinds of separators are used, i.e., celgard separator of diameter 19mm and glass fiber separator of thickness 16mm. The separators prevent internal contact between the electrode materials. Before making the cells, the separator sheets were cut out and dried in the vacuum oven at 80°C overnight. The electrolyte used in lithium cells was 1M lithium hexafluorophosphate solution in ethyl carbonate and dimethyl carbonate (1M $LiPF_6$ in 1:1 EC:DMC). Five drops of the electrolyte was dripped onto the separator sheet. The lithium disc of diameter 16mm was placed on the wet separator and the spacer disc is placed on the anode. The spring is placed on the spacer disc and the components are covered with a cap. The coin cell was then sealed by using a crimper located inside the glovebox. The coin cell components are handled by tweezers. Care must be taken to use plastic tweezers after dripping the electrolyte to prevent short circuiting of the cell. The cells were tested after a period of 2 to 3 hours after fabrication, so the separators had enough time to soak up the electrolyte. For magnesium cells, lab cells were used, refer to section 3.2.

4.4. Side Experiments

A few side experiments were done out of curiosity. THF, the solvent for the magnesium electrolyte is also a popular solvent and is known to dissolve polymers. The experiment was carried out and the polymer and the monomer dissolved in THF resulting in a clear orange solution (refer to figure 4.3).

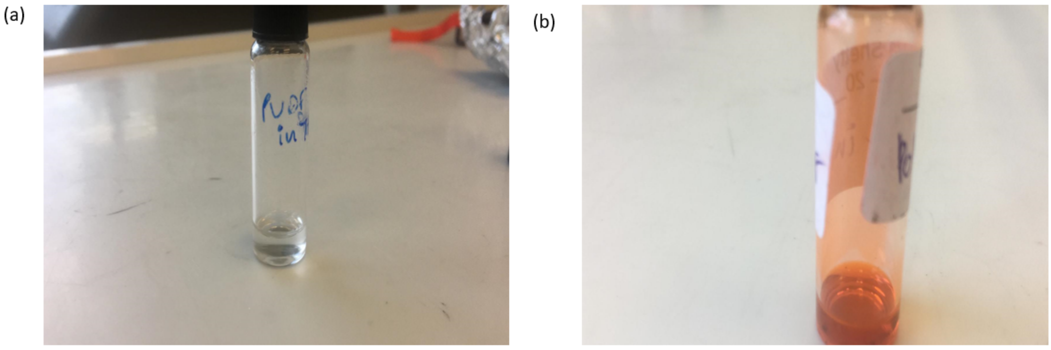

Figure 4.3: (a) PVDF dissolved in THF and (b) Polymer dissolved in THF

The next step was to determine if THF dissolved the binder as well. The binder should dissolve in the solvent of the cathode (NMP) and not in the solvent of the electrolyte. This test was carried out and it was found out that PVDF dissolves in THF, resulting in a clear solution (refer to 4.3). Dissolution of binder in the solvent of the electrolyte can impact the performance of the battery negatively. The coating does not cohere adequately to the substrate, which results in poor contact. This affects the electronic conductivity, ionic conductivity, the capacity, and the cycle life of the battery [15]. Finding an alternative to PVDF was important because even if some of the active material was lost in the solvent, the binder would prevent all of the active material from dissolving in the electrolyte. Hence, binder is important for a battery to work. Because the binder and the active material dissolved in THF, it was concluded that the magnesium cells didn't work because of binder dissolution and loss of active material in the electrolyte. Polytetrafluoroethylene (PTFE) binder based coating is also done and tested and is described in section 4.2.3.

Since PVDF was used as the binder in NMP and chlorobenzene based coatings, it was not known if PVDF dissolved in chlorobenzene, since PVDF dissolved easily in NMP. If PVDF did not dissolve in chlorobenzene, then the binder is an inert filler. This test was carried out and both PVDF and PVDF-HFP did not dissolve in chlorobenzene. Experiments following this information did not employ any kind of binder when chlorobenzene was used as the solvent.

4.5. Battery testing

It is essential to do CV measurements at very low scan rates to observe a high capacity, because only then will the ions attach itself to the electron withdrawing groups (EWG) of perylene. At higher scan rates, the movement of ions across the electrodes is faster and the current observed is higher. The Y-axis of a CV curve is the current and the X-axis is the voltage. The data is plotted as a function of current per mass of active material versus the voltage. Experiments were started with lithium cells, since it widely studied in the research group. The scans are conducted at a low scan rate ($0.1 \mathrm{mVs}^{-1}$) so as to give the working electrode sufficient time for the reactions to take place.

In this section, cells were made by dissolving only the active material in chlorobenzene. No PVDF and carbon black has been used in any of the cells described in this section. The monomer was taken in a glass vial, and chlorobenzene was added drop by drop just until all of the active material was dissolved. The rest of the procedure followed the same process as described in section 4.2.2. Only the monomer has been tested against lithium and magnesium from hereon, as the supply of the polymer was limited.

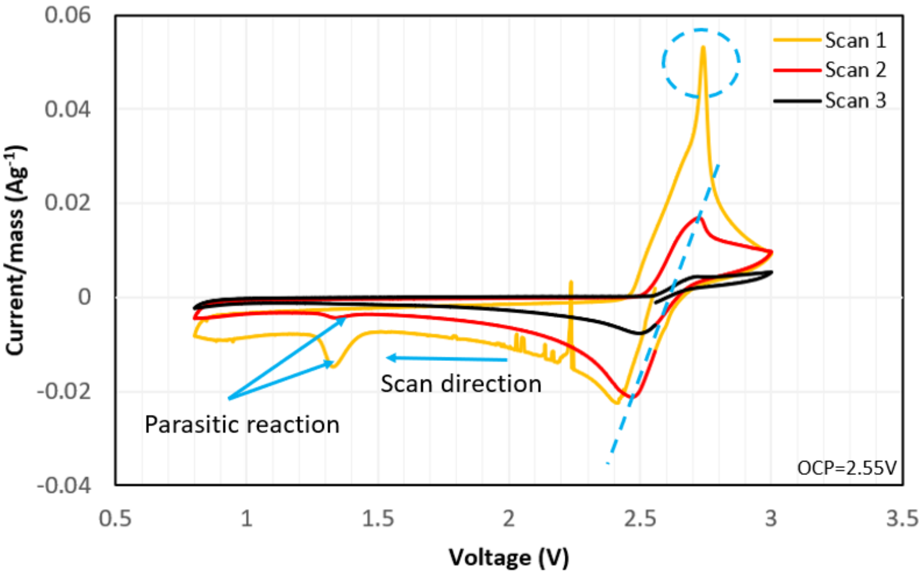

Figure 4.4: Monomer versus Lithium (only monomer)

The voltage range for the CV curve shown in figure 4.4 is set from 0.8V to 3V. The scan starts and ends at the OCP value (2.55V). The same voltage range has also been set in figure A.1 but in that case, some of the capacity may also be contributed by the conductive additive. The monomer is electrochemically reversible at 2.7V and it is denoted by the blue dashed line. In the first cycle, an unwanted reaction takes place at ~1.3V during the first discharge. The peak is also observed in the second cycle and disappears in the third cycle. At ~2.2V, some spikes are observed and these are most likely due to contact problems. The peak denoted by the blue dashed circle in the first cycle is bigger than the first discharge peak. Thus, it is a parasitic reaction and the reversibility extent of the same is not known. However, scan 2 and scan 3 are reversible, and exhibit a lower capacity and this is due to the parasitic reactions observed in the first two cycles

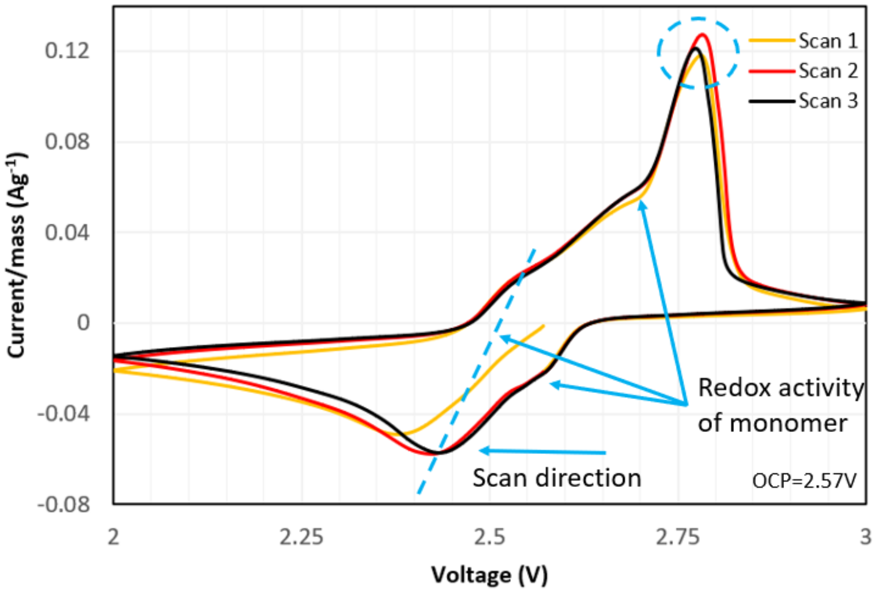

Figure 4.5: Monomer versus Lithium (different voltage range)

From the previous Monomer versus Lithium CV curves, no capacity due to active material was observed until 2.4V. To avoid the parasitic reaction(s) observed in the previous CV curves, the voltage range was set from 2V to 3V. The scan starts and ends at the OCP value (2.57V). Lithium insertion in perylene takes place at

2.45V and 2.6V. Lithium extraction takes place via three reaction mechanisms; at 2.55V, 2.7V, and 2.75V. The reaction is fully reversible and no capacity loss is observed in all the three cycles. The sharp peak observed from figure 4.4 is not present. This confirms that the sharp peak was due to the parasitic reaction observed at 1.3V in figure 4.4. Two peaks are observed during lithiation and three peaks are observed during de-lithiation. This depends on the kinetics of the reaction and on the structure of the monomer.

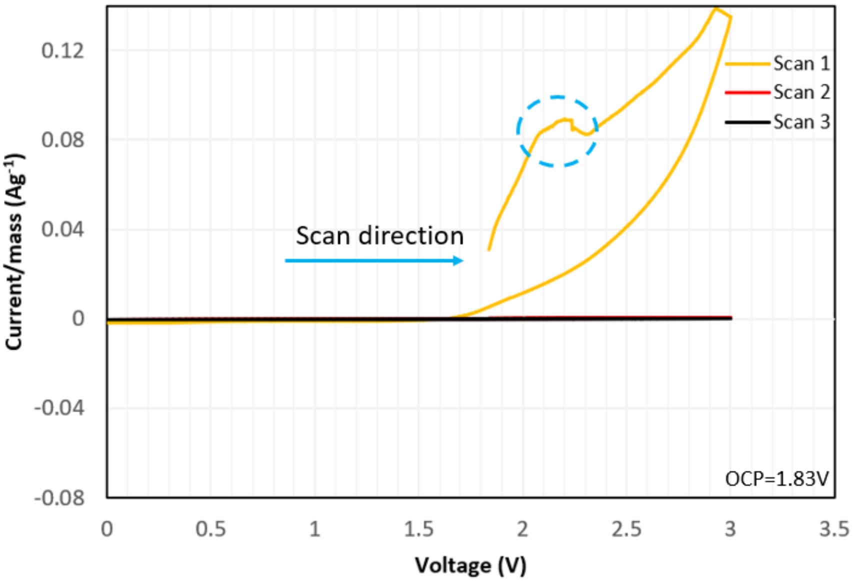

Figure 4.6: Monomer versus Magnesium (only monomer)

Figure 4.6 shows the scan of monomer versus magnesium from 5mV to 3V. The scan rate was 0.1mVs^{-1}. The scan starts and ends at the OCP value (1.83V). The large voltage range was chosen so that once the redox activity of the monomer was observed, then another cell could be made again under similar conditions and scanned in the same voltage range. Initially, the cell was charged in order to remove any residual magnesium that may have entered the perylene during cell construction. That's why the voltage has been increased first. A small peak is observed at 2.3V after which the perylene is destroyed. The peak also corresponds to the standard electrode potential at 2.37V (Mg/Mg^{2+}).

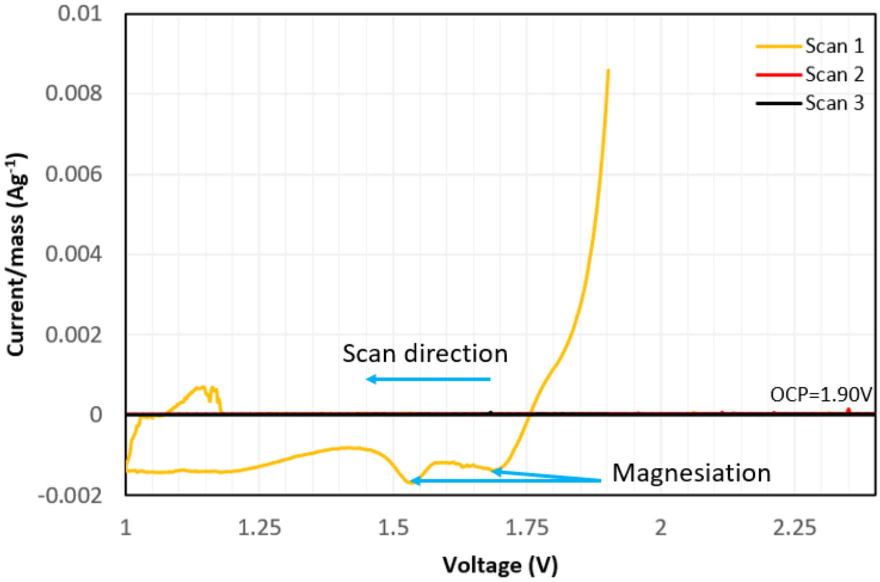

Figure 4.7: Monomer versus Magnesium (different voltage range)

Figure 4.7 shows another CV scan of a magnesium cell with monomer as the active material. The scan starts and ends at the OCP value (1.90V). The voltage range is set from 1V to 2.4V and since it is a fully charged cell, the cell is discharged first. The CV was done at a scan rate of $0.1 \mathrm{mVs}^{-1}$. When the measurement starts, a positive current is observed. This is because there is some magnesium in the cathode. Had the measurement first scanned up and then down (charge first and then discharge), a trend similar to figure 4.6 would be observed.

At 1.55V and 1.7V, small peaks are observed and this corresponds to the magnesiation. 1.55V corresponds to 2.22V vs Li/Li^+ and 1.7V corresponds to 2.37V vs Li/Li^+. From the previous lithium scans conducted, this seems like the peaks could definitely correspond to magnesiation. No capacity is observed while charging the cell and the reason behind this is unknown. The cell was shorted soon after even though the cell had not been disturbed during the measurement.

4.6. Conclusion

From the CV scans done on magnesium cells, it can be seen that the cell dies in between. It looks like a short circuiting, but how this happens is not known. The possible reasons for this to take place are listed below:

- Formation of SEI layer on the surface of the anode preventing magnesium ion diffusion across the electrodes. Presence of chloride and phenyl ions on the surface of the anode hinders the movement of magnesium ions.
- Since chlorobenzene is used as the solvent to dissolve the active material, it could also react with THF in the electrolyte. Chlorobenzene reacts with magnesium in the presence of THF to form phenyl magnesium chloride, a Grignard's reagent. The formation of phenyl magnesium chloride may also cause disturbances within the cell.
- Since the magnesium discs are stored in air, magnesium oxide is formed on the surface of the electrode. Prior to cell fabrication, the electrode discs were sanded thoroughly to remove the oxide formation. Although this is unlikely, it still cannot be ruled out entirely
- The OCV shown by a pristine cell is ~1.8V. The disturbances observed during the CV could have something to do with the way the cell was fabricated.

5

Conclusions & Recommendations

This chapter will answer the research questions and sub-questions based on the results obtained. Recommendations based on the author's experience during the study is also given.

The goal of the thesis was to see if the organic material, perylene was electrochemically active in magnesium ion batteries. The research sub-questions help in answering the main research question. The main research question is:

Is perylene electrochemically active in a magnesium battery?

5.1. Research sub-questions

The research sub-questions answered in this section are based on the experimental results discussed in chapter 4.

Is perylene electrochemically active in a lithium battery?

Yes, the polymer and the monomer is active in lithium-ion batteries. The research was started with lithium because it is extensively studied in the SEE research group. Testing the polymer against lithium served as a basis for the monomer tests. No concrete with the polymer has been established because the polymer was supplied in a limited quantity and at a certain point, the testing had to be stopped. Further tests were carried out with the monomer. The monomer displays reversible electrochemical activity at 2.7V. In figure 4.5, it is a bit unsure if the peak is reversible, but in figure 4.4, the second and third cycles are reversible.

is there any difference in the redox activity exhibited by the polymer and the monomer in both lithium and magnesium systems?

As mentioned before, concrete results with the polymer was not established due to technical problems. But essentially, based on the tests done so far, there is no difference observed in the electrochemical activity between the polymer and the monomer. The polymer is preferred over the monomer when cycle performance is the topic in question.

Is perylene stable in a magnesium cell employing the magnesium-APC electrolyte?

No, perylene is not stable against the magnesium APC-THF electrolyte. The polymer and the monomer dissolve in THF, the solvent of the electrolyte (refer to chapter 4). This is not ideal because it results in loss of active material in the electrolyte, thus hampering the performance of the battery. The PVDF binder also dissolves in THF. With both the active material and the binder lost in the electrolyte, perylene is probably not the best cathode material for non-aqueous magnesium batteries.

What can the poor capacity of the perylene based magnesium system be attributed to?

The poor capacity of perylene can be attributed to dissolution of the PVDF binder and perylene in the magnesium APC-THF electrolyte. It is not ideal to have the binder dissolve in the electrolyte. Since the active material also dissolve in the electrolyte, using a different binder will prevent all of the active material from getting lost in the electrolyte.

Chlorobenzene is used as the solvent to dissolve the active material. Reaction of chlorobenzene with magnesium in the presence of THF results in the formation of phenyl magnesium chloride. Formation of phenyl magnesium chloride on the surface of the magnesium anode may form a passive layer preventing the migration of ions across the electrodes.

Does the electrolyte decompose on the surface of the anode? If yes, how does it affect the performance of the battery?

The answer to this is not known because the magnesium anode was not tested for surface composition. But according to literature, the electrolyte dissociates into phenyl ions, aluminum ions, and chloride ions which form a passive layer on the magnesium anode, thus preventing ion migration.

In answer to the main research question- yes, perylene is electrochemically active in magnesium batteries. Discharge peaks at 1.5V and 1.7V is observed. However, care must be taken to construct magnesium cells in a more careful way to prevent accidental short circuiting.

5.2. Recommendations

Recommendations are based on the bottlenecks encountered during the project. Few of the learning's can be taken into consideration for future research on this topic. Some of the points to be considered are:

- Since the chevrel phase magnesium system was not optimized, the inability to charge the cell could be due to contact issues. It is suggested to use PTFE as the binder for a better performance.
- The voltage window of the chevrel phase cathode can also be increased to see if magnesium extraction takes place at higher voltages. Care must be taken to prevent electrolyte decomposition at higher voltages.
- Since perylene dissolves in THF solvent, it would be useful to test it in lithium ion systems that employ perylene as cathode material.
- Since the active material dissolves in the solvent of the electrolyte, it would be useful to employ cage-like structures for the cathode. Cage-like structures would "trap" the active material, preventing all of the active material from dissolving into the electrolyte.
- To study the cyclic performance of an organic material based cathode, it is best to use the polymer instead of monomer. Lithiated monomer dissolves in the electrolyte more easily. A simple test can be done to confirm this- insert a lithium disc in a glass vial, put a tiny amount of monomer, and some liquid electrolyte. The monomer will take longer to get lithiated, but eventually it will get dissolved in the liquid electrolyte.
- It is also advisable to make an electrolyte that does not dissolve the binder and the active material. Perylene definitely does have a big scope in the field of battery research, but with magnesium, perhaps, aqueous electrolytes can be explored.
- In the CV scan described figure 4.5, two peaks are observed during lithiation and three peaks are observed during de-lithiation. It would be useful to do an in-situ NMR and in-situ infrared to locate the exact position of the ions in the structure of the monomer.
- In the future, it would be useful to do x-ray photoelectron spectroscopy (XPS) measurement on the magnesium anode. This can help determine if there is a passive film formation which prevents ion migration across the electrodes. If this is known, further steps can be taken to optimize the system.
- Exploring solid electrolytes for magnesium batteries can prevent dissolution of perylene and PVDF in the solvent of the electrolyte.

Bibliography

[1] D. Gielena and et al., "The role of renewable energy in the global energy transformation," *Energy Strategy Reviews*, vol. 24, pp. 38–50, 2019.

[2] Z. Yang and et al., "Electrochemical energy storage for green grid," *Chemical Reviews*, p. 3577–3613, 2011.

[3] G. J. Simandl and et al., "Magnesium - raw materials, metal extraction and economics - global picture," 2007.

[4] A. Ponrouch and et al., "Multivalent rechargeable batteries," *Energy Storage Materials*, pp. 253–262, 2019.

[5] N. Elgrishi and et al., "A practical beginner's guide to cyclic voltammetry," *Journal of Chemical Education*, pp. 197–206, 2017.

[6] P. Ranque, "New polymers as binders or electroactive materials for li-ion batteries," Doctor of Philosophy Thesis, L'UNIVERSITE DE PAU ET DES PAYS DE L'ADOUR, Pau, France, 2018.

[7] U. Akpan and G. Akpan, "The contribution of energy consumption to climate change: A feasible policy direction," *International Journal of Energy Economics and Policy*, vol. 2, no. 1, pp. 21–33, 2012.

[8] S. Pryor and R. Barthelmie, "Climate change impacts on wind energy: A review," *Renewable and Sustainable Energy Reviews*, vol. 14, no. 1, pp. 430–437, 2010.

[9] R. Eisenberg, "Addressing the challenge of carbon-free energys," *ACS Energy Letters*, pp. 1521–1522, 2018.

[10] N. Spoorwegen. Sustainable energy. [Online]. Available: https://www.ns.nl/en/about-ns/sustainability/energy/sustainable-energy.html

[11] W. Wang and et al., *Electrochemical cells for medium- and large-scale energy storage: fundamentals.* Elsevier, 2015.

[12] L. Kavanagh and et al., "Global lithium sources-industrial use and future in the electric vehicle industry: A review," *Resources*, pp. 1–29, 2018.

[13] J. Warner, *The Handbook of Lithium-Ion Battery Pack Design.* Elsevier, 2015.

[14] S. O. Amrouchea and et al., "Overview of energy storage in renewable energy systems," *International Journal of Hydrogen Energy*, vol. 41, pp. 20 914–20 927, 2016.

[15] J. Song and et al., "Mapping the challenges of magnesium battery," *The Journal of Physical Chemistry Letters*, pp. 1736–1749, 2019.

[16] P. Saha and et al., "Rechargeable magnesium battery: Current status and key challenges for the future," *Progress in Materials Science*, pp. 1–86, 2014.

[17] O. Pena, "Chevrel phases: Past, present and future," *Physica C: Superconductivity and its Applications*, pp. 95–112, 2015.

[18] E. Levi and et al., "Phase diagram of mg insertion into chevrel phases, $mg_x mo_6 x_8$ (t = s, se). 1. crystal structure of the sulfides," *Chemistry of Materials*, pp. 5492–5503, 2006.

[19] P. Saha and et al., "A rapid solid-state synthesis of electrochemically active chevrel phases ($mo_6 t_8$; t = s, se) fore rechargeable magnesium batteries," *Nano Research*, pp. 4415–4435, 2019.

[20] R. University. Icp-oes. [Online]. Available: https://www.ru.nl/science/gi/facilities-activities/elemental-analysis/icp-oes/

[21] A. W. Bernhard Häupler and U. S. Schubert, “Carbonyls: Powerful organic materials for secondary batteries,” *Advanced Energy Materials*, pp. 1–34, 2015.

[22] A. Iordache and et al., “Perylene-based all-organic redox battery with excellent cycling stability,” *Applied Materials and Interfaces*, pp. 22 762–22 767, 2016.

A

Electrochemical Testing

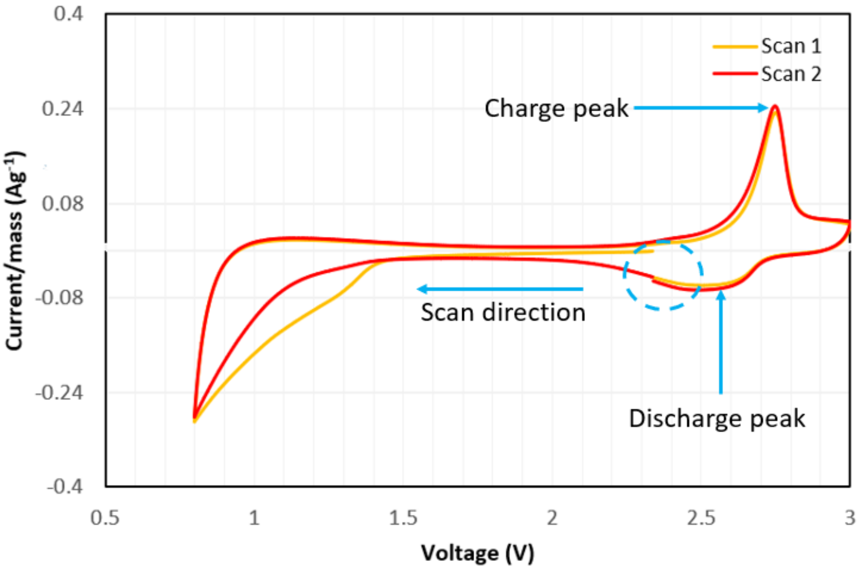

Figure A.1: Monomer versus Lithium

In figure A.1, insertion in pyrelene goes via two reaction mechanisms; at 1V and at 2.5V, whereas the extraction goes only via one step, i.e., at 2.75V.

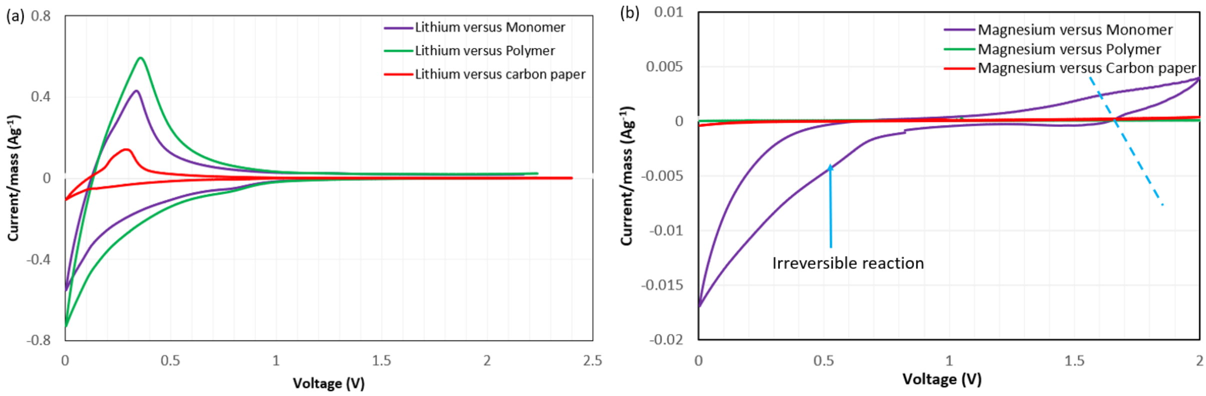

Figure A.2: Monomer, polymer, and carbon paper versus (a) Lithium and (b) Magnesium

The voltage range was set from 5mV to 2.5V. From figure A.2a, no capacity is observed from the monomer and the polymer. At voltages close to 0V, the perylene is destroyed.

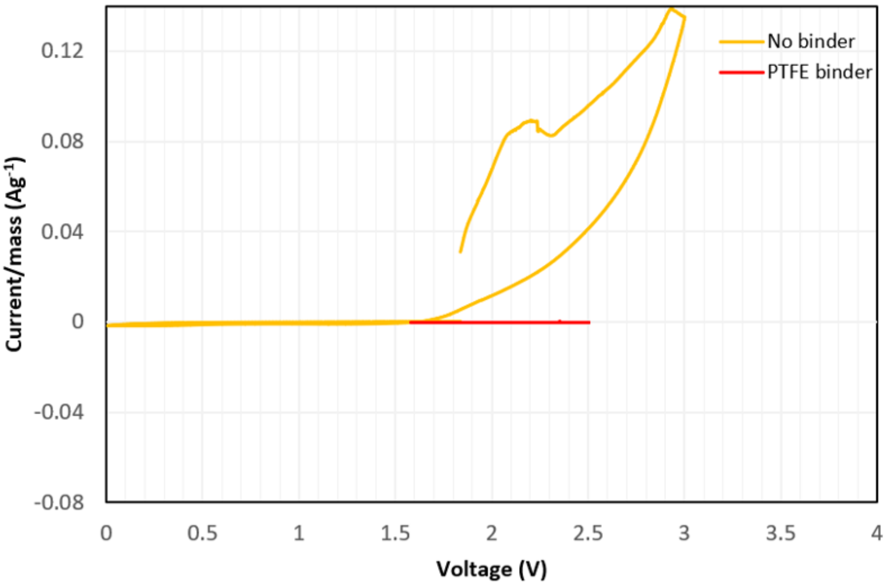

Figure A.3: Comparison between PTFE binder and no binder electrode

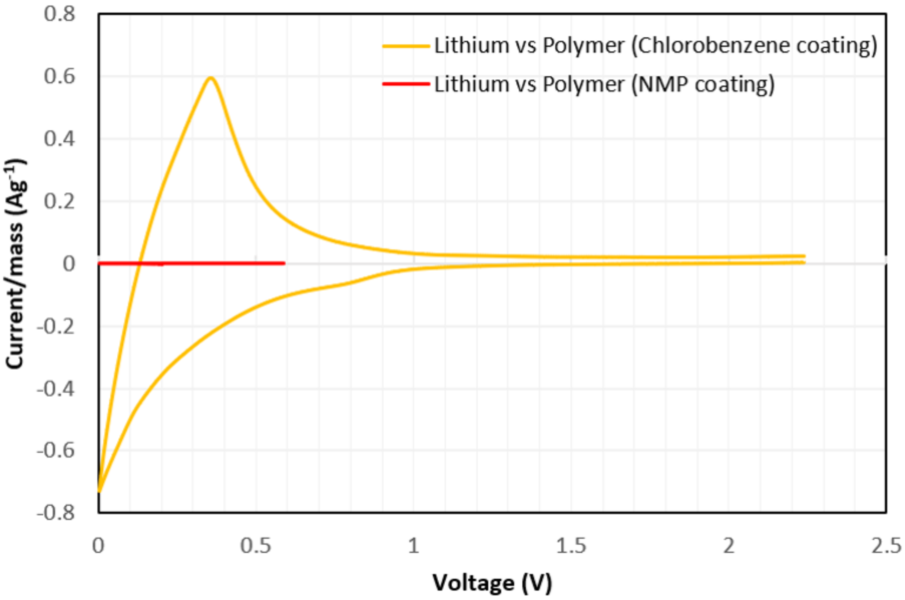

Figure A.4: Comparison between solvents- NMP and Chlorobenzene