Advanced electrodes for hybrid electrochemical capacitors

Rohit Satish

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**ADVANCED ELECTRODES FOR HYBRID
ELECTROCHEMICAL CAPACITORS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

04-August-2016

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Date

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Abstract

The aim of this thesis is to study a new kind of energy storage solution known as “Hybrid Electrochemical capacitor” which allows for the integration of two existing technologies Lithium ion batteries and supercapacitors. The resulting device has the promising properties of both these devices, and can further be fine-tuned to meet the demands of autonomous industry vehicles and Plug in Hybrid Electric Vehicles.

The thesis achieves the above aim by the development and study of electrode materials that can meet the requirements of hybrid electrochemical capacitors. Initial studies are based on the narrowing down of appropriate intercalation materials which can be used as electrodes for a hybrid capacitor. This is achieved in three steps. A benchmark is set using a high Lithium ion conducting type electrode followed by fundamental understanding of the effect of electrode polarity on the energy density of hybrid capacitors. A working prototype cell is constructed using the above rule. Further improvements on the hybrid capacitor are planned by the use of high capacity Lithium rich layered materials.

Apart from battery electrode the thesis looks to develop activated carbon from a bio-degradable source with low cost and low environmental impact. The bio waste material chosen in this thesis is human hair. Human hair was chosen because it is cheap to obtain and environmentally benign also the hair follicles are composed of loosely attached flakes which present a possibility of high surface area activated carbon. Dependence of the activation mechanism on the surface area and pore size distribution is studied. The final aim of this section is to develop a supercapacitor material with a high surface and optimum pore size distribution so that the energy stored in the capacitor electrode can be maximized. All the materials studied during the course of this thesis, were carefully characterized to study structural morphological and electrochemical properties

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Abbreviations

AC	Activated Carbon.
BET	Braunauer Emmett Teller.
CNT	Carbon Nano Tube.
DOE	Department of Energy.
ED	Energy Density.
EDLC	Electrochemical Double Layer Capacitor.
EPH	External Parallel Hybrid.
ESH	External Serial Hybrid.
EV	Electric Vehicles .
EXAFS	Extended X-ray Absorption Fine Structure.
HEC	Hybrid Electrochemical Capacitor.
HRTEM	High Resolution Transmission Electron Microscope.
ICE	Internal Combustion Engine.
IPH	Internal Parallel Hybrid.
ISH	Internal Series Hybrid.
LIB	Lithium Ion Battery.
LIC	Lithium Ion capacitor (can be used interchangeably with HEC).
LLC	Lithium Rich layered oxides.
LMO	LiMn_2O_4 .
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$.
MWCNT	Multi walled Carbon Nano Tube.
NEXAFS	Near Edge X-ray Absorption Fine Structure.
PD	Power Density.
PHEV	Plug-in Hybrid Electric Vehicles.
SEI	Solid Electrolyte Interface.
SLAC	Stanford Linear Accelerator.
SSRL	Stanford Synchrotron Radiation Lightsource.

SWCNT	Single Walled Carbon Nano Tube.
TEM	Transmission Electron Microscope.
XANES	X-ray Absorption Near Edge Structure.
XAS	X-ray Absorption Spectroscopy.
XRD	X-ray diffraction.

Chapter 1

Thesis Rationale

The purpose of this chapter is to develop a perspective on the current scenario of energy storage. It clearly states the need for detailed studies on hybrid electrochemical capacitors, by comparing it with current energy storage solutions. It is identified as feasible solution for application in Plug-in hybrid vehicles. The energy and power density targets for hybrid capacitors is then matched to achieve an EV range of 40 mile and 60 miles respectively. The chapter also clearly outlines the objective and scope of this work with respect to the nature of materials studied and the properties to be focused on. To the reader it also provides a brief dissertation overview which acts as a summary to each of the following chapters entailing the core studies performed in each one of them. The chapter concludes by enumerating the outcomes and novelty of each of the studies performed during the course of this thesis.

1.1 Problem Statement

1.1.1 Background

The last decade has seen a tremendous growth in the energy consumption of the world [1,2]. About 80 % of this energy is still produced using non-renewable sources of energy, [1] like coal, petroleum and natural gas, which are largely used because of the high throughput of energy that can be obtained per unit mass. All of the non-renewable sources of energy although convenient to use, cause severe damage to the environment, in the form of climate change, global warming, pollution, deforestation, large scale species extinction [2-6].

Renewable sources of energy like solar, wind energy etc. are an easy solution for most of the energy related issues faced today. But most of these have an inherent flaw, in that they have an intermittent nature and cannot be used to directly power appliances through the day. For example, the peak demand of electricity is during the night time, a time when solar power cannot augment the grid supply. Energy storage technologies are hence directed at storing the renewable sources of energy during times of high input and then augment the grid during high demand.

1.1.2 Perspective

In an effort to solve the above issue the past decade has seen an immense growth in research pertaining to energy storage solutions [7-9]. Two of the most dominant technologies in this field are Lithium-ion batteries (LIB) and Supercapacitors.

LIB's are capable of storing energy greater than 100 Wh kg^{-1} and are the main energy source for portable electronics industry. Although Li-ion batteries exhibit exceptional energy density, they undergo sudden failure when charged and discharged at high power ratings. This is attributed to the fact that the rocking chair mechanism used to store charge, involves the physical insertion and extraction of the charge carrier ion (Li) from the host structure leading to volume changes in the host. At a high power load, the stress build up in the molecule cannot be dissipated with time hence the structure collapses leading to battery failure. Supercapacitors on the other hand store energy *via*. physical adsorption and

desorption in an electrochemical double layer hence high power reaction are easily possible in this case as no chemical reaction occurs. But as the charge storage happens by the formation of a double layer only on the surface the specific energy of such devices is of the order of $\sim 10 \text{ Wh kg}^{-1}$.

1.1.3 Exploiting the Niche- Motivation

Certain energy storage applications like automated industrial vehicles, small power tools and Plug-in Hybrid electrical devices require a high energy density $\sim 60 \text{ Wh kg}^{-1}$ coupled with an ability to charge fast. Initial tests have used Li ion batteries or supercapacitors for this purpose. While using Li ion batteries guarantees high energy storage capabilities. It leads to capacity fading gradually when cycled at high power conditions.

This is because of gradual disintegration of the host structure. Supercapacitors are more

Figure 1. 1 Ragone Plot showing the energy density and power density of various energy storage technologies, the superimposed region labelled HEC represents the energy and power density gap that HEC devices are meant to fill. Figure Courtesy (US. defense Logistics Agency)

suited for such applications, as they do not undergo any capacity decay when cycled even at high power. But in order to achieve the required the mass of the supercapacitors would be ~ 10 times that of Li-ion batteries.

To reduce the mass of the device it is necessary to increase the energy density. This can be achieved by a technique called hybridization. Wherein a new cell is constructed with a

combination of a supercapacitor and battery electrode. This technology is mainly aimed as a replacement for the current supercapacitors. Hybrid capacitors or HECs have been shown to display energy densities almost 3-4 times of conventional supercapacitors at comparable power densities. Thus making their study and optimization an important scientific contribution to the field of energy storage. The energy and power density of each of the energy storage technologies is summarized in figure 1.1.

The thesis hence, is aimed at both the development and understanding of advanced high energy electrodes for HEC application. It involves the construction of high power faradaic components (operating on an intercalation chemistry) coupled with the synthesis of an economically viable and an environmentally benign, high energy supercapacitor.

1.2 Thesis Target

The target application of HECs is to be a viable solution to power Plug-in Hybrid vehicles. Plug-in hybrids are electric vehicles that share properties from both a standard hybrid vehicle which consists of an electric motor with an internal combustion engine (ICE), and an EV which consists of only an electric motor which can be charged from the grid. Hence unlike conventional hybrids, PHEV devices can substitute electricity from the grid instead of gasoline.

Examples of this technology are the 2014 Ford Fusion Energi which can go about 21 miles by only using electricity and the 2014 Chevy Volt which can travel 38 miles before the ICE kicks in. The use of electricity makes the travel much cleaner and cheaper. The average cost to drive 100 miles on electricity is only 3-5 \$ as compared to ~13-15 \$ for driving hundred miles on gasoline[1]. The United States Advanced Consortium on Batteries(USACB) has established that in order for PHEVs to be commercially viable in the future the driving range of these vehicles needs to be extended so as to reduce the working of the ICE only during high load bearing and high acceleration conditions. The values calculated by the consortium are listed below. The values are also compared with existing values for energy and power density of Hybrid capacitors, reported in literature (Figure 1.2).

Table 1. 1 Requirements of a Plug-in Hybrid Electronic Vehicle as dictated by the United States Advanced battery Consortium

	10mile PHEV	40 mile PHEV
Energy (Wh kg ⁻¹)	65	99.16
Power (kW kg ⁻¹)	0.833	0.383
Weight (kg)	60	120 kg

It can be noted from figure 1.1 that Li ion batteries have sufficient energy storage capabilities but lack in terms of power density. While on the other hand the supercapacitors lack in terms of energy density. HEC devices are placed ideally so as to be able to easily provide for the energy density and power density required for powering PHEV devices.

1.3 Objectives and Scope

The research scope for this work is the development of a hybrid capacitor, which can be a next generation replacement to supercapacitors and also successfully power a 40 mile and 60 mile PHEV.

The objectives set in order to achieve the above can be briefly enumerated as follows.

- Understanding and optimizing the role of faradaic type intercalation compounds in charge storage in hybrid capacitor.
 - Exploration and setting up of a baseline performance for a representative intercalation type electrode with commercially available activated carbon.
 - Studying the effect of electrode polarity on energy density and development of a rubric to decide polarity depending on the power needed from the cell.
 - Application of the above rule to construct a representative intercalation type compound.
- Development of a highly porous, high surface area high carbon structure with exceptional energy storage capabilities.

- Selection of appropriate carbon material as a starting material for constructing activated carbon with high electrochemical activity.
- Studying the effect of activation methods and conditions on the final morphology of activated carbon.
- Developing a pore-size distribution which is hierarchical in nature. Hence maintaining optimum electrolyte contact, and high charge transfer kinetics.
- Developing and studying new chemistries for radical improvement of hybrid

Figure 1. 2 : Comparison of previous data collected on hybrid capacitors based on Non-aqueous electrolytes; PHEV target 1 corresponds to a 10 mile PHEV, and PHEV target 2 corresponds to a 40 mile PHEV. The references for each of the above data points are summarized below.

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capacitor energy storage capabilities.

- Understanding the charge storage chemistry of high capacity materials like Lithium rich layered oxides (capacity double of conventional cathode materials) using *in-operando* X-ray diffraction, synchrotron based X-ray absorption studies. Also to explore the little known oxygen anionic redox reaction occurring in the bulk of such materials using O K-edge near edge X-ray Absorption Fine structure (NEXAFS) studies.
- Studying the effect of introducing high capacity metal oxides into the activated carbon *in-situ* during the carbonization process. This technique has the potential to improve the net energy stored by the activated carbon.
- Fundamental studies on understanding the charge storage mechanism of each of the electrodes.

1.4 Dissertation Overview

The thesis addresses

Chapter 1: Thesis rationale

The chapter outlines the objectives and scope of this thesis. It provides a dissertation overview wherein the aims and objectives of each of the chapters are explained in brief. It also clearly defines the final target for this thesis.

Chapter 2: Literature review

The chapter is aimed at developing a basic understanding of a hybrid capacitor and its components. And previous strategies to improve the performance of these kind of cells. It outlines various classes of materials which have been used as an intercalation host in hybrid configurations, specifically addressing the energy density and power density of each. The chapter helps to determine classes of materials that can provide promising electrochemical performance in a hybrid capacitor. The second half of the chapter involves the study of activated carbon from bio-waste. A list of sources and activation techniques are compared

listing out the pros and cons of each.

Chapter 3: Experimental Procedure

The chapter discusses the principles underlying the synthesis or characterization technique employed. It also explains the various modes of data fitting and data analysis, explaining the rationale behind choosing any technique and highlighting the Pros and Cons of each technique.

Chapter 4: Study of the faradaic component of Hybrid capacitors

This chapter focusses on the study of materials storing charge through a faradaic process in a hybrid capacitor. The chapter can be further divided into 4 sections.

- *Section 4.1* Lithium conducting type garnet materials were investigated by coupling it with activated carbon[10].
- *Section 4.2* The chapter goes on to explore the usage of vanadium based phosphates ($\text{Li}_3\text{V}_2(\text{PO}_4)_3$) which could act as both cathode and an anode, this unique property allows us to develop a rubric as to the conditions suitable for using a faradaic intercalating material as an anode or cathode[11].
- *Section 4.3* From the conclusions drawn in the previous chapter a high voltage cathode was selected to be the electrode of choice when using a hybrid device for maximum energy density at moderate power loads. LiVPO_4F was tested as a high potential electrode[12].
- *Section 4.4* In order to further increase the energy storage capabilities of Hybrid capacitors. Lithium rich layered oxides were explored as a possible high capacity alternative to conventional cathodes[13]. Before application into a hybrid cell the materials was tested *in-operando* using X-ray diffraction X-ray absorption and NEXAFS. These studies have provided a wealth of information on the local changes in the molecule while cycling. Taking us one step closer to the practical application of Lithium rich layered materials in hybrid capacitors

Chapter 5: Construction and application of hierarchically porous activated carbon obtained from Human hair

Human hair was selected as a source of activated carbon due to its natural morphology and weak forces holding its natural flaky structure. The chapter studies the effect of activation on the pore structure and surface area of the final activated carbon sample. Using this information, the activated carbon sample was optimized to have a hierarchical pore size distribution. It also aims to shed light on the improvements afforded by using an optimized activated carbon sample rather than a physically activated, expensive and environmentally hazardous carbon. Comparisons were made between a standard supercapacitor and a hybrid capacitor in order to establish the increase in energy density afforded by using a faradaic electrode coupled with a supercapacitor[14].

Chapter 6: The big picture

This chapter aims at understanding the results together so as to put them in perspective, it aims at highlighting the improvements in hybrid technologies by the results generated in this work. At the same time, it also directs a sight to shortcomings faced during the project and outlines a future plan to alleviate the same. The chapter has been divided into the following 3 sections.

- Section 6.1 Co-relating the previous results to form the big picture.

The section draws together the threads of the thesis comparing the various systems studied against each other, as well as against commercial materials and previous literature indicating any improvements made. We were able to achieve an energy and power density which can be considered sufficient to power 60 km per charge Plug-in Hybrid Vehicles (ED values defined by US advanced battery consortium)

- Section 6.2 Reconnaissance results

These results are included in this chapter as an effort to emphasize other materials which can be used as hybrid capacitor materials upon further optimization. The

nature of these results are purely reconnaissance based. As these materials helped to pave the way to study the materials discussed in the results. The depth of study into the above materials did not warrant an entire chapter on them.

- Section 6.3 Future Plan

The section aims at defining the future of Lithium ion based hybrid capacitors. It outlines the current target achieved and future research needed to improve the performance and scalability of such cells. The section also includes an outline and preliminary results on future fundamental scientific studies required to understand high capacity faradaic materials and also impregnation of activated carbon with metal oxide molecules.

1.5 Findings and Outcomes/Originality

This research led to several novel outcomes like:

1. Application of Garnet type $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$: such garnet structures have been known to have a high Li ion conductivities (stuffed garnets with the formula $\text{Li}_7\text{Nd}_3\text{W}_2\text{O}_{12}$ have been used as a solid lithium ion electrolyte) [10, 15-19]. The study had a two-fold application, initial short term goals include the study of lithium garnets in a lithium ion battery and improvement of its electronic conductivity using *in-situ* carbon coating. These results were then applied while testing this material as a possible faradaic component for hybrid capacitors. The second goal of this work was to setup a baseline in terms of energy density and power density, against which future results can be benchmarked.
2. Understanding the role and contribution of each of the electrodes: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was chosen as it could act as both a cathode and anode [11, 20-26]. The results obtained in the experiment were used to establish that at high power loads (> 2 kW). The faradaic component should be applied as the anode material. And in case of low to moderate power applications hybrid devices can deliver higher energy when the faradaic component was used as the cathode. Such empirical studies had never been carried out for hybrid batteries and are essential for development of high energy

devices [12].

3. Exploring the charge storage mechanism of Lithium rich layered oxides: During the course of initial examination it was observed that Lithium rich layered cathodes exhibit a higher capacity when compared to commercial cathode materials [13, 27-31] $\sim 250 \text{ mAh g}^{-1}$. Hence, these were considered as an excellent choice for a high energy density electrode. The materials undergo a complex reaction mechanism including transition metal redox and oxygen anionic redox. We explored the reaction mechanism of these materials by developing *in-operando* X-ray diffraction experiments. We were able to explore phase changes occurring during cycling. Further experiments were designed to conduct *in-operando* X-ray absorption studies using which we were able to understand local structural changes occurring in the material. Also we were able to conduct near edge XAFS studies to observe the occurrence of oxygen anionic redox reaction.
4. Development of activated carbon from human hair [32, 33], we could achieve a hierarchical pore size distribution by tailoring the activation conditions. This promotes complete wetting by the electrolyte which furthers a more efficient use of the high surface area. The design also allowed us to create ion buffer zones in large mesopores which vastly improve the charge transfer kinetics of the human hair based activated carbon when compared to commercial activated carbon [14].

1.6 References

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Chapter 2

Literature Review

This chapter aims at developing an understanding of the current status of research on hybrid electrochemical capacitors. It also provides a basic understanding the concept of hybridization and its needs. During the course of this chapter a brief introduction is provided initially for batteries and supercapacitors which form the basis of understanding hybrid systems. It later goes on to highlight the workings of a hybrid capacitor, focusing on the different types of hybridization protocol and their pros and cons. Also effort has been made to outline any prior work in literature relating to hybrid electrochemical capacitors, initially exploring alternatives for systems based on aqueous electrolytes and then discussing in detail the intercalation materials that have been used as a possible anode or cathode in hybrid electrochemical capacitors using non aqueous electrolytes.

Also one of the major setbacks to hybrid electrochemical capacitors is the use of activated carbon which has not be fine-tuned to provide a high energy density. The later part of this review is aimed at developing an understanding of the activation process and the various parameters involved in tuning the available surface area and pore size distribution

2.1 Li-ion battery

2.1.1 Background

Lithium ion batteries (LIB) have been at the forefront of energy storage research for the past decade. The main reason for this is the high energy density, high operating potential and highly tunable nature. These devices power almost the entire mobile electronics industry because of their high energy density of 100-150 Wh kg⁻¹.

The basic LIB consists of four components, a cathode, anode, electrolyte and separator. Commercial cathode materials consist of various kinds of materials ranging from layered oxides like LiCoO₂, spinel LiMn₂O₄ and Olivine materials like LiFe(PO₄). The anode materials commercially viable till today mainly consists of carbonaceous materials like graphite. The choice of electrolyte depends on the kind of system. For the purpose of this thesis we will be focusing solely of organic electrolytes which mainly consist of Lithium salts like LiPF₆ dissolved in carbonate based solvents. These electrolytes are chosen because of their relatively large potential window. The separator generally consists of polymer films or woven glass fibers which allow for the conduction of ionic species through them but at the same time have a high electronic resistivity [1, 2]. The electrochemical energy stored in Li-ion batteries is *via*. a rocking chair mechanism which can be elucidated as shown in equation 2.1

Where $x \approx 0.5$, $y=0.6$ (the formula pertains to a LiCoO₂ cathode and a graphite anode)

2.1.2 Working

The working chemistry of a standard LIB used today revolves around simple redox chemistry. As the cell is charged the transition metals in the cathode undergo an oxidation reaction which leads to a unit increase in the charge of the molecule, to maintain charge neutrality the cathode material donates a Li-ion into the electrolyte solution and an electron in the external circuit. The potential applied across the circuit then allows for the movement

of this lithium ion to the anode where they are then again reduced to metallic lithium using the electron travelling in the external circuit. The process is illustrated by the schematic in figure 2.1.

During discharge the Li atoms are oxidised from the anode and travel through the electrolyte and get reinserted into the cathode material. The lifetime and the net capacity of a Li-ion cell depends on this reaction occurring reversible with minimal losses.

Figure 2. 1 : Schematic of a standard Lithium ion Battery with graphite as the anode and LiCoO_2 as the cathode material, electron flow is shown in the external circuit, whereas Li ions migrate through the Li conducting organic electrolyte. Reproduced with permission from B. Scrosati et al. Journal of Power Sources, **2010**. 195(9): p. 2419-2430.

2.1.3 Alternate charge storage routes for Lithium ion batteries based on anode chemistries

In the previous section the mechanism discussed w.r.t to Li ion batteries, pertains to the rocking chair mechanism followed in the case of intercalating type host materials. The two other possible mechanism that can be employed for the purpose of lithium storage can be outlined as follows

- Conversion
- Alloying

Both these mechanisms show high discharge capacity when compared to intercalating materials. But they have been known to shown to an extremely high change in volume

during charge and discharge. These extreme changes lead to a low cycle life. Making materials storing charge by these mechanisms not appropriate for Hybrid capacitor applications

2.2 Supercapacitors

2.2.1 Background

Supercapacitors are devices that are especially designed to provide large bursts of power in short time durations. These devices are largely made from high surface area activated carbon (1000-2000 m²g⁻¹). The energy density of most of these devices is low (~2-10 Wh kg⁻¹). But they have extremely high power densities of the order of 2-5 kW kg⁻¹ [4]. In comparison to normal parallel plate capacitors these devices display a much higher capacitance which can be easily explained using the following relation.

$$C \propto \frac{A\epsilon_r\epsilon_0}{d} \quad \text{eq 2.2}$$

Where,

C is the capacitance of the device in Fg⁻¹.

A is the surface area of the electrode in m².

d is the distance between the two electrodes m.

ε_r Is the relative static permittivity.

ε₀ Is the permittivity of free space (8.854 E-12 F m⁻¹)

Using high surface activated carbon allows the increase in capacitance by increasing the area manifold when compared to a parallel plate capacitor. Activated carbon is generally obtained from petroleum sources such as coal tar and pitch, but recently there has been a growing research trend towards the use of bio-waste based activated carbon.

2.2.2 Working

Supercapacitors can be broadly divided as

- Electrical double layer capacitors: These are capacitors that store charge

electrostatically using the reversible adsorption of ionic species from the electrolyte on the surface of the electrode. Charge separation occurs upon the polarization of the electrode – electrolyte interface to form what was described by Helmholtz in 1853 as double layer capacitance. The capacitance can be calculated using equation 2.2. The theory was later modified by Guoy and Chapman to suggest the formation of the charged interface as a diffuse layer at the electrode electrolyte interface. The capacitance depending on the choice of electrolyte ranges from 5-20 $\mu\text{F cm}^{-2}$ [3]. Specific capacitance obtained have been generally observed to be greater in the case of aqueous electrolytes but organic electrolyte based EDLC supercapacitors store a higher amount of energy. This is attributed to the wider working potential of organic electrolytes. The energy stored by a supercapacitor is calculated using the equation.

$$E = \frac{1}{8 \times 3.6} CV^2 \quad \text{eq 2.3}$$

Where

C is the capacitance of the material in F g^{-1}

V is the working potential (Volt)

E is the energy Wh kg^{-1}

Since the total energy stored is squarely dependent on the potential range. A slight increase in the working potential leads to a significant increase in the net energy stored.

As a result of the electrostatic nature of the formation of EDLC no faradaic reactions occur at the electrode. This means that the electrode kinetics is instantaneous and the lack of ions inserting into the bulk of the structure ensures that no structural deformations occur while cycling preventing any capacity fade. Another important difference when compared to batteries is that the charge storage mechanism is in no way dependent on the choice of the solvent used unlike in LIBs. Where the carbonate based solvents allow for the formation of a stable solid electrolyte interphases which further stabilizes the electrode. Hence we are free to choose solvents that can operate at even below -40°C . Hence, most of the attention

in the field of supercapacitors is directed to the optimization of the surface of the electrode [4].

- Pseudo-capacitors: Certain capacitors use extremely fast transition metal redox reaction to store charge. Due to the fast kinetics these materials very often present with profiles very similar to EDLC type capacitors. Metal oxides such as RuO_2 and MnO_2 and certain conducting polymers [5-7] have been shown to exhibit this behavior. The specific capacitance of pseudo-capacitors is observed to be considerably higher when compared to carbon based supercapacitors. But the use of redox reactions for charge storage leads to problems in long term stability of the electrode material.

2.3 Hybrid Electrochemical Capacitors

2.3.1 Background

Recent times have seen an increased demand for high energy and high power energy storage devices that will be able to power Plug-in hybrid electric vehicles (PHEV) and purely electric vehicles. Hybrid electrochemical capacitors are a step towards satisfying this demand as they have the ability to deliver relatively high energy outputs at high power loads. An HEC can be schematically represented as Figure 2.2.

Figure 2. 2 Schematic representation of a Li- hybrid electrochemical capacitors. Adapted with permission from G.G. Amatucci, F *et al.* Journal of the Electrochemical Society, 2001. 148(8): p. A930-A939.

2.3.2 Working

Currently there is no general understanding of the charge storage mechanism at play in case of hybrid capacitors, it is largely considered to be mixture of both battery and supercapacitor charge storage techniques. There are two possible ways the cell could store Lithium based on the choice of polarity of the electrodes. Keeping in mind all the discussions below are based on organic electrolytes.

1: Battery material as cathode: During the charge cycle the Li-ions in the electrolyte can physically adsorb onto the surface of the activated carbon electrode at the same time the cathode material de-intercalates Li out of its host structure. During the discharge process the Li ions are de-adsorbed from the surface of the activated carbon into the electrolyte and the Li ions already present in the electrolyte are re-intercalated back into the battery host structure. This configuration allows for the adsorption of the much smaller Li ion species on the activated carbon surface. While the much larger PF_6 ions do not participate in the charge storage mechanism. One of the major problems in this process is the lack of charge carriers for energy storage.

2: Battery material as anode: During the charge cycle the Li-ions from the electrolyte are intercalated into the battery host structure whereas the PF_6 ions from the electrolyte are physically adsorbed on the surface of activated carbon. During discharge the process reverses itself. One of the leading problems with this configuration is the lack of charge carriers in the system. A possible way to go around this issue can be to employ a technique which has been well established for graphite based Li-ion electrodes called pre-lithiation. During pre-lithiation the anode materials is coupled with a Li metal electrode and discharged hence filling the host structure with Li. This Lithium stuffed anode is then placed in the hybrid capacitor configuration, increasing the net number of charge carriers in the system.

2.3.3 Approach to hybridization

Hybridization of a battery and a supercapacitor can be carried out in several different ways depending on the application. A summary of the possible approaches to achieve hybridization is shown in figure 2.3.

Hybrid systems connected externally are called external hybrids. These can further be divided into external series hybrids (ESH) and external parallel hybrids (EPH). A single

Figure 2. 3 Schematic representing the types of hybrids. Used with permission from D. Cericola *et al.* *Electrochimica Acta*, 2012. 72: p. 1-17.

cell containing both the battery and supercapacitor components is called an internal hybrid these can again be classified as an internal series hybrid and an internal parallel hybrid. Each of these type of devices is explained in detail below.

External serial hybrid systems

This configuration has not been extensively studied till date, a possible approach to study these systems is discussed by Burke et al. When the two type of devices are coupled in series as expected the voltage across the circuit adds up while the same amount of current flows through both the devices. The device with the lower energy density is the limiting factor in this setup both in terms of net energy and the tolerance to voltage swings that can be tolerated by the device. For this setup to be practical enough the battery electrode needs to be made much larger than the supercapacitor electrode to improve high current performance. In conclusion this type of hybrid system is too bulky and lacks any practical use.

External Parallel Hybrid Systems

This idea was initially suggested as early as 1968 by Ragone [8]. Since then this field has received a lot of attention especially towards improving the pulse capabilities of batteries which could be used to apply short bursts of power to crank engines at low temperatures. A combination of a battery and a supercapacitor can considerably reduce the size of the battery to be used. The size and materials used in the battery need to be optimized so that it can charge a supercapacitor quickly at the same time be able to store enough charge for three crank attempts. Since batteries have much higher energy densities when compared to supercapacitors. An ideal solution would be to have a small battery pack coupled with a larger supercapacitor device.

The parallel combination is advantageous in other applications also such as regenerative braking wherein the supercapacitor can charge quickly due to the energy released during breaking of an automobile and in turn charge a battery. This stored energy can be reused during periods when high acceleration is warranted. An added advantage of adding of adding a supercapacitor in parallel to a battery system is that it acts as a filter system therefore any transient currents that might have passed through the battery leading to material degradation, now passes through the supercapacitor electrode. This dramatically increases the battery life and thereby increasing the range of the vehicle.

Internal serial Hybrid batteries

This configuration is the main area of experiments in this thesis, they can alternatively be called Hybrid Electrochemical Capacitors, and in this case one electrode is a battery type while the other is an EDLC (electrical double layer capacitor) type electrode, depending on their working potential the components can be used as a cathode or an anode.

Internal Parallel hybrid systems

IPH or bi-material electrodes consist of both a faradaic and non-faradaic component in a single electrode. One of the interesting examples of this combination is given by Cericola *et al.* [9]. The work looks to compare two systems one using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and activated carbon and the other employing LiMn_2O_4 and activated carbon. This setup when tested against ISH hybrid combination with the same materials resulted in higher recorded energy densities. Certain limitations occur in the construction of these kind of hybrid devices. Including the engineering of the contact between the two materials and their compatibility with each other. Activated carbon is stable over the potential range used by most non aqueous electrolytes hence most of the research needs to be aimed at the battery electrode. LTO and LMO are potential candidates and the LTO/AC system has been commercialized as BatCap the system can store (90-32 Wh kg⁻¹ at 50-6000 W kg⁻¹).

An interesting direction to develop this kind of hybridization would be to establish a composite *in-situ* during the synthesis process which will ensure good kinetics across the surface contact points between the materials.

Results published in literature in the past decade are focused on the study of Internal Serial Hybrid (ISH) devices. This is so because of the infant stages of hybridization. ISH devices help us to understand the mutual dependence of both the electrodes and the complex interplay of supercapacitor and battery components. Upon further understanding of the reactions between the components and the mechanism of charge storage and its dependence on both electrodes, these hybrids can become more prevalent players in the energy storage market.

2.3.4 Comparison between a hybrid device and a Lithium ion battery or supercapacitor

Figure 2.4 compares a hybrid capacitor with a battery and a supercapacitor, and helps to gain perspective as to the energy density that is expected from an ideal Hybrid capacitor. Most of the research conducted on hybrid capacitors are based on water based electrolytes because of the high ionic conductivity of water when compared to non-aqueous systems.

But it can be observed that experiments conducted using hard carbon/graphite or Lithium insertion host materials in non-aqueous electrolytes indicate a higher energy density because of a relatively higher working potential [2,9]. On comparison it can be noted that the energy density of batteries is almost double that of hybrid capacitors. Hence Hybrid capacitors are in no way a replacement for LIB instead they can be treated as next generation supercapacitors. The next section briefly looks at the experiments conducted on hybrid capacitors and aims at forming an understanding the nature of materials which can be considered to be suitable for Hybrid capacitors.

Figure 2. 4 Comparison between internal serial hybrids based on activated carbon and different faradaic materials. The specific energy is reported against the cell voltage. As comparison the specific energy of an idealized EDLC, an idealized internal serial hybrid and an idealized Li ion battery are reported the figure is used with permission from D. Cericola et al. *Electrochimica Acta*, 2012. 72: p. 1-17.

2.4 Study of materials applied in Hybrid Electrochemical Capacitors

One of the major pitfalls towards wide scale application of Hybrid electrochemical capacitors is the lack of focused studies on materials that are solely designed for this application. The choice of activated carbon as the supercapacitor electrode is natural because it is cheap and easy to synthesize. The selection of the battery component needs understanding of the nature of properties needed for hybrid capacitors. The next section highlights these properties in detail.

2.4.1 Selection criteria for the faradaic component in Hybrid capacitors.

Initial studies on hybrid capacitors were conducted using aqueous electrolyte, the electrode materials generally used are limited to metal oxides, hydroxides, and sulphates. These devices have been shown to show excellent high power capabilities as highlighted in the next section. But the use of water as the electrolyte leads to limitations on the potential window that can be used in these cells. This in turn limits the energy density of the cell.

A more important area is the study of insertion based host materials that can be used in non-aqueous media which can deliver energies three to four times higher than water based electrolytes. A high performance Li ion insertion host material is necessary to deliver high energy capabilities over a prolonged duration. In comparison with pseudo-capacitors these are able to accommodate Li ions *via* a two phase process which allows for the maintenance of a constant potential output during the charge and discharge.

The choice of a proper insertion host material can thereby increase the energy density of the HEC manifold. Summarizing from a few keystone developments in the HEC based research area a few rules of thumb can be set aside while choosing a proper host material.

- (i) Most commercial organic electrolytes consist of a lithium salt like LiPF_6 dissolved in a mixture of carbonate based solvents. These mixtures are stable in a potential window of 0.7V to 4.5 V *vs.* Li metal. Hence it is considered to develop a device which functions in this potential window. If the material is discharged below 0.7 V the carbonates in the electrolytes start to decompose to form a solid electrolyte interphase between the electrode and electrolyte, this layer helps to form a

passivating layer on the electrode but at the same time adds to the mass transfer resistance of the material, thereby reducing the net capacity of the material and severely affecting its high power performance. At potentials higher than ~ 4.5 V vs. Li the electrolytes undergo certain side reaction and force the electrode to release oxygen present in its lattice this leads to destabilization of the host material and leading to failure. Therefore, complete half-cell studies need to be performed on the host material before assembly to ensure that it can be used in a LIC [21].

- (ii) In case aluminum is used as the current collector for the testing it should be ensured that the discharge potential does not go below 0.5 V vs. Li. Below this potential Li begins to start alloying with aluminum leading to an irreversible loss of Lithium from the system, reducing the amount of charge the system can store.
- (iii) Carbonate based electrolyte solvents used today have been shown to have inferior ionic conductivity as compared to solvents used in supercapacitor systems today. An example of this are electrolytes based on acetonitrile solvents these have been shown to have an order of magnitude higher ionic conductivity when compared to carbonate based electrolyte. But they suffer from certain safety flaws such that they are flammable at high temperatures and are not stable at low potentials. This safety concern further limits the choice of electrolyte for HECs
- (iv) Another issue that plagues a majority of Li-HEC devices is the electrode materials suffer from low electronic conductivity leading to a high degree of polarization during cycling. If in the discharge cycle the redox potential of the materials is reduced to 0 V vs. Li it leads to Lithium plating on the surface of the electrode which can further lead to short circuiting of the cell.
- (v) Utilization of nanostructured materials as possible battery materials has been seen to improve the overall performance because of the extra available surface area. But the availability of all this extra area also adds to the possibilities of very vigorous side reactions with the electrolyte.
- (vi) Non faradaic electrodes, i.e. EDLC based electrodes store charge by physically adsorbing a charged species on their surface to form a double layer. The energy stored by these electrodes is solely dependent on the surface morphology and pore structure. Because of this simple physical charge storage mechanism, they have

been shown to exhibit cycle lives greater than 500000 cycles. To complement this, the Li insertion type electrode needs to be extremely stable during the entire working potential range [21].

- (vii) The choice of anion used in the electrolyte also greatly influences the capacity of the HEC. The ionic content of the electrolyte needs to be optimized to achieve higher performance. Specific capacity of Li-HEC's have been shown to vary a great deal depending on the nature of salt used, for example for LiPF_6 , LiCF_3SO_3 , LiClO_4 and LiBF_6 the reported values are 176, 172, 252, 286 mAh g⁻¹ respectively [21]. While designing a Li-HEC device one has to be mindful that the concentration of Lithium in the electrolyte strongly controls the ionic conductivity of the electrolyte. The host material chosen should be able to counter this change in Li molarity of the solution.

2.4.2 Aqueous systems

Systems based on Manganese Dioxide

Huo and Tsuo were the first to study this system which used MnO_2 as the anode material and activated carbon as the cathode the testing was conducted in an aqueous electrolytes [10, 11]. During the charging process MnO_2 is oxidized coupled with exchange of protons in the aqueous medium. The system shows promise in terms of high capacitance and cycle life, studies have also been conducted to explore the effect of morphology on the capacitance of MnO_2/AC [12-14]. A capacitance of 31 F g⁻¹ is observed. In terms of application the system is limited due to the usage of an aqueous electrolyte.

Systems based on Nickel oxides and hydroxides.

This system was extensively studied initially by Varakin *et al* [15]. Activated carbon is mostly used as the negative electrode with Nickel Hydroxide electrodes being used as positive electrodes dipped in alkaline electrolytes. The electrochemical cell uses the Ni (II) to Ni (III) oxidation process to store charge. The material displays initial issues with conductivity. This has been alleviated by the use of conductive additives.

Systems based on Lead compounds

These are derived from the well-established Lead Acid battery industry. Activated carbon is employed as the negative electrode. A mixture of lead oxide and lead sulphate is used as the cathode materials with sulphuric acid acting as the electrolyte. The system exploits the Pb(II)/ Pb(IV) redox couple. They have been shown to be stable for more than 10000 cycles. But the usage of lead leads to questions about the safety of the battery.

2.4.3 Non Aqueous Systems

2.4.3.1 Anodes

1: β -FeOOH – is analogous to hollandite type α -MnO₂ which has been shown to have reversible capacity of $\sim 300 \text{ mAh g}^{-1}$ [15] when used in Li ion batteries. β -FeOOH can be synthesized using a conventional hydrothermal method. It has a 2*2 tunnel like structure which facilitates fast Li kinetics. Half-cell studies at low current rates of 5 mA g^{-1} show a capacity of $200\text{-}240 \text{ mAh g}^{-1}$. It was paired up with activated carbon for Li-HEC testing after appropriate mass balance was applied on both the electrodes. A maximum cycle life of 800 cycles at 10 C was recorded. At low power loads an energy density of 45 Wh kg^{-1} was recorded on a single electrode basis, which is double of that recorded for AC/AC systems [9, 16, 17].

2: Transition Metal oxides

2.1 V₂O₅ – Vanadium based compounds have long attracted attention from the Li ion battery community because the large range of available oxidation states in vanadium. V₂O₅, assuming an insertion of 2.2 moles of Li, is able to deliver 325 mAh g^{-1} [18-20]. Capacity fading is one of the main problems that is faced by V₂O₅. Several approaches have been used to improve the cycle life of V₂O₅ based batteries including modification using conductive coatings or stabilizing agents. One of the important technique which has shown promise is the development of 1-D nanostructures of V₂O₅. Using half-cell studies as the basis Li-HEC was constructed with Single walled CNT as the counter electrode.

The cell is shown to be stable for 500 cycles while being able to deliver a maximum energy density of $\sim 18 \text{ Wh kg}^{-1}$ at 315 W kg^{-1} [21]. Although appreciable the performance of V_2O_5 does not make it a competitive anode for HEC applications because of the large capacity

Figure 2. 5 Represents the framework of V_2O_5 as viewed along the b axis. K. Momma and F. Izumi. Journal of Applied Crystallography, 2011. 44(6): p. 1272-1276.

decay observed in half cell studies wherein within 50 cycles the materials could retain $\sim 45 \%$ of its initial capacity. Attempts have been made to introduce 1 dimensional nanostructured V_2O_5 but no considerable improvements are observed.

2.2 $\alpha\text{-MnO}_2$ – MnO_2 is a unique material which has been widely investigated for applications in both li ion batteries and supercapacitors [22-26]. This is because of the pseudo-capacitive nature of charge storage in MnO_2 . One conformation which is of special interest is the hollandite type tetragonal MnO_2 these are generally synthesized using a hydrothermal route and crystallize into nanorods [27]. Cycled from 1.5 to 3.8 V vs. Li a reversible capacity of 130 mAh g^{-1} is recorded. Li HEC fabricated using AC as the cathode and $\alpha\text{-MnO}_2$ as the anode deliver a maximum energy density of 9 Wh kg^{-1} at a power density of 87 W kg^{-1} [27]. MnO_2 suffers from poor cycling performance this is because of the low electronic conductivity of the pristine material. Later efforts were directed to develop a Li-HEC with $\text{MnO}_2/\text{MWCNT}$ composite as the cathode and MWCNT's as the anode, the electrolyte used is also changed to one with higher ionic conductivity like LiClO_4 in EC:DEC. The recorded energy density is 33 Wh kg^{-1} [28]. Even after adding conductive additives and changing the nature of the Li salt, improvements in cycle ability and high power performance could not observed.

2.3 TiO₂ (Anatase)- Various polymorphs of TiO₂ have been applied in the energy storage [29]. One of the most common polymorphs of TiO₂ available is Anatase TiO₂, it offers advantages such as a stable redox potential, and a good cycle life. But alternately it suffers from a huge irreversibility of the order of 75 mAh g⁻¹ in the first cycle also the relatively high redox potential of 1.7 V vs. Li makes it an impractical anode for Li ion batteries. But because of their high degree of stability these are suitable for Li-HEC formulation. Tests were conducted by using anatase TiO₂ as the anode and activated carbon as the cathode material a maximum energy density of ~42 Wh kg⁻¹ and a power density of ~0.8 kW kg⁻¹ [30]. But the large Li consumption during the first charge could still not be alleviated. Research has also highlighted the use of mesoporous anatase TiO₂ with MWCNT's this has been shown to have an energy density of ~80 Wh kg⁻¹ [31].

2.4 Bronze TiO₂ – over the years the bronze phase TiO₂ has shown most promise because of its ability to store a large amount of charge using a two phase mechanism [32-34]. It is prepared using a simple hydrothermal technique wherein anatase TiO₂ is exposed to a

Figure 2. 6 (1) Crystal structure of TiO₂ as viewed along the b axis (2) Displays the electrochemical data corresponding to the performance of TiO₂ in a Lithium half-cell. It has been adapted from V. Aravindan et al. Chemical Reviews 2014

strongly alkaline medium at $\sim 130^\circ\text{C}$ in a hydrothermal autoclave. The reaction process leads to the formation of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanorods. They are subsequently washed with a strong acid to form $\text{H}_2\text{Ti}_3\text{O}_7$ the hydrogenated compound is further heated at $\sim 500^\circ\text{C}$ to obtain bronze phase TiO_2 . The resultant B- TiO_2 has a monoclinic structure, as depicted in Figure 2.6. The titanium oxygen network leads to the formation of tunnel like structures which is indicative of facile Li insertion [35-41]. Li-HEC was fabricated with activated carbon as the counter electrode a maximum energy density of 23 Wh kg^{-1} was obtained and a maximum power of $\sim 2.3\text{ kW kg}^{-1}$ could be applied on the system. Other studies are also conducted on the dependence on nano-structure and the nature of separator used during the cell assembly it has been instrumental in showing that bulk TiO_2 powders do not have any significant electrochemical activity.

2.5 LiCrTiO_4

Lithium chromium titanate is not highly reported as an anode due to the high toxicity of chromium [42-44]. It has theoretical capacity of 157 mAh g^{-1} and an insertion potential of

Figure 2. 7 : Crystal Structure of LiCrTiO_4 . The tunnel like structure is indicative of good battery performace. (2) Electrochemical performance of LiCrTiO_4 adapted from V. Aravindan *et al.* Chemical Reviews, 2014.

1.5 V vs. Li. It belongs to the spinel class of materials which have been known to have an open 1D tunnel like structure shown in figure 2.7. This structure facilitates the movement of Li ions to and fro from the structure.

It has been tested in a Li-HEC configuration and has proved to be the most promising anode material till date. An energy density of 23 Wh kg⁻¹ and a power density of 4 kW kg⁻¹ is recorded for the bare materials, and is stable for ~ 9000 cycles.

2.6 Li₄Ti₅O₁₂

Has spinel framework with the general formula AB₂O₄. It has garnered a multitude of interest in terms of an anode candidate for Li-ion batteries. The reason for this is its unique structure, it can undergo intercalation of ~3 moles of Lithium into the host structure without any volume change [45]. It loses viability as a Li ion battery material because of its relatively high redox potential of 1.5 V vs. Li[46]. But this is not an issue for Li-ion capacitor devices. LTO has been tested with activated carbon as the counter electrode and has been able to deliver excellent performance. Naoi *et al*[47-50] have shown that LTO

Figure 2. 8 Energy and power density of LTO when used in Hybrid capacitor. Used with permission from K. Naoi et al. Journal of Power Sources, 2010. 195(18): p. 6250-6254.

can be used even at very high current rates up to 300 C. Figure 2.8 (ref [49]). The hybrid electrochemical capacitor is reported to have an energy density 4 times that of a

symmetrical supercapacitor. LTO has been reported to have low electronic conductivity when compared to other battery materials, hence its usage in Li-HEC devices warrants the modification of the material by either coating it with a conductive layer or by the suspending it in a conductive matrix, this reduces the net tap density to a certain extent.

2.4.3.2 Cathodes

1: Spinel Oxides

1.1: Lithium Manganese dioxide (LiMn_2O_4)

Lithium manganese dioxide is a spinel type material which has recently garnered attention because of crystal structure which allows for the facile movement of lithium atoms through the 1-D tunnels as shown in figure 2.9 below[51]. A maximum energy density of $45 \pm 5 \text{ Wh kg}^{-1}$ at a power rating of 30 W kg^{-1} has been reported for $\text{LiMn}_2\text{O}_4/\text{AC}$ systems [9, 52-55].

The manganese atoms in LiMn_2O_4 are a mix of +3 and +4 oxidation states during the charge process. The Mn (III) has been shown to be vulnerable to Jahn-Teller distortion which leads to dissolution of Manganese into the electrolyte when the electrode is cycled above 4 V leading to a gradual loss in capacity. Depending on the counter electrode used in the

Figure 2. 9 Crystal structure of LiMn_2O_4 indicating a spinel structure.

Li-HEC setup the capacity fade could be a serious issue. One possible solution is the partial doping of Manganese with other transition metals like Ni discussed below.

2.2: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Ni doped Lithium manganese oxide (LNMO) was first studied as a possible cathode material as a Li-HEC cathode material by Li *et al*[56]. The material is composed of Mn (IV) ions. Mn(III) ions have been replaced by Ni(II). A half-cell capacity of 125 mAh g^{-1} is observed. Li-HEC device was optimized with an LNMO to AC mass ratio of 1:3. And cycled between 0-2.8 V. A maximum energy density of 55 Wh kg^{-1} was recorded for the sample. Other examples of using LNMO have been modified using a solid state ceramic route, wherein a small fraction of Mn^{3+} is present along with Mn^{4+} this has been shown to increase the capacity to 133 mAh g^{-1} at the same time increasing the maximum energy density of the Li-HEC device to 56 Wh kg^{-1} [57]. Both the above studies have shown that LNMO can withstand operations at high currents (up to 20 C) but they lack in terms of a high cycle life this is mainly due to the side reactions occurring with the electrolyte during cycling.

Figure 2. 10 Figure Indicating the performance of LNMO at varying current rates. Reproduced with permission from ref[56]

2: Layered Oxides

2.1: $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{O}_2$ - layered oxides have long been considered an ideal choice for Li-ion batteries because of their large reversible capacities. But these materials suffer when operated at high currents ultimately leading to cell failure. Karthikeyan *et al.*[27] was the

first to study $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{O}_2$ as a potential layered cathode for Li-HEC applications. In spite of a favorable structure for facile Lithium migration it has been shown to have a near insulating nature, hence the authors have suggested the formation of composites with conducting polymers. The $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{O}_2$ -PANI-Ppy electrode was then cycled with activated carbon as the counter electrode in an organic electrolyte. The electrode displayed an energy density of 49 Wh kg^{-1} . This is in stark contrast to the low value of 10 Wh kg^{-1} which is obtained when only the bare materials is tested in a HEC setup. The layer of conducting polymers helps to form a conducting substrate which allows for facile electron migration between the current collector and the active material. At the same time coated active material is able to provide a cycle life of ~ 5000 cycles without any significant decay.

2.2: Li_2MoO_3 is an example of a high capacity layered oxide because of the multiple oxidation states of Mo. A hypothetical capacity of 340 mAh g^{-1} can be obtained considering a two electron transfer. Kobayashi *et al.* [58] developed a simple solid state technique for the synthesis of Li_2MoO_3 . Li_2MoO_3 is said to have a rhombohedral structure as shown in

Figure 2. 11 Representation of Li_2MoO_3 . The material displays a layered structure with alternating MoO_6 and Li layers

figure 2.11 but the nature of the stacking is highly dependent on sintering conditions. Park *et al* [59] successfully implemented the formation of a HEC by using Li_2MoO_3 -AC composite in combination with hard carbon as the counter electrode [60]. But Park *et al.* have employed Li_2MoO_3 as a sacrificial cathode which helps to lithiate the hard carbon

anode during the initial cycles. The Li_2MoO_3 does not contribute electrochemically in any way towards the performance of the cell but helps to reduce the task of separately lithiating the anode before application.

2.3: $\text{Li}_2\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_3$ (NMC) has received recent attention as a potential high voltage cathode in Lithium ion batteries. It was first developed by Ohzuku *et al.*[61] as a possible replacement of LiCoO_2 as the dominant cathode material. HEC with NMC as the cathode materials was first tested by Yoon *et al.* [62] using AC as the counter electrode the HEC device was able to deliver double the 60F g^{-1} while the AC/AC device was able to deliver only 27F g^{-1} .

Figure 2. 12 Structural representation of a Lithium rich layered cathode material. The transition metal layer is marked with by blue octahedra it contains Ni, Mn and Co statistically distributed. Li layers occupy alternate layers.

3: Phosphates

3.1: LiFePO_4 - has an olivine structure as illustrated in figure 2.13. These materials have a possible 2 dimensional Li ion channel but the presence of the phosphate tetrahedral leads to the confinement of Li ion channels only along the b axis. As shown in figure, the structure is explained in detail by Padhi *et al.*[63].

Figure 2. 13 Representation of the crystal arrangement in LiFePO_4 . The materials is known to have olivine structure with edge shared FeO_6 octahedras, further connected to alternate layers using PO_4 tetrahedra. The structure leads to the formation of 1D tunnels in the material. Li atoms are located in these tunnel like zones.

Electrochemical activity of LiFePO_4 was first discussed by Padhi *et al.* [63, 64] the materials was an interesting alternative cathode material for Li ion batteries because of the much improved thermal stability of iron phosphates and a flat insertion potential at 3.4 V vs. Li. The material shows a theoretical capacity of 170 mAh g^{-1} . The most important quality of LiFePO_4 is that it is environmentally benign when compared to LiCoO_2 [65-68]. It was initially commercialized by battery companies like A123, Sony. The material suffers from low electronic conductivity because of the $-I$ effect of the phosphate group, in order to commercially use LiFePO_4 the pristine power needs to be mixed with a conducting additive such as carbon while at the same time the particle size needs to be small enough so as not to have a high localized resistance. The olivine phase LiFePO_4 as shown in figure 2.13 was first applied in an HEC setup by Wu *et al.* [69] wherein the HEC device was compared to an AC/AC supercapacitor cell to compare high power performance. Further studies by Chen *et al.* [70] compared the performance between Li-HEC devices based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with the composite electrodes of LFP and AC, a 53 % improvement in capacity was established. Na *et al.* [21] reports the highest energy density of 69 Wh kg^{-1} using an LFP electrode by using a composite of AC-LFP vs MCMB cycled between 2-4 V [21]. Despite its obvious advantages as an environmentally benign cathode material the low Li diffusion

kinetics of Li iron phosphates forces researchers to mix it with conducting agents to increase conductivity of the pristine material which in turn leads to a decrease in tap density of the electrode.

3.2 LiCoPO₄- a high voltage insertion cathode shares the same olivine framework as LiFePO₄, the operating potential of this electrode is ~ 4.8 V vs. Li which is above the potential window for conventional carbonate based electrolytes [71, 72]. At these high potentials the phosphate group disassociates into the electrolyte. Vasanthi *et al* [73] managed to synthesize LiCoPO₄ using a polyethylene glycol assisted approach the best energy density obtained in Li-HEC setup is 112.9 Wh kg⁻¹. The high energy density is not because of the material but instead is attributed to the pseudocapacitance provided by an impurity phase Co₃O₄. While the pristine material when tested provided an energy density of ~ 2.9 Wh kg⁻¹ at a power density of ~ 0.19 kW kg⁻¹ [73]. It is important to note that olivine materials can be seen to have a facile Li ion migration pathways but in general are found to be non-conductive also the use of metals like Co as a component of the host material might lead to concerns about the toxicity of the material.

4: Fluorophosphates

Fluorophosphates are compounds structurally very similar to the phosphate compounds. The addition of fluorine occurs on the transition metal octahedral leading to relatively smaller TM-F bonds which leads to a distortion of the octahedral also addition of fluorine

Figure 2. 14 Pictorial representation of a representative Fluorophosphate

leads to the increase in operating potential of the material. Fluorophosphates have a 3 dimensional tunnel like structure as shown in figure 2.14 which is indicative of good Li ion diffusion through the host structure

4.1 $\text{Li}_2\text{CoPO}_4\text{F}$: Addition of fluorine in the host structure allows for a much more stable structure compared to the phosphate analogues[74], accompanied by a higher insertion potential fluorophosphates can be a high energy high power battery material. During electrochemical cycling the cathode undergoes single phase Li insertion/extraction process rather than a two phase mechanism observed in case of phosphates[74, 75]. Half-cell tests indicate a gradual decline in the capacity of the material. Karthikeyan *et al*[76]. was the first to apply a high potential fluorophosphate as a possible Li-HEC electrode pairing it with activated carbon as the anode. The cathode delivered an energy density of 47 Wh kg^{-1} when tested between 0-3 V. The material shows a high energy density paired with a cycle life of 30000 cycles.

Even though the material shows promise, it can be observed that the use of toxic materials like Co implies that it cannot be used on a commercial scale. During the process of this thesis we explore the substitution of Co with V which has a similar open cage structure and a high insertion potential of 4.2 V vs. Li. The results are explained in detail in chapter 4.

5: Silicates

Study of iron phosphates indicated that safe and environmentally benign materials can be used as battery materials even if they exhibit low electronic conduction values by the addition of conducting additives like carbon. The phosphate backbone is able to provide the structural stability in the potential window without a need to form passivating layer. In the same vein it becomes necessary to study the substitution of phosphates with silicates, a similar stabilization as seen in the phosphate should be observed in this case. The lower electronegativity of the silicates leads to a low electronic band gap which leads to a more conducting material [77, 78].

5.1 $\text{Li}_2\text{MnSiO}_4$: Mn based silicates are considered noteworthy because of the eco-friendly nature of this materials, but it is plagued by issues of low electronic conductivity and on continued cycling the materials collapses forming an amorphous phase. [78]. Karthikeyan

et al. [79] studied the possible use of this materials as an insertion materials for application in cathodes. It was concluded that silicates can be applied in cathode materials but with excess carbon to act as conducting channels in the material. Karthikeyen *et al.* [79] was the first to synthesize a Mn based silicates so as to carbon coat it *in-situ* and applied this material to Li-HEC application. The maximum energy and power densities observed are 54 Wh kg⁻¹ and 1.5 kW kg⁻¹ when cycled between 0-3 V.

5.2 Li₂FeSiO₄ : Iron based silicates have been shown to have comparatively better electronic properties when compared to their manganese analogues[77]. Early research into the feasibility of this materials was carried out by Manthiram *et al.* [80]. The results obtained suggest that iron based electrodes can operate at a high potential exploiting the +3/+4 redox couple at the same time assuming that 2 Li ions can be reversibly extracted from the structure a theoretical capacity of 333 mAh g⁻¹ can be calculated. But the material failed to work in practical scenarios because of structural instabilities at high potential. Iron +3/+4 redox is not known to be extremely stable and reversible, which might also be a cause attributing to the low performance. Karthikeyen *et al.*[81] on the other hand applied lithium iron silicates in an HEC configuration and achieved excellent results. This is because in the case of HEC devices the battery materials do not undergo deep discharging or charging cycles. The system tested was carbon coated Li₂FeSiO₄/AC. Maximum energy density of 43 Wh kg⁻¹ and maximum power density of 1.4 kW kg⁻¹. The material is shown to be stable in a potential window of 0-3 V for up to 1000 cycles.

2.4.4 Structures considered for HEC battery electrode

After a thorough literature review we have narrowed down to the use of 4 types of crystal arrangements that can be applied as a possible battery electrode for Hybrid electrochemical capacitors. They are outlined below

1: Garnet structures: Have been studied in detail for a period of time as solid Li ion conductors and have been known to have excellent diffusion kinetics. Apart from this tungsten based garnet oxides have been shown to have a low stable insertion potential. These properties can be helpful in increasing the energy and power density of the HEC device.

2: Polyanionic phosphate base materials: Phosphate based materials have been shown to be stable and environmentally benign. During the course of this thesis two specific homologues $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and LiVPO_4F were used in order to study the following fundamentals about HEC's

- $\text{Li}_3\text{V}_2(\text{PO}_4)_3$: has been reported to have good lithium ion diffusion kinetics when applied in Lithium ion batteries. Due to the use of vanadium as the active TM it can be applied as both a cathode and an anode material in HEC configurations. This unique characteristic allow for the setting up of a rubric in order to determine the effect of polarity on the total amount of energy stored. The values can then be calculated at different power densities in order to achieve an empirical rule deciding the polarity of the faradaic component based on power density so as to achieve maximum energy density.
- LiVPO_4F : Fluorophosphates have been used because of the open cage structure displayed by them. The material has a high and flat insertion potential (4.2 V vs. Li). These characteristics not only allowed for the improvement in the net energy density and power density of the HEC device when compared to previous literature but also lays the groundwork to understanding the complex interplay between the battery and the supercapacitor electrode during cycling.

3: High capacity lithium rich Layered oxides: Using studies based on $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ it can be inferred that using cathode materials as potential battery materials has a positive influence on the high power performance of the cell. After the optimization of the activated carbon electrode. Lithium rich layered oxides (LLC) with their high capacity and high degree of cycle stability were seen as a natural progression. Initial fundamental studies have been conducted on ruthenium based LLCs with the general formula $\text{Li}_2\text{Ru}_{0.75}\text{M}'_{0.25}\text{O}_3$. M is 3d transition metal. During the course of this thesis a variety of substitutions of M are initially studied but focused attention has been directed towards Ti, Fe and Sn because of their superior performance. Due to their high capacity LLC's can be applied both in IPH and ISH devices. Fundamental studies were conducted on the samples to understand and optimize the materials for HEC applications.

2.5 Carbon based supercapacitor materials for HEC application

Apart from a stable battery electrode, a HEC device requires the construction of a high surface area supercapacitor material with high energy storage capacity which is also reasonably cheap. Activated carbon with a highly porous structure is the perfect material for this purpose [82]. Activated carbon can be formed using carbon rich precursors by carbonizing the source in an inert environment, physical activation employs the use of activating agents like steam or CO₂ for selective oxidation of certain areas in order to form pores on the surface

A wide range of carbon precursors can be used to develop activated carbon, but the most economical choice is to use activated carbon from bio-waste sources such as food waste, human waste or agricultural waste (Table 2.1). Depending on the starting structure of the material an appropriate activation technique can be applied to the material. A brief outline of the activation techniques generally used is provided

2.5.1 Activation techniques

1: Physical activation: Is the most common form of activation. It involves the modification to natural carbon after its synthesis. The main activating agents in this type of activation are steam and carbon dioxide, used singly or in conjunction with each other. These agents extract carbon atoms from the structure of the porous carbon. Although this method is highly economical in terms of raw materials, it leads to a pore structure which is not well formed with an extremely low yield of activated carbon. Making it unsuitable as an activation process that can be used for activating carbon for electrochemical energy storage applications [83].

2: Chemical Activation: Employs the use of strong oxidizing agents or de-hydrating agents to modify the activation process. The chemicals generally used are phosphoric acid, zinc chloride, potassium hydroxide and potassium carbonate. Such activation process' are called chemical activation[84]. These techniques allow to modify carbon with minimum wastage at the same time perform the reactions at low temperatures. But this technique requires post processing to remove any chemical impurities after that are left on the carbon

sample after activation. Over the course of the past decade a large sample space of bio-material based carbon sources have been used these are summarized in table 2.1. It can be noted from Table 2.1 that bio-based carbon sources are capable of delivering high surface area activated carbon.

Table 2. 1 List of activated carbons, the activating agent used for activation and the total observed surface area.

Source	Activating Agent	Surface Area m ² /g	Reference
Coconut Shell	H ₃ PO ₄ , ZnCl ₂	1350	[85]
Olive Stone	Phosphoric Acid	1218	[86]
Dates	H ₃ PO ₄ (60 %)	1162	
Wood(180 F g ⁻¹)	KOH	1598,2059	[87] [88] [89]
sugar cane bagasse(300 F g ⁻¹)	H ₃ PO ₄ ,ZnCl ₂	1500	[90]
sunflower seed hull(311 F g ⁻¹)	H ₃ PO ₄ ,ZnCl ₂	1235	[91]
Pistachio-nut shell-based	KOH	1900	[92]
Argan Seed Shells	KOH	2100	[93]
Sorghum Pith	NaOH	35	[94]
Oil palm fruit	KOH	1704	[95]
Sucrose	CO ₂ gas	3000	[96]
Carageenan	KOH	2502	[97]

Pine Cone derived carbon	KOH	3950	[98]
Corncob bio- waste	KOH	1210	[99]
Dead Leaves	K ₂ CO ₃	1058	[100]
Tobacco rods	KOH	1761	[101]
Cotton Stalk	Phosphoric acid	1481	[102]
General Agricultural Waste	ZnCl ₂	970	[103]
Cocoon Silk	Nitric acid reflux method	-	[104]
Bio-Char from banana	Hydrothermal activation	138	[105]
Ground Coffee powder	Nitrogen activation	1867	[106]
Sawdust	Steam Activated	1250	[107]
Paper Pulp	Hydrothermal activation	2850	[108]
Chicken Feather	KOH	1398	[109]
Chicken Egg shell membranes	KOH wash followed by HCl wash	221	[110]
Hemp	Hydrothermal activation assisted by sulphuric acid	2287	[111]

2.5.1 Factors controlling the capacitance of activated carbon based electrodes

The amount of charge that can be stored on the surface of activated carbon can be controlled by the following factors

- Surface area of the activated carbon: The key to increase the capacitance of a supercapacitor material is to increase the specific surface area of the material while maintaining electrical conductivity of the sample. Graphitic carbon is an ideal choice for this. These forms of carbon can be activated or templated or formed into fibers to achieve a high surface area[112, 113].
- Nature and distribution of pores on the surface of activated carbon: Pores on the surface of activated carbon help to greatly enhance the surface area of the activated carbon, they can be broadly divided into three categories micropores (<5 nm), (mesopores 5-50nm), macropores (>50 nm). An optimum distribution of pores facilitates good interaction between the electrolyte and the surface of activated carbon. [114]. Pore structure of the material can be controlled by the nature of the activating agent, temperature of carbonization and time for carbonization. Longer activation time and higher activation temperatures lead to a wider mean pore size [115].
- Surface Functionalization: the nature of the functional group on the surface of activated carbon controls the ability of the electrolyte to wet the activated carbon. Also the presence of electron accepting or donating groups on the surface enhances the electronic conductivity of the carbon sample [116, 117].

Initial research on increasing the capacitance of activated carbon was aimed at the increase of pore volume to increase the specific surface area and by refining the activation process. However it was observed that the increase in capacitance is limited for even the most porous samples. Studies on a series of carbon materials based on their surface area indicate there is no linear co-relation between specific surface area and capacitance [113, 118, 119]. It was initially identified that the pores smaller than 2 nm which contribute to the specific surface area are not accessible to the ionic species of the electrolyte, as research has shown that these species are surrounded by highly stable solvation shell. The energy required to remove the solvation shell is of the order of a few kJ's [120-122]. From this it can be understood that pore size larger than 2 nm which is bigger than the ionic species should influence the capacitance to a high degree. It was observed that having a large portion of the pores in the mesoporous range does not afford improved performance. A maximum capacitance of 100-120 F g⁻¹ for organic electrolytes and 100-150 F g⁻¹ for aqueous

electrolytes is recorded [123, 124]. Hence it can be assumed that a balanced ratio of meso to micro pores is needed to achieve a high capacitance.

It was predicted by Song *et al.* [125] and Lee *et al.* [126] that a hierarchical pore size distribution might considerably improve the rate performance and capacitance of porous carbon structures. The design of the hierarchical pore structure is based on different interaction properties of pores with electrolytes depending on the size of the pores. These interactions can lead to shorter ion transport distance, low resistance and large charge storage density [127]. The physical and chemical properties in the macropores can be considered as synonymous with the electrolyte present in the bulk with the lowest resistance. The macropores and meso pores can also act as ion buffering channels which store electrolyte in them thus effectively reducing the distance that needs to be travelled by ions during charge and discharge. Wang *et al.* [127]. was successful in developing a 3D aperiodic hierarchical structure using carbide derived carbons. The results of the experiment are presented below

Figure 2. 15 Figure indicates the development of a 3D aperiodical hierarchical pore structure development in carbide derived carbons using a templating technique. Copied with permission from ref[122]

For the purpose of this thesis the use of carbide derived carbons is not feasible because it is neither sustainable nor economical[115]. But maintaining a pseudo hierarchical structure

is of interest. Human hair has been chosen as the carbon source material and studies are conducted on the pore structure depending on the nature of activating agent used. We were able to achieve a capacitance of 115 F g^{-1} using a NaOH assisted activation technique. The final carbon structure has large macropores on the outside with smaller mesopores at the core [117].

2.6 Conclusion

The Literature review has been instrumental in devising a plan on the basis of which the aims and objectives of this thesis are based. It can be concluded that only the application of an intercalation chemistry is suitable for HEC applications. Among intercalation compounds on the basis of working potential, high capacity, long cycle life and future application four categories of materials have been selected, lithium garnets, vanadium based phosphates, vanadium based fluorophosphates, lithium rich layered compounds. Further the second section 2.5 helps to provide insight on previous studies on the development of activated carbon from bio-sources. The section also discusses about using a hierarchical pore size distribution in the final activated carbon to achieve maximum energy density.

2.7 References

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Chapter 3

Experimental Methodology

This chapter aims to identify the synthesis and characterization techniques used during the course of this thesis. At first the chapter identifies and briefly explains the synthesis techniques used and also sheds light on the rationale for the selection of the techniques. It follows with a brief description of the structural and morphological characterization performed on the material prior to its electrochemical testing. These include PXRD, electron microscopy, spectroscopic and thermal characterization. The process of initial characterization is helpful to screen materials which are not suitable for high power battery operations. The material is later assembled into an electrochemical cells and put through a series of tests such as cyclic voltammetry, galvanostatic charge discharge cycling, and impedance spectroscopy. To better understand the structural evolution of materials while operating as a battery. In-operando X-ray diffraction studies and X-ray absorption studies were conducted at SSRL (Stanford Synchrotron Radiation light source)

3.1 Synthesis

3.1.1 Solid State Synthesis

Solid state synthesis involves the heating of individual constituents at high temperatures in order to form a final product. It is the most heavily used synthesis procedure, mainly attributable to the fact that it requires little or no pre-preparations. The reaction mixture is mixed and pelletized to ensure good contact and then placed in ceramic containers and heated in the presence or absence of oxygen depending on the final state of the product.

Principle

Solid state synthesis has its roots deeply buried in solid state chemistry. The formation temperature and pressure of a final product is determined by studying its phase diagram. The final temperature applied to the sample is decided using the Tarmans rule “that the maximum temperature should be less than $2/3^{\text{rd}}$ of the melting point of any of the individual constituents” [1]

At room temperature the individual constituents are unable to react to form the final product in any appreciable time. The reaction conditions required are heavily dependent on the reactant properties such as surface area, thermodynamic free energy change and reactivity. As the reaction temperature is increased the individual reactants are able to interact with each other to form the desired products. Due to the dependence on solid diffusion kinetics the process is generally very slow unless the reaction is an ion exchange reaction.

Advantages

- 1: Involves little or no pre-preparation.
- 2: Allows control of the oxidation state of the final product depending on the environment chosen for the reaction

Disadvantages

- 1: There is no control over reaction kinetics
- 2: High temperature synthesis leads to a waste in energy

- 3: It needs optimization to ensure that the reaction is complete
- 4: High temperature leads to sublimation of certain materials leading to a loss of raw material during the heating process.
- 5: No specific morphology can be obtained

Application

During the process of this thesis, high temperature synthesis through the ceramic route was carried out using a Carbolite muffle furnace and a Carbolite Tube furnace with an Argon gas environment (Figure 3.1). This technique was employed in synthesis of a range of materials ranging from layered oxides, spinel oxides, garnet structures also the Argon based tube furnace assisted the formation of oxygen sensitive compounds like $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and LiVPO_4F

Figure 3. 1 : Carbolite Tube Furnace used for heating materials under a constant flow of Argon

3.1.2 Hydrothermal synthesis

Hydrothermal techniques involve the dissolution of reactants in water or any other suitable solvent (solvo-thermal reaction) the mixture is then sealed in a teflon container which is enclosed in a stainless steel autoclave. The reaction mixture is heated to above the boiling point of water, leading to conditions of extreme pressure in the teflon vessel. These conditions lead to the formation of high surface area nano-materials (Figure 3.2).

Principle

The solvent properties such as di-electric constant and solubility of various solvents change dramatically at supercritical conditions. The critical temperature and pressure of water are 374 °C and 22.1 MPa respectively. The di-electric constant of water at normal pressure and temperature is recorded at 78. At this value polar ionic solutes can easily dissolve in water. The dielectric constant of water decreases rapidly on increasing temperature and decreasing pressure. At supercritical conditions this value falls to below 10 at these values the di-electric constant becomes a contributing factor towards the rate of the reaction (electrostatic theory) [2]. Hence supercritical water provides an excellent reaction zone for nanoparticle formation because of primarily two reasons[3].

- 1: High nucleation rate because of the lowering of the overall solubility of the solvent at supercritical conditions
- 2: Enhancement of the reaction rate.

Figure 3. 2 Schematic indicating the process of performing a hydrothermal synthesis.

Advantages

- 1: Hydrothermal reactions allow for the facile synthesis of metal oxide nano-powders.
- 2: The supercritical conditions allow reaction rates which 10^3 times faster than conventional reaction techniques.

Disadvantages

- 1: Hydrothermal techniques pose a significant safety issue because of the excess pressure conditions present during the reaction.
- 2: The morphology of the resultant structure cannot be controlled to a high degree

Application

During the course of this this thesis hydrothermal synthesis has been applied a number of times for the synthesis of nano platelets. the hydrothermal synthesis technique employed involved the addition of a system to induce mechanical agitation during the synthesis process this allows for more control on the aspect ratio of the nano-fibers formed [4]. We successfully used this technique for the synthesis of $\text{H}_2\text{Ti}_3\text{O}_7$ and VO_2 nano-platelets, both of these compounds have been shown to have remarkable capacity and high capacity retention (Appendix II). The reaction vessel used was a 20 ml stainless steel acid digestion autoclave procured from Parr Scientific products, USA. The heating of the autoclave was performed in a convection oven.

3.2 Characterization

3.2.1 X-ray diffraction

Background

Max Von Laue was the first to discover that X-rays could be used to study crystalline materials. The individual layers in a crystalline material act as miniature diffraction gratings for X-rays. These days X-ray diffraction has become an increasingly common technique to study crystalline materials. It is based on the constructive interference of monochromatic X-rays with a crystalline sample. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed towards the sample surface.

The interaction of the incident X-rays with the sample is considered constructive interference when the conditions satisfy the Bragg's law

$$n\lambda = 2d \sin \theta \quad \text{eq 3.1}$$

Where,

n is an integer

λ is the wavelength of the X-rays

d is the inter-planar spacing generating the diffraction

θ is the diffraction angle.

The diffracted X-rays are then detected, counted and processed. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered materials. Conversion of the peak positions to a d-spacing format allows the comparison of the diffraction pattern with a database of crystal structures.

Working

X-ray diffractometers are consist of three basic elements

1. Source : X-rays are generated in a cathode ray tube by heating a filament to produce electrons. These electrons are then accelerated towards a target by applying a high voltage. When the electrons have enough energy to dislodge electrons from the inner shells of the target characteristic X-ray spectra are produced. The spectra consists of several parts but the most important being K_{α} and K_{β} . The wavelength of the X-rays generated is characteristic of the target material and is almost monochromatic in nature. Filtering, by foils or crystal monochromators is required to generate perfect monochromatic X-rays. Copper is the most common target $CuK_{\alpha} = 1.5418 \text{ \AA}$.
2. Sample Holder : Most commonly the sample holder is stationary stage which can be rotated or not depending upon the measurement requirement. The stage is so placed that maximum X-rays can be received by the detector. Depending on the nature of the sample the holder varies. For most common powder measurements the holder is a simple container transparent to X-rays, in the case of the thin films or single crystal measurements the geometry of the holder changes to suit the measurement. In general during sample preparation care needs to be taken to ensure that the sample surface is smooth and flat such that the normal from the surface of the sample subtends an equal angle at the source and detector. Also another fact to be taken care of is that excessive compaction of a powder sample might lead to the development of preferred orientation in the crystals which will lead to the production of erroneous diffraction data.
3. Detector : As the incoming radiation impinges on the sample and the Bragg's law is satisfied (constructive interference occurs). A detector records the X-ray signal and

converts the signal to a count rate which is then analysed by the user. Broadly classified there are mainly two types of detectors a scintillation detector and a gas filled detector. A scintillation detector has a large number of losses which makes the energy resolution of this kind of detector poor making it unsuitable to differentiate between $K\alpha$ and $K\beta$ radiation. But it has high quantum yield making it ideal for point intensity measurements. A gas filled detector uses an inert gas like Ar or Xe, incoming X-ray photons ionize the inert gas into Ar^+ and an e^- . The energy required to ionize the inert gas is much lower than the energy of the X-ray photons, hence a few photons can ionise a large amount of the gas generating a large number of electrons. These electrons are then accelerated onto a wire which is kept at a potential of about 1 kV. The burst of electrons on the wire is converted to a voltage pulse which is then shaped and counted by the electronics. Gas filled detectors have a good energy resolution but display a loss in linearity at high count rates.

Application

X-ray diffraction was one of the most heavily used characterisation techniques used during the course of this thesis. It served as a tool to study the nature of the phase formed. Diffraction measurements coupled with Rietveld refinement allowed for calculation of crystallographic parameters for the battery materials. Apart from powder samples we were also able to scan electrode materials after failure to calculate any changes in the lattice parameters which lead to the collapse of the framework structure.

Another aspect explored during the course of this thesis was the use of *in-operando* X-ray diffraction as a tool to understand the structural evolution in battery materials during electrochemical cycling. Certain hurdles were encountered during this type of testing because during the testing the electrode needs to be protected from external environmental factors making it necessary to construct a new *in-operando* cell which would allow X-ray penetration into the electrode material while shielding the electrode materials from contamination. The construction of the *in-operando* cell is described in detail in Chapter 4.

3.2.2 Spectroscopy techniques

3.2.2.1 X-ray Absorption spectroscopy

X-ray absorption involves the shining of high energy X-ray beams generated in a synchrotron onto the sample to be probed, the X-rays tend to excite a core electron from its inner shell. The absorption by the element can be measured by comparing the intensity of the initial beam to the transmitted beam, this is done by measuring the fluorescence given off by excited atoms as an electron fills a vacant energy orbital (core hole), or by measuring the excited electrons as the core is filled (Auger electron). As one measurement is collected the energy is slightly modulated sequentially in order to collect a complete spectrum over

Figure 3. 3 Experimental station at SSRL. The beam line is dedicated station to perform high energy X-ray absorption Spectroscopy studies.

the desired range. A standard X-ray absorption spectra is illustrated in figure 3.4 [5].

The spectra can largely be divided into two portions

1. X-ray Absorption Near Edge Structure (XANES) - This region mainly consists of two portions the pre-Edge and the edge. The pre-edge is the region before the

Figure 3. 4 A sample spectra indicating the regions of interest in a normal XAS spectrum. The above curve corresponds to that collected for the Ru K edge in RuO_2

absorption edge where the absorption coefficient decreases with increasing photon energy. The edge is when a sudden jump in the absorption coefficient is absorbed. The edge value is highly dependent on the nature of the material and its local coordination structure [6].

2. Extended X-ray Absorption Fine Structure (EXAFS) - This region largely pertains to any interactions that the electrons have after they are ejected from the atom. This measurement is highly sensitive to information about the surrounding atoms around the central atom [6].

Application

XAS techniques are extremely useful for battery applications as they can estimate the changes in local structure around a selected element. Also qualitative analysis of the XANES spectra indicates any change in the oxidation state of the element selected.

During the course of this thesis XAS studies were used to study Lithium rich layered materials (Chapter 4) these materials have been known to exhibit issues on prolonged cycling. To study this an *in-operando* setup was designed using modified coin cells. The

cells were cycled in the set potential region while XAFS patterns were accumulated every 20 minutes.

These experiments were carried out at SSRL, on beamline 4-1 which is dedicated for X-ray absorption spectroscopy studies (figure 3.3). The beamline can operate along a large energy range from 5.5 keV to 38 keV with a resolution of 10^{-4} and a spot size of $4 * 18$ mm. It uses a Si (220) monochromator. The instrument is able to collect absorption data both in fluorescence (Lytle detector) and transmission modes, for the study on lithium rich materials it was mainly used in the transmission mode. During the course of the study the K-edges of Iron, Ruthenium and Titanium were recorded *in-operando*. Standards containing RuO_2 (Sigma Aldrich), Fe_2O_3 (Sigma Aldrich) and TiO_2 (Sigma Aldrich) were also recorded in order to put the near edge spectra in perspective. Pure metallic foils were used as standards so that the spectra's obtained could be compared with each other.

The obtained patterns were further analyzed by the Demeter suite of XAS tools[7]. Athena [7] was used to analyze the pattern by normalizing the absorption coefficient, calibrating and aligning the reference channels for all the scans. The general trend of the XANES portion of the curve can be easily interpreted at this stage, further fitting was done using Artemis [7]. The fitting is instrumental in calculating any changes in the coordination environment of the d-block elements in question. The results of the experiment are explained in detail in chapter 4.

3.2.2.2 Raman Spectroscopy

Can be used to observe vibrational rotational and other low frequency vibrations occurring in a molecule. It can be used to fingerprint a certain kind of bonding or molecule present in the sample. It is based on the in-elastic scattering of light usually from a laser source. Photons are absorbed on the surface of the sample and then re-emitted with a small shift in frequency this phenomenon is called the Raman effect and can be used to study the type of molecule present[8].

Working

The Raman effect is based on deformations to an electric field E by molecular polarizability α . The laser beam can be considered as an oscillating electromagnetic wave with electric vector E . As the laser impinges on the sample it induces a change in the dipole moment of the molecule given by $P = E\alpha$ which deforms the molecule. Because the molecule is deformed periodically it starts to vibrate at frequency called the fundamental frequency ν_m . Oscillating dipoles can emit radiation in three possible ways

1: Elastic or Rayleigh scattering: the sample surface absorbs the incoming laser radiation which has a frequency of ν_0 . After excitation the molecule returns back to its basic vibrational state and emits light with the frequency of ν_0 . This type of interaction is called Rayleigh scattering and is the dominant signal at low wavenumbers. This type of molecule has no active Raman modes.

2: A photon with frequency ν_0 is absorbed by a Raman active molecule which at the time of interaction is vibrating at its basic vibrational state. Part of the energy of the incoming photon is transferred to the Raman-active mode with frequency ν_m and the resulting frequency of scattered light is reduced to $\nu_0 - \nu_m$. This Raman frequency is called Stokes frequency.

3: A photon with frequency ν_0 is absorbed by a Raman-active molecule, which at the time of interaction is already at an excited vibrational state. The excess energy of the Raman active mode is released. And the molecule reverts back to its basic frequency and the resulting frequency of scattered light goes up to $\nu_0 + \nu_m$. This Raman frequency is called Anti Stokes.

About 99.999 % of all incident photons in a spontaneous Raman experiment undergo Rayleigh scattering. This type of signal is practically of no use for molecular characterization. To use the useful 0.001 % of the signal special additions need to be made to the instrument to block out signal from Rayleigh scattering.

Instrumentation

A Raman spectroscope can be considered to be made out of the following parts (Figure 3.5)

1. Excitation source (laser)
2. Sample illumination system and light collection optics
3. Wavelength selector
4. Detector

Figure 3. 5 Representation of the schematic of the components in a Raman Spectroscope

The sample is usually illuminated with a laser beam in the ultra violet or the visible region. The wavelength laser source used during the course of this thesis was fixed at 480 nm which is in the visible range. The light after scattering on the sample is focused with a lens and is sent through an interference filter or spectrophotometer to obtain a Raman spectrum of the sample. During data collection the main issue of significance is the separation of the intensities caused by Rayleigh scattering when compared to Raman scattering.

The most common mode is to physically limit the range of the collected spectra to not collect any data due to Rayleigh scattering. Commercially available interference filters can be used for this purpose. But it limits low frequency data acquiring limit of Raman spectroscopes to 100 cm^{-1} .

Earlier detectors used consisted of mostly single channel photo multiplier tubes. But it was noted that data collection using this setup took too much time to allow Raman spectroscopy to be a commercially viable fingerprinting technique. Hence today most of the detectors in use are multi-channel detectors like photo-diode arrays or commonly used charge-couple devices.

In order to improve the signal to noise ratio our experiments were carried out using a stimulated Raman setup which employs the use of a very strong laser pulse. Pulsed lasers are able to transform a much larger portion of incident light into useful Raman scattering hence substantially improving the signal to noise ratio. Stimulated Raman scattering is an example of non-linear Raman spectroscopy. Very strong laser pulses with electric field strength $> 10^9\text{ V cm}^{-1}$ transforms up to 50 % of all coherent laser energy to stokes frequency of $\nu_0 - \nu_m$. The stokes beam is aligned along with the incoming radiation. This helps to amplify only the Raman signal from the molecule. Weaker Raman active modes are not present. The stokes beam is so strong that it also leads to secondary excitation. Hence it can be observed that stimulated Raman enjoys at least 4-5 times magnitude enhancement of Raman signal as compared to spontaneous Raman scattering.

Application

1: Carbon coating on battery materials: while synthesizing battery materials for Li-HEC applications it was observed that most materials suffered from a relatively low electronic conductivity. This was remedied by carbon coating the sample. The technique has, in the past improved conductivity and is essential for the working of commercial battery materials such as LiFePO_4 . Using Raman spectra, we were able to probe into the nature of carbon present in these coatings to study the distribution of both sp^2 and sp^3 type carbon. A higher sp^2 content indicating increased electronic conductivity. Hence the scans were

predominantly limited in the range of 1300-1400 cm^{-1} . The tests were carried out on a Witec Alpha 300 SR using a 480 nm Argon Laser.

2: Study of activated carbon: activated carbon was synthesized using cheap carbon sources. Raman spectroscopy was employed to understand the nature of the carbon formed after activation and determine a relative ratio of graphitic to disordered carbon

3.2.2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is surface analysis tool which has its roots in the discovery of the photoelectric effect by Einstein in the year 1921. The technique was perfected much later in the year 1981 by Kai Siegbahn.

There are three main parts of the instrument (figure 3.6),

1. Source: Is the source of monochromatic X- rays that are directed towards the sample. These X-rays are generally generated using an X-ray gun. A heated tungsten filament is used to generate electrons which are then heated towards an anode target with accelerating potential of 220 kV or higher. Interaction with the target leads to the emission of characteristic X-rays. Targets generally used are made up of aluminum or magnesium because they generate a steady stream of X-rays which are almost monochromatic [9-11].
2. Sample: The source X-ray beam strikes the surface of the sample which is mounted on a suitable holder. Any sample stable in high vacuum conditions can be studied using an XPS. Thin films and foils can be easily mounted onto the machine. The analysis of powder sample requires the spreading of the powder material on a double sided tape and then treating it like a thin film. Most XPS setups have a chiller attached to the sample chamber which can be cooled up to $-50\text{ }^{\circ}\text{C}$ for samples which are unstable at room temperature. Liquids can be analyzed once they have condensed onto a substrate or directly onto the probe. Electrically conducting samples need to be grounded before start of the experiment [12].
3. Detector: Upon interaction with the sample the incoming X-rays eject photoelectrons from the surface of the sample. The intensity of the photoelectrons is easy to record, but calculating the binding energy for each of electrons is a

complicated process. The KE is usually measured with a hemispherical device paired with an electron lens. Ideally the analyzer should be able to resolve 0.1 eV for electrons with high kinetic energy ($>1000\text{eV}$). Various detector designs have been used in the past and have been discussed in the following references [9, 13-18]. Two common approaches are to use a hemispherical electrostatic analyzer or a cylindrical mirror electrostatic analyzer. In these techniques the electrons are spatially resolved based on their kinetic energy, this is done by pre-retarding the electrons coming into the analyzer using the magnetic lens at the entrance. Because the electrons entering the analyzer all have a kinetic energy in a narrow range, the analyzer operates in a constant resolution mode. The actual kinetic energy scanning is done by manipulating the voltages at the pre-retardation region. Electrons which match the tuning conditions of the spectrometer pass through the pre-retardation section and through the analyzer are then directed to a channeltron electron multiplier detector, which behaves as an amplifier by generating multiple electrons per each electron impacting the detector (10^6 - 10^8). The electron pulses are directed to a photo luminescent screen which counts the number of photoelectrons hitting the screen.

Working Principle

The governing equation for XPS studies is based on Einstein's theory of photoelectric emission

$$h\nu = KE + BE + \phi_s$$

Where

$h\nu$ is the energy of the source radiation.

KE is the energy of the photon that is ejected from the sample surface after the source radiation interacts with it.

BE is the minimum amount of energy required to eject an electron from a specific orbital.

ϕ_s is the work function of the spectrometer and is constant for a given device.

Figure 3. 6 Schematic of X-ray Photon Spectroscopy instrument

Binding energy (BE) is characteristic of each core atomic orbital of an element. Making XPS an extremely useful fingerprinting tool. A general XPS spectra has been shown in figure 3.7. The spectra pertains to a scan of an activated carbon sample obtained from human hair[19]. Each peak in the spectra corresponds to photoelectrons emitted from a particular core level with a characteristic BE.

Figure 3. 7 X-ray Photoelectron survey spectra of an Activated carbon sample obtained from human hair

Binding energy of a material is dependent on the following factors

1. The number of protons in the nucleus.
2. The distance between the core electrons and their nuclei.
3. The density of electrons around the respective atom, ion, molecule, or solid.
4. The electron-electron interactions present.

Application

XPS is an element specific and surface sensitive measurement, making it an ideal choice to check for any impurities on the surface of a sample. For example in ref [19] XPS was used to establish the presence of N_2 on the surface of the activated carbon.

Apart from fingerprinting XPS can be used as an analytical tool to establish any change in the chemical environment of a specific element (change in oxidation state). This data is obtained by conducting high resolution scans over a narrow energy band around the reported BE of the element in question. An increase in oxidation state implies that the net nuclear charge of the remaining electrons increases which leads to an increase in the binding energy for the next electronic ejection. This phenomenon leads to a term called chemical shift wherein the spectra shifts to a higher or lower energy.

Although XPS is an extremely useful tool for elemental characterization of surfaces up to a depth of 20 nm, but it is not suited to probe the bulk of the material. Also certain battery materials are sensitive to the ultra-high vacuum conditions that are applied on the sample during analysis.

3.2.3 Microscopy techniques

3.2.3.1 Scanning Electron microscopy (SEM)

The SEM is one of the most versatile instruments available for microstructure analysis of materials. The primary reason for the usefulness of an SEM is the high resolution that can be obtained when bulk objects are examined. Advanced research instruments claim to go down to a resolution of 10 nm. Another important feature of the SEM is the three

Figure 3. 8: The figure helps to identify the components in the JEOL JSM 7600 F and relating it to the schematic of a general microscope

dimensional appearance of the specimen, which is a direct result of a large depth of field and shadow-relief effect of secondary and backscattered electrons. An SEM can be divided into the following sub-systems (figure 3.8)

1. **Electron gun:** Involves the use of a tungsten or lanthanum boride filament which is heated to a high temperature. This results in the production of an electron beam. This beam can be accelerated between 1- 40 keV. Several types of electron guns are used on current SEMs. These guns vary in the amount of current they can produce, the size of the source, the stability of the emitted current and the lifetime of the source. The tungsten filament based guns have a lower lifetime when compared to a LaB_6 gun[20].
2. **Electron lenses:** The electron column consists of an electron gun and two other lenses. The diameter of the electron beam from the electron gun is too large to be used directly on the sample and obtain sharp images. Electron lenses are used to reduce the diameter of the electron beam and focus the beam on the surface of the sample. Most SEM can generate a spot size less than 10 nm, while still carrying sufficient current to form a sharp image. As the beam emerges from the final lens, it interacts with the near surface region up to a depth of $1\mu\text{m}$ and generates signals used to form an image. The actual image generation requires the scanning system to construct an image pint by point[20].

3. Deflection System: In order to produce contrast in an image, the signal intensity from the beam-specimen interaction needs to be measured point by point. The function of the deflection system is to scan the beam along a line and displace the line position for the next scan, so that rectangular raster can be generated. Two pairs of electromagnetic deflection coils are used to control the raster of the beam. The first pair bends the beam off the optical axis of the microscope and the second pair bends the beam back onto the axis at the pivot point. The magnification of the specimen image is the ratio of the linear size of the viewing screen, to the linear size of the raster of the specimen[20].

4. Electron Detectors: The interaction of the electron beam with the sample leads to the generation of a variety of signals, which may be used to modulate the intensity of the viewing CRT and produce an image. The two dominant signals used for the formation of the image are secondary electrons (SE's) and backscattered electrons which are collected by the Everhart-Thornley (E-T) electron detector. It consists of a scintillator, a light pipe and a photomultiplier tube. The detector is located to the side of the specimen. The detector is electrically isolated from the rest of the microscope and has a wire mesh screen in front of at a potential of about +300 V. The positively charged screen draws the low energy secondary electron into the detector. All electrons entering the detector are accelerated by a voltage of +12 kV placed on the aluminum coating of the scintillator. The amplified energy SE now travel down a light pipe to the photomultiplier tube which converts the light to an amplified electrical signal. Variations in the signal as the beam is swept across the sample is used to form a high resolution representation of the surface[20].

Application

The SEM used during this thesis was the JEOL 7600F as shown in figure 3.8. The purpose of SEM based studies were to predominantly study the morphological properties of the materials synthesized. It was essential in studying the aspect ratio of VO₂ nanorods depending on the rate of agitation during synthesis (Appendix II). Apart from studying nano-structures. SEM based studies helped to determine the nature of particle agglomeration during synthesis. Certain degree of elemental mapping is also possible by using the EDX setup attached to the 7600 F. This was especially useful while studying

partial substitution effects in Lithium rich layered compounds.

3.2.3.2 Transmission electron microscope

It is a technique wherein a thin beam of electrons is fired through a thin sample, interacting with the sample as it goes through. The ejected electrons are analyzed either using a fluorescent detector or by sensors such as CCD camera. The resolution of a TEM device is much higher than the best light microscope this is mainly because the source of illumination in the case of a TEM is a stream of electrons instead of photons in the visible spectrum. The low wavelength of electrons leads to a very high resolution (0.2 nm) allowing a TEM to resolve even rows of individual atoms. The following section describes the three important components of a TEM[21]

Components of Transmission Electron Microscope

- 1: Illumination system: it consists of an electron source such as a tungsten filament. At high accelerating voltages the filament acts as an electron gun injecting electrons towards an anode the diverging electron beam then moves into the first and second condenser lenses which focus the electron beam on the sample
- 2: The objective lens and the stage
- 3: The TEM imaging system: Physically it includes the intermediate and projector lens. After the image is initially magnified by the objective lens (X50) it is further magnified by the first intermediate, this lens allows for the selection of the type of image that can be obtained, initial image or diffraction pattern in the back focal plane of the objective lens.

During the course of this thesis the dominant role of transmission electron micrographs has been to identify the orientation of different planes in a polycrystalline materials, successfully image nano-structures which could not be resolved by a SEM. HR-TEM was also used to identify the thickness of conductive coatings on a pristine sample. All the measurement was conducted on a JEOL JSM 2100 F

3.2.4 Thermal analysis

3.2.4.1 Thermo-gravimetric analysis (TGA) – Is used to determine the decomposition temperature of materials, to determine high temperature stability or any other accompanying phase change at high temperatures. It measures the change in mass as a function of temperature or time in a controlled environment with controlled temperature conditions.

Construction

A TGA consists of a sample pan connected to a high precision balance. The pan resides in a gold lined furnace and is heated or cooled during the time period of the experiment. A sample purge gas flows through the furnace, generally an inert gas or air is used for this purpose depending on the final outcome required. The pan measures any change in mass with temperature. This experiment can be used to quantify a variety of reaction which include but are not limited to loss of water, loss of solvent, decarboxylation, pyrolysis, oxidation, decomposition

Application

During the course of this thesis. TGA was conducted using a TGA Q500 (Texas instruments) a list of experiments conducted are

- 1: To evaluate the amount of carbon coating on $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$.
- 2: To evaluate the carbon coating amount $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.
- 3: To evaluate the thermal stability of activated carbon.

3.2.5 BET analysis

Brunauer-Emmett-Teller (BET) [22] is a technique based on the adsorption of certain inert gases on the surface of a medium. Using the amount of gas adsorbed on the surface, parameters such as surface area, pore size and pore size distribution can be calculated. (Quantochrome NOVA 3200).

The concept involved is an extension of the Langmuir theory which looks at monolayer molecular adsorption the BET theory extends this theory to multilayer adsorption of inert gases the theory is based on the following assumptions.

1. Adsorption can occur only on well-defined sites on the surface of the sample.
2. There are no chemical interactions between the adsorbate and the adsorbent and each molecule on the surface can act as an adsorption site for an incoming molecule.
3. The uppermost layer of the molecule is in equilibrium with the gas phase.
4. The process of desorption is a thermodynamically limited process, implying that external energy needs to be provided to remove a layer of adsorbate from the surface of the adsorbent. This heat of adsorption is similar for all the adsorbed layers.
5. At saturation pressure the number of layers on the molecule are assumed to be infinite

During the process of the experiment various isotherms are collected at different pressures these isotherms are plotted and the BET surface area is then calculated from the plot. As shown below.

BET equation

$$\frac{1}{v\left[\left(\frac{p_0}{p}\right) - 1\right]} = \frac{(c - 1)}{v_m c} \left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \quad eq\ 3.2$$

Where,

p and p_0 are the equilibrium and saturation pressure

v is the amount of the gas that is adsorbed during the experiment

v_m is the monolayer adsorbed quantity

c is the BET constant

The above equation is of the form a straight line, hence plotting term 1 against term 2 and fitting this curve to straight line will give us the amount of materials that is adsorbed on the surface of the material.

Application

BET analysis was mainly used to understand the pore structure of activated carbon synthesized using various carbon sources derived from bio-waste products. The sample was thoroughly dried in a vacuum chamber before the BET experiment. Prior to the experiment the mass of the sample was noted. The sample is loaded onto the BET tubes and fixed onto the degasser for a period of 4-6 hours at 130 °C. The sample is then scanned over a range of pressures to obtain the adsorption and desorption isotherm. These values are further plugged into the BET equation to calculate the surface area of the sample. Also using tertiary methods, the experiment can generate the pore size distribution in given sample. This information is helpful in understanding the dependence of pore size on the capacitance offered by the sample of activated carbon.

The information obtained from a BET measurement is purely physical, and does not give any information about the chemical nature of the samples surface which in some cases can influence the capacitance greatly. Hence care should be taken when using surface area measurements as a yard stick for electrochemical activity.

3.3 Electrochemical Analysis

3.3.1 Cyclic Voltammetry (CV)

Is one of the most basic and fundamental tests carried out on battery materials to test their feasibility. The effectiveness of CV results from its capability to rapidly observe redox behavior over a wide potential range.

CV consists of cycling the potential of an electrode in an un-stirred electrolyte and measuring the resulting current response. The potential of the working electrode is measured against a reference electrode which remains inactive during the testing process. The potential applied across these two electrodes can be considered as the excitation signal. The signal for a CV is a linear potential scan with a triangular waveform. The voltammogram is generated by monitoring the current generated in the working electrode while it is swept through a potential window. The important parameters to be considered for a CV are (i) The cathodic and anodic peak potentials, (ii) cathodic and anodic peak currents, (iii) the cathodic half peak potential and half wave potential.

Lithium based single electrode tests generally show an OCV of ~3.0V vs. Li depending on whether the cell is to be tested as an anode or cathode the first potential sweep is negative or positive respectively. Assuming the test conditions for a cathode material. The electrode is scanned in a positive direction from 3 V. When the potential is sufficiently positive to oxidize the transition metal in the electrode material according to the following equation.

The anodic current shows a rapid increase until the concentration of the pristine cathode material reduces substantially causing the current to peak and then slowly decays as the solution surrounding the pristine material is slowly depleted by its electrolytic conversion to an oxidized state. At the end of the charge range specified, the scan is reversed and the slowly discharged back its original state according to the following reaction [23-25].

Apart from studying the redox state of the battery material CV traces are instrumental to observe reversible electron transfer reaction and at the same time observe any side reactions occurring on the surface of the electrode, which is instrumental in then deciding a modified

testing window for the materials so as to avoid any major degradation in terms of capacity of working potential[24, 25].

CV tests were conducted as a preliminary electrochemical test on all materials mentioned in the thesis. Observation of the CV trace was instrumental in qualitatively determining the ease of lithium intercalation or de-intercalation by observing the shape of the curve and the difference between the anodic and cathodic curve. A CV trace is very sensitive to the type of mechanism of charge storage as can be seen in literature, charge stored by a fast mechanism such as adsorption leads to a rectangular profile while a relatively slow intercalation process leads to a duck shaped profile[24, 25]. The primary device to conduct CV experiments used in this thesis was the SOLARTRON 1256E. The device is capable of sweeping a wide potential range and has a minimum current resolution of 1 nA. Also it is able to change the scan rates of the potential sweep a technique which can then be used to empirically determine an approximate Li-ion diffusion coefficient [26].

3.3.2 Galvanostatic Cycling (GCD)

Galvanostatic charge discharge tests involve the application of a constant current across a cell to charge and discharge the working electrode within potential window. Typical GCD traces are shown in figure 3.9. GCD profiles are instrumental in providing a qualitative answer towards the charge storage mechanism. It can be used to calculate the amount of time it takes for a cell to charge and discharge which translates to the capacity of the cell (mAh). Charge discharge profile shape can be further divided into the following categories.

- (i) Lithium insertion through a two phase mechanism- In this case the charge discharge profile can be charged quickly up to the redox potential of the transition metal following which, a flat plateau is observed which indicates the presence of two phases in the material *i.e.* a lithium rich phase and a lithium deficient phase which exist simultaneously. During this period the cell provides a constant potential making it ideal for energy storage. Figure 3.9(a) is an illustration of the charge discharge profile of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode conducted in a non-aqueous electrolyte using Li metal as both the counter and reference electrode.
- (ii) Charge storage by adsorption/desorption on the surface – capacitive materials store charge by adsorbing the charge carrier ions on the surface. No chemical reaction occurs

between the electrolyte and the electrode and charge is stored purely by the formation of an electrical double layer. Figure 3.9(b) illustrates the profile of such a material (activated carbon in a non-aqueous medium using Li metal as both the counter and reference electrode) it can be observed that in this case the potential of the cell is a linear function of the current and no plateau is observed, also another inference from literature is that there is little or no capacity loss in supercapacitor materials even when a high current load is applied across the cell, because of the purely physical nature of the reaction.

Figure 3. 9 (a) Characteristic charge discharge profile of a material storing charge by a faradaic mechanism; (b) Characteristic charge discharge profile of a supercapacitor material.

Apart from charge storage mechanisms, galvanostatic charge-discharge studies can be aimed to understand the behavior of energy storage materials over a long time by cycling them repeatedly. GCD studies can be modified to understand the dependence of the capacity of the material on the current load applied (rate performance testing). Hence making this technique essential for identifying battery materials that can be suited for Li-HEC applications.

During the construction of a Li-HEC the capacity values from a GCD curve is essential to calculate the mass the mass balance between the supercapacitor and battery electrode. Figure 3.10 is an illustration of a GCD curve for a Li-ion capacitor using LTO as the anode and AC- (derived from human hair) as the cathode. From the figure 3.10 it is easily

discernable that the curve is an amalgamation of both supercapacitor and battery electrodes and depending on the current one of the mechanism dominates [27].

All GCD testing was carried out in either a SOLARTRON 1256E or a NEWARE battery testing system.

Figure 3. 10 A characteristic galvanostatic charge discharge profile displayed by a Hybrid capacitor

3.3.3 Impedance Spectroscopy

Is a technique to characterize the electrical properties of materials and their interfaces with electrically conducting electrolytes. For conducting an impedance spectroscopy measurement, a single frequency voltage or current is applied to a system and the corresponding phase shift and amplitude are recorded. Real or imaginary parts of the resultant output are calculated by passing it through an analogue circuit or a Fast Fourier transform function. Commercial instruments are available which allow a frequency range of 1 mHz to 1 MHz. The analysis of an impedance spectra is highly dependent on the use of a proper circuit used to fit the experimental data. A representative impedance spectra of an

insertion based material is shown in figure 3.11. [28] The results are plotted as a Nyquist plot between Z'' and Z' (imaginary and real parts of the impedance respectively). Impedance spectra need to be measured when the electrode is in equilibrium. The plot has features which is representation of the time constants recorded during the overall intercalation process. The parts of the spectra can be summarized as follows, (i) A pronounced semi-circle appears at high to medium frequencies which reflects the resistance for Li^+ ion migration through the surface films and film capacitance,[29-32] (ii) Another smaller circle is observed at medium frequencies which has been hypothesized to refer to charge transfer resistance and interfacial capacitance. In the case of ultra-thin electrodes this semi-circle is not observed. For thicker electrodes like the ones used during this thesis it is generally present. This curve is not potential dependent instead it is attributed to the time constant related to charge transfer. The thinner electrodes are more oriented and less porous. The total active surface area is smaller, and the inter-particle contacts with the current collector

Figure 3. 11 : Standard impedance plot of a battery type material.

are better. These lead to a reduction in charge transfer resistance related to the electron transfer and the interfacial capacitances of these electrodes. Hence for thin electrodes both

the semi-circles are merged into one.[29, 30, 33] (iii) A sloping line which at low frequencies behaves similar to Warburg impedance, reflects solid state diffusion characteristics. (iv) The sloping line becomes steeper at the lowest frequencies enabling the measurement of differential intercalation capacity of the electrode at a fixed potential.[29, 30, 33].

3.4 Electrochemical cell assembly

3.4.1 Construction of the electrode

1: Slurry casting

It is the most used technique for the fabrication of electrode coatings, this technique allows the user to control the thickness of the coating in a given area, which in-turn controls the mass loading of the cells. The process of synthesizing a coating is given below.

1. The active material is mixed with PTFE (poly tetra fluoroethylene) and conductive carbon like super P (TIMCAL) in the required ratio. The mixture is thoroughly ground so as to form a uniform powder with no clumping in the sample.
2. N-methyl pyrrolidone (NMP) is used a solvent to disperse these materials. NMP is added drop by drop to ensure that the solution retains optimum viscosity.
3. Depending on the nature of the electrode material the slurry can be cast immediately or stirred overnight before casting.
4. After the slurry is ready, it is cast of an Aluminum or copper foil depending upon the desired operating potential.
5. A doctor blade is used to spread the slurry on the foil while maintaining the thickness required.
6. The sample is dried in an oven at 60 °C in the presence of air for 8 hours
7. The dried electrode foil is then passed through a calendaring instrument which simultaneously heats and presses the electrode material into the copper or aluminum foil.
8. The electrodes are cut in the desired size and dried again in vacuum at 80 °C in a vacuum oven at 1 bar vacuum.

9. The electrodes are weighed to calculate the amount of active material.
10. The electrodes are then assembled into a coin cell or Swagelok cell[©] depending on the purpose.

2: Pellet type electrodes

1. The active material is mixed with conductive carbon (Super P TIMCAL) with Teflonized acetylene black.
2. Ethanol is added as a dispersing medium into the mixture while constantly mixing the components.
3. The mixture slowly turns into a pellet, make sure that the pellet is homogenous by repeatedly mixing the contents.
4. The pellet is then placed on a 0.25 mm thick stainless steel mesh (Goodfellow, 20 mm diameter) and pressed using a 20mm die set under a pressure of approximately 7-8 tons using a hydraulic press. The electrode is then dried in vacuum at 80 °C
5. The formed electrode can be assembled into a coin cell.

3.4.2 Testing Setup

All testing done during this research is limited to the usage of two kinds of setup which will be discussed in detail below underlining their specific use advantages and possible compromises that may be incurred.

1: **CR2016 coin cell setup**: this involves a stainless steel casing with a 20 mm diameter. The specifics of the cell are described below.

Advantages

- 1: It is the most cost effective way to test new active materials because it ensures good contact between the current collector and stainless steel.
- 2: This setup allows for an excellent sealing against moisture and oxygen.
- 3: It is safe to test Li based half cells which contain lithium metal because of the low amount of lithium present there is no visible fire hazard that may occur.
- 4: The active material the separator and the Lithium foil or counter electrode are pressed together so as to maintain the pressure necessary to facilitate good electronic contact.

Disadvantages

1: Coin cells are not good for post-mortem studies on active materials to determine the reason for failure, as opening the cell often leads to electrode damage.

2: Swagelok Cells©

These are specialized cells made for lithium battery research they are composed of five parts as shown in Figure 3.12. These cells have an advantage that they do need to be crimped like coin cells but instead work on a nut lock system. Because of the ease of assembly, it is convenient to employ these kind of cells to perform post-mortem analysis of battery parts and also to use these cells as a pre-lithiation tool as in the case of anode materials.

Figure 3. 12 : Photograph of a Swagelok© cell

3.5 References

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Chapter 4

Study of Battery materials for HEC applications

The chapter focusses on studying the battery electrode for HEC applications.

The study can be divided into 4 sections

- 1. Garnet structures exhibiting a high Li-ion diffusion coefficient- $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$.¹*
- 2. Phosphate based high voltage insertion material- $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ²*
- 3. Fluorophosphate based materials with 3D diffusion paths- LiVPO_4F*
- 4. High Capacity Lithium rich layered oxides- $\text{Li}_2\text{Ru}_{1-x}\text{M}_x\text{O}_3$*

The studies on the garnet type material were conducted to achieve a benchmark performance for hybrid capacitors. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was studied in order to develop a relationship between power density and electrode polarity. The fluorophosphates were tested as an optimized high voltage insertion voltage electrode material. Lithium rich layered cathodes are explored as game changing cathode materials because of their large capacity. All the materials used in this section were initially characterized using a variety of techniques such as X-ray diffraction, electron microscopy and electrochemical characterization. Apart from these experiments in-operando X-ray diffraction and X-ray absorption experiments for Lithium rich cathodes were designed.

¹ Portions of this Chapter were published substantially in - Satish, R., Aravindan, V., Ling, W. C., Goodenough, J. B., & Madhavi, S. (2014). *Advanced Energy Materials*, 4(9).

² Portions of this chapter were published substantially in -Satish, R., Aravindan, V., Ling, W. C., & Madhavi, S. (2015). *Journal of Power Sources*, 281, 310-317.

4.1 Study of garnet Structures as Li-HEC electrodes

4.1.1 Introduction

Conventional graphite anodes are an established part of the LIB industry. These have been able to show a high insertion capacity of $\sim 350 \text{ mAh g}^{-1}$. But they suffer from a drawback that they undergo Li plating at high current rates. To avoid this safety hazard, the search for alternate anode materials is essential. Several prospective materials have been proposed as anode insertion materials to accommodate Li ions reversibly, without considerable structural deformation. The list of materials is summarized in figure 4.1. For example TiO_2 anatase (1.7 V vs. Li with a theoretical capacity of 335 mAh g^{-1}) [1], monoclinic TiO_2 -Bronze (1.5 V vs. Li with a theoretical capacity of 335 mAh g^{-1}) [2], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\sim 1.5 \text{ V vs. Li}$ theoretical capacity of 175 mAh g^{-1}) [3-5], LiCrTiO_4 ($\sim 1.5 \text{ V vs. Li}$ theoretical capacity of 157 mAh g^{-1}) [6].

Figure 4. 1 Comparison of anodes on the basis of their reported insertion potential and capacity. The figure has been reproduced with permission from ref [10].

The above host materials all show impressive properties but these suffer in terms of energy density when compared to graphite because of the relatively high insertion potential. A

high potential insertion material restricts the choice of cathode materials that can be paired with these materials. So despite their superior performance the net energy density delivered by these materials would be reduced. One way that this can be improved is the use of conversion or alloying based materials, these have been shown to exhibit high capacities which can successfully offset the issue caused by high operating potentials[7]. But, because of a large amount structural changes during cycling these materials are not highly suited for applications such as HEC [8]. This situation shows the importance of developing anode materials that can be successfully used in both batteries and hybrid capacitors.

One of the possibilities that has been recently hypothesized by Goodenough *et al.* [9, 10] is the use of garnet type materials. Garnet materials have received a lot of attention as possible alternatives for solid electrolytes [11] with ionic conductivity greater than 10^{-4} S cm^{-1} at ambient conditions.

A garnet molecule is described by the molecular formula $\text{Li}_{3-7} \text{A}_3\text{B}_2\text{O}_{12}$, in this structure the lithium atoms occupy three separate sites namely square anti prismatic, octahedral and tetrahedral sites in a 3:2:3 ratio. A representation of the structure of the molecule is shown in figure 4.2. The tetrahedral Li sites are bridged by empty octahedras sharing opposite faces with two tetrahedral sites, this arrangement of sites allows for connectivity between

Figure 4. 2 3D representation of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$. The Li atoms can be seen to occupy tetrahedral sites.

two tetrahedral Li atoms through the octahedral site, leading to the formation of a 3D interstitial space in the molecule. This interstitial space depending upon the nature of B and C can accommodate up to 9 Li atoms. But studies have put an empirical limit of 7 Li atoms on the molecule[9].

In this study the focus is primarily on a garnet molecule with the formula $\text{Li}_3\text{X}_3\text{W}_2\text{O}_{12}$. These garnet structures crystallize in a cubic structure as illustrated in figure 4.2. Initial attempts were made to synthesize a range of lithium stuffed garnets by using a variety of cations. The diffraction pattern and the electrochemical analysis of these variants is shown in Appendix I. Due to the low electrochemical activity of the Y and Mo variants further research was focused only on $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ [12]. The reasons for narrowing are studies on this single Lithium stuffed garnet structure are detailed as follows.

- The presence of tungsten allows us to exploit the $\text{W}^{4+/6+}$ furthering a multi electron reaction at a low potentials of 0.8 V vs. Li. Allowing the insertion of four Li atoms into the host structure
- The presence of lanthanide like Neodymium allows for structural stability during cycling. Other cheaper alternatives such as Yttrium and Molybdenum have not been successful as shown in Appendix I. Hence restricting our discussions to Nd based garnets.

4.1.2 Motivation

- The high molecular weight of the selected lithium garnet is indicative of a low theoretical capacity, this fact is counteracted by the fact that the materials is able to reversible insert and extract 4 Li ions from the host structure.
- Using the tungsten +4/+6 redox couple facilitates the exploitation of extremely low insertion potential ~ 0.8 V vs. Li. A low insertion potential is of little significance when used in a single electrode configuration. But in the case of future applications it can be noted that a low insertion potential anode is necessary to achieve high energy density. In the case of Li-HEC device this allows us to exploit a large potential window increasing the energy stored in the system.

- The presence of Neodymium decreases the theoretical capacity of the materials but at the same time is necessary to maintain structural integrity. Through the purpose of this work we aim at understanding charge storage mechanism of Lithium rich garnets and in the future alleviate the need of heavy lanthanides in the host structure.
- Initial research into Lithium rich garnet structures similar to that reported here shows an incredible decrease in their discharge capacity after the first cycle [9, 13]. This chapter aims at understanding the reason for this irreversible capacity loss at the same time reduce it[10].

4.1.3 Experimental Procedure

Synthesis

A conventional solid state ceramic route was used to synthesize the pristine material[14]. The chemical reaction governing the reaction is as follows

Stoichiometric amounts of Li_2CO_3 (Merck, Germany), Nd_2O_3 (Aldrich, USA), and WO_3 (Aldrich, USA) were mixed and thoroughly ground using a mortar and pestle. The powder is pelletized in stainless steel die with 20 mm diameter with a hydraulic press. The pellet is then fired at 750 °C for 2 days. To avoid sublimation of Li during high temperature sintering. 10 % excess Li_2CO_3 is added to avoid shortage of Li in the system. The pellet was removed re-ground and re-pelletized and re-heated at 880 °C for three days. The final resultant is $Li_3Nd_3W_2O_{12}$. The obtained powder was then ball-milled using a high energy ball mill (SPEX 8000D, USA) for 1 hour. The size reduced powder is suspended into a sucrose solution and continuously stirred at 80 °C to yield a composite powder. Finally, the composite powder is heated in the presence of Ar at 600 °C for 2 h to carbonize the sucrose[12].

Characterization

X-ray diffraction measurements were carried out using a Bruker D8 advanced powder diffractometer equipped with a copper target generating CuK_α radiation. The diffraction pattern is subjected to Rietveld refinement using TOPAS V4 software package. Morphological and surface topography was examined using a FE-SEM (JEOL JSM 7600F) carbon coating on the sample and crystallinity of the sample was analyzed using HR-TEM (JEOL JSM 211F). Raman spectra of the bare sample was recorded using a WITEC Alpha 300 SR (argon laser 480 nm). Thermo-gravimetric analysis on the pristine and carbon coated sample and pristine sample was done using TGA Q500.

Electrochemical cell Assembly

Electrochemical studies were performed in a standard CR-2016 coin cell configuration. Electrodes were synthesized for three samples, pristine, ball milled and carbon coated. Active material is mixed with conducting carbon and binder (Teflonized acetylene black) in the ratio of 8:1:1. The composite is pressed onto a 200 mm^2 stainless steel mesh which serves as a current collector. The test cell was fabricated using porous glass fiber separator (Whatman Cat No. 1825-047 UK) and flooded with 1M LiPF_6 dissolved in a 1:1 volume ratio of ethylene carbonate (EC): di-methyl carbonate (DMC). CV studies were conducted using a Solartron 1256E and battery analysis was conducted using a NEWARE battery testing system.

4.1.4 Results and Discussions

Materials Characterization

The material was synthesized using a solid state method coupled with a sucrose assisted carbon coating process to enhance the conductivity of the sample. In order to determine the effect of size reduction on the electronic properties of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ three separate sample were tested listed in Table 4.1.

Table 4. 1 $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ with varying degree of processing

Sample 1	Pristine $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$
Sample 2	Ball milled $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$
Sample 3	Carbon coated and ball milled $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$

All the samples were characterized using X-ray diffraction in order to confirm phase purity and analyze if the size reduction lead to any change in the lattice parameters of the material. It was observed that all three samples consisted of single phase of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$. Only differences observed were in case of the intensity recorded for each sample which is because of relative size of the particles. Also the carbon coated on $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ is amorphous and does not contribute to any excess reflections in the diffraction pattern. From the nature of the peaks (figure 4.3) it can be inferred that the sample is highly crystalline.

Figure 4. 3 Rietveld refined X-ray diffraction pattern. Reproduced with permission from ref [10]

Rietveld refinement was carried out for sample 3 the results are summarized below in figure 4.3.

Figure 4. 4 Schematic indicating the size reduction of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ as it is ball milled.

The pattern was refined to a cubic structure with the space group $\text{Ia}\bar{3}\text{d}$ at full occupancy of Li, Nd, W, O at 24d-A, 24c-B, 16a-C and 96h sites [15]. The lattice parameter obtained after refinement of the powder pattern is $a = 12.445(1) \text{ \AA}$ [10].

Micrographs representing each stage is illustrated in figure 4.4. It can be observed that the particles size reduces from 2-3 μm to $\sim 100\text{-}200 \text{ nm}$.

Such a drastic size reduction leads to appreciable changes in the electrochemical properties of the sample. Reduction in particle size is synonymous with an increase in net surface area of the electrode exposed to the electrolyte which might give rise to parasitic reactions leading to a loss in capacity. The carbon coating serves as both a conducting layer and protective layer against parasitic reactions that might occur at low potentials.

SEM micrographs and HR-TEM images of the carbon coated sample are illustrated in figure 4.6 it can be noticed that the carbon coated sample has a largely aggregated structure which is expected because of the high temperature ceramic route used. Figure 4.6 (b) indicates an isolated edge of a particle. The following points can be noted from the image. The particles seem to have regularly spaced grating which is indicative of a highly crystalline sample. Also on the outer surface of the particle it can be observed that there is

a uniform amorphous layer of carbon with a thickness of ~ 2 nm figure 4.6(b) . The carbon coating is aimed at improving the conductivity of the base material.

The amount of carbon coated on the sample is tested using a thermo-gravimetric setup. The sample is heated in the presence of air. The results of which are summarized in figure 4.5 (1). The calculated weight loss corresponding to the amount of carbon in the sample is ~ 2.2 wt %. Indicating that the sample contains 2.2 wt % of carbon in it. It is important to control the carbon percentage in the electrode in order to optimize the volumetric density of electrode materials. TGA data was also collected for the pristine sample to rule out any

Figure 4. 5 (1) indicates the TGA of LNO indicating the total amount of carbon present in the sample ; (2a) Indication of the Raman spectra of LNO without carbon coating, (2b) Raman spectra of LNO after coating. Used with permission from ref [10]

thermal decomposition (Appendix 4).

The quality of the carbon coated on the sample is extremely important as it establishes the electronic conductivity improvements in the sample. Raman spectra recorded for both the bare sample and the carbon coated sample is illustrated in Figure 4.5(2). The purpose of this experiment is to study the presence and nature of the D and G peaks occurring at 1320 and 1580 cm^{-1} respectively. It can be easily discerned from the graph that these peaks are absent in the case of the bare sample whilst in the carbon coated sample they are visible. The D peak corresponds to a disordered phase in carbon while the G corresponds to a graphitic phase of carbon. The G mode is said to have a E_{2g} symmetry where the Eigen vector is said to involve the in-plane movement of the sp^2 carbon atoms [16]. The D mode

Figure 4. 6 (a) FE-SEM micrograph of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$;(b) TEM micrograph of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ indicating a uniform carbon coating on the sample. Used with permission from ref [10]

is said to have an A_{1g} symmetry which involves phonons from the K zone boundary. This mode is not allowed in the case of perfect graphite and hence can be observed only in the presence of disordered carbon [17]. Another imported feature of these Raman bands is that the ratio of the intensity of the two peaks is an indication of the amount of each type of carbon present in the sample. I_d/I_g was calculated to be 0.98 which indicates that the fraction of sp^2 carbon is higher than sp^3 carbon, hence carbon coating will have a positive effect on conductivity of the sample [18-20].

In order to confirm the positive effect of carbon coating on the sample. The three samples were assembled into half cells using Li metal as both the counter and reference electrodes and an organic electrolyte (1M LiPF_6 in 1:1 EC:DMC) the results of which are shown in figure 4.7. Note that the carbon coated sample is superior to the bare sample and the ball milled sample. Hence, further testing is limited to sample 3.

Figure 4. 7 Comparison of the charge discharge profile of pristine, ball milled and carbon coated LNO

Electrochemical testing

LNO was initially tested in a half-cell arrangement with Li as both the counter and working electrode. The testing was done between 0.2 -1.2 V vs. Li. The reaction occurs by the following process

The CV of $Li_3Nd_3W_2O_{12}$ is represented by Figure 4.8. During the first discharge process two broad peaks are observed at ~0.76 V and 0.34 V vs. Li, which corresponds to the reduction of $W^{6+/5+}$ (2 moles of Li) and $W^{5+/4+}$ (2 moles of Li), respectively.

During the charge cycle two sharp peaks are observed at 0.4 V and 0.9 V vs. Li. These peaks are accompanied by small shoulder peaks. The peak splitting of each of the peaks is because of the Li insertion mechanism. Li ions are electrochemically inserted into tetrahedral 24d- A sites bridged by empty 48g octahedral units [9, 14, 21]. In the second cycle, a small shift in the peak position towards a higher potential and reduction of area

Figure 4. 8 Sketch indicating the cyclic voltammetry curve of LNO when cycled between 0.2 V to 1.2 V vs. Li. Reproduced with permission from ref [10].

under the CV curve during the cathodic scan is observed, which can be attributed to the formation of a SEI layer and structural rearrangement after the first cycle. However, no shift was observed in the anodic scan. Repeated cycling for the next 5 cycles shows perfectly reversible behavior. The energy difference between the two redox states is 0.3 eV which indicates the presence of a localized d electron which make the material a poor electronic conductor [10, 14]. Further stressing the need of carbon coating on the materials in order to ensure facile electron conduction.

Figure 4.9(a) is a representation of the first two charge and discharge cycles of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ in a single electrode setup. The tests were conducted at 100 mA g^{-1} . The profile corroborates the electrochemical data obtained from the CV measurements. A discharge capacity of $\sim 250 \text{ mAh g}^{-1}$ was recorded for the first discharge. This drops to $\sim 145 \text{ mAh g}^{-1}$ in the second cycle. The cell is cycled between 0.2-1.2 V vs. Li. The irreversible capacity has been reduced considerably when compared to previous literature

Figure 4.9 (a) First two charge discharge cycles of C-LNO; (b) Capacity retention behavior in the first 300 cycles. Reproduced with permission from ref [10]

[9] but still leads to the loss of $\sim 100 \text{ mAh g}^{-1}$. The irreversible capacity loss can be mainly attributed to the formation of a stable SEI layer on the surface of the anode [22, 23]. In order to confirm that the loss in capacity is not due to some irreversible transformation in the sample. *Ex-situ* diffraction measurements were carried out on the electrodes after the first cycle. The results are highlighted in Figure 4.10. It can be observed that the structure of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ remains intact. The cell was cycled for more than 300 cycles (figure 4.9 b) and no considerable drop in capacity is observed, this also indicates that no major structural changes are taking place in the host structure during cycle and the irreversible

capacity loss at the end of the first cycle can be attributed to the formation of an SEI layer on the surface.

Figure 4. 10 Comparison of X-ray diffraction pattern of pristine LNO, after first discharge, after first charge. * reflections correspond to reflections caused by the stainless steel electrode. Reproduced with permission from ref [10]

The formation of this SEI layer then passivates the surface of the anode against any further reactions with the electrolyte at potentials lower than 0.7 V vs. Li a similar reaction is observed in the case of graphite wherein the formation of a stable SEI layer on the surface of the anode is essential for the application of graphite in LIBs. To confirm good Li ion conduction through the host structure it was charged and discharged at different current rates the profiles for which have been sketched in figure 4.11(a, b). It can be easily observed from this data that the shape of the charge discharge profile remains unchanged at even 8 C indicating a robust insertion type material that can be used in a HEC. On comparing the capacity of the carbon coated $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ with a plain powder [9] tested at 1C it can be noted that the pristine powder material was only able to deliver a reversible capacity of 75 mAh g^{-1} while the carbon coated electrode was able to deliver 128 mAh g^{-1} . This

improvement in net capacity delivered, can be attributed to the size reduction of the particles and the subsequent carbon coating

Figure 4. 11 (a) Dependence of charge stored in LNO on the current rate applied.;(b) Rate performance of LNO. Reproduced with permission from ref [10]

Full cell testing

Before testing it in a HEC device. Preliminary tests were conducted as $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ as a potential anode in a Li ion battery with LiMn_2O_4 as the counter electrode. The capacities of both the electrodes were evaluated in a half cell setup. The electrochemical information

Figure 4. 12 (a) Charge discharge profile of LNO/Li from 0.2 -4.3, charge discharge profile of LiMn_2O_4 /Li from 3 -4.3 V, charge discharge profile of LiMn_2O_4 /LNO; (b) Magnified image of the charge discharge profile of LiMn_2O_4 /LNO; (c) Capacity retention and coulombic efficiency measured at 100 mA g^{-1} ; (d) Capacity retention and coulombic efficiency measured at 500 mA g^{-1} . Reproduced with permission from ref [10]

was then applied to calculate both an appropriate potential range and an appropriate mass balance between the cathode and anode (2.03:1). To illustrate the tungsten and manganese redox couple GCD studies were conducted and the results charted in Figure 4.12 (a). As

expected the full cell ($\text{LiMn}_2\text{O}_4/\text{C}-\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$) has a CV profile which is the same as that of the anode. This is attributed to the fact that due to a higher polarization ($\Delta V = 540$ mV) the anode is dominant over the cathode (200 mV). The GCD traces showed the operating potentials of the full cell at ~ 3.4 V vs. Li. This operating potential is clearly indicative that a low potential anode can be used in a full cell setup to generate high energy lithium ion batteries. The full cell was cycled between 2.95 V to 3.9 V (figure 4.12b). It was observed that there is some irreversible capacity loss after the first cycle. The full cell

Figure 4. 13 Rate performance of the $\text{LiMn}_2\text{O}_4/\text{LNO}$ full cell. Reproduced with permission from ref [12]

was able to deliver a capacity of 115 mAh g⁻¹ and an energy density of 390 Wh kg⁻¹. The observed energy densities are much higher than observed for lithium ion batteries elsewhere [12]. The capacity fade that is observed for the cell is attributable to the Jahn teller distortion experienced by Mn leading to manganese dissolution into the electrolyte and eventual loss in capacity. The full cell was cycled at 100 mA g⁻¹ and 200 mA g⁻¹ the results are summarized in figure 4.12(c, d) it is noted that it displays excellent columbic efficiency in both the cases. In the case of the lower current loading Figure 4.12 c it can be noted that a 100 % efficiency is reached in a few cycles. This is because in the initial cycles the SEI layer has not been fully established on the surface of the anode. Both the cells show excellent reversibility retaining 71 % of the initial charge when cycled at 100 mAh g⁻¹ and 93% of the initial charge when cycled at 200 mA g⁻¹.

Rate performance tests were conducted for the full cell LiMn₂O₄/ C-Li₃Nd₃W₂O₁₂ cell cycled between 2.95-3.9 V at various current densities as shown in figure 4.13. 100 mA g⁻¹ is assumed to be 1C. As expected increase in current loading leads to a minimal capacity fade. The full cell shows a capacity of ~100 and 60 mAh g⁻¹ at 2 and 8C respectively. This clearly illustrates the higher capabilities of the system. Increase in the high power performance is because of the size reduction and carbon coating which facilitates easy electron conduction through the material at high current rates. This study clearly proves that low insertion potential garnet structures can be used for high current applications. After successful application in a Li ion battery configuration Li₃Nd₃W₂O₁₂ was applied in a HEC. Half- cell studies are conducted on commercial activated carbon (NORIT) and C-Li₃Nd₃W₂O₁₂ [12]. Activated carbon recorded a capacity of 33 mAh g⁻¹ [18] while Li₃Nd₃W₂O₁₂ recorded a reversible capacity of 140 mAh g⁻¹. New electrodes were constructed after balancing the mass according to the equation.

$$Q = C_1 \times m_1 = C_2 \times m_2 \quad \text{eq 4.1}$$

Where,

Q is the net charge stored in each of the electrodes

C₁ is the capacity of activated carbon

m₁ mass of the activated carbon

C₂ is the capacity of Li₃Nd₃W₂O₁₂

m₂ mass of Li₃Nd₃W₂O₁₂

m_2 is fixed at 3 mg, the calculated value of m_1 is 12.72 mg. The electrodes are assembled in a 2016 coin-cell arrangement with $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ as the anode and activated carbon as the cathode, the electrolyte used is 1M LiPF_6 dissolved in a 1:1 by volume mixture of EC:DEC and glass fiber separator. The cell was cycled between 0.75 to 3 V. The charge discharge profile is plotted in figure 4.14 (a).

The charge storage mechanism can be explained as follows. During the charge process the Li ions from the electrolyte intercalate into the Li insertion host while the PF_6^- ions are attracted towards the activated carbon electrode. During the discharge process the Li ions are extracted from the insertion host back into the electrolyte. And the PF_6^- ions desorbed from the surface of the activated carbon.

The energy density of the full cell was calculated 33.7 Wh kg^{-1} . The corresponding power densities is calculated to be 0.77 kW kg^{-1} . All calculations are done by using the mass of both the electrodes. The calculation of the energy density of the cell is unique because

Figure 4. 14 Charge discharge profile of LNO/AC hybrid capacitor. The grey area indicates the area under the discharge curve and is used to calculate the energy density of the cell; (b) Ragone plot of LNO/AC hybrid

conventional techniques using a standard fixed operating potential and calculating its product with the capacity of the cell cannot be used here, because of the changing slope of

the charge discharge profile. Using the midpoint of the potential range is also not an option and doing so can sometimes lead to inflated or reduced values. Hence in order to calculate the energy density of HECs it is best to calculate the area under the charge vs potential curve as shown in figure 4.14a. This calculation leads to the most accurate energy density values. The cell is tested at varying power density values and the results collaborated with the resulting energy density. A compilation of the information is shown in figure 4.14 b. The Ragone plot indicates that as the power density is increased there is a steady drop in the energy density of the cell which is expected behavior.

To gain a deeper understanding of this behavior the charge discharge profiles for three current rates are plotted in figure 4.15. It can be seen that there is a complex interplay between two competing mechanism. At low current rates of 50 mA g^{-1} it can be observed that the profile is similar to that expected from a materials storing charge by a faradaic mechanism. This is because at low current rates it feasible for the Li ions to actually

Figure 4. 15 Rate performance of LNO/AC hybrid capacitor.

intercalate into the battery material. On the other hand when tested at high current rates like 200 mA g^{-1} it can be observed that the cell displays a profile similar to that expected from a pure supercapacitor this is due to the fact that at such high rates only surface diffusion occurs at both electrodes.

Considering the above system as an internal serial hybrid type device the net energy density of the cell is limited by the supercapacitor electrode in this case the activated carbon electrode. While the maintenance of high power output at high energy values is dependent on the battery electrode. It can be observed from the Ragone plot in figure 4.14 b that the drop in energy density is less severe when compared to previous literature for example AC/TiP₂O₇ (ED=13 Wh kg⁻¹, PD 371 W kg⁻¹) [24], AC/LiTi₂(PO₄)₃ (ED= 14 Wh kg⁻¹, PD= 180 W kg⁻¹) [25], LiMn₂O₄/AC (ED=25 Wh kg⁻¹, PD = 325 W kg⁻¹) [26] indicating that the insertion host has a robust structure and is able to intercalate Li ions even at high current rates.

4.1.5 Conclusion

HEC are devices that use a combination of a battery electrode and a supercapacitor electrode in order to achieve energy densities and power densities in a niche spot between these two technologies, as discussed by [8, 27]. In this section the problem statement has been isolated to the study of probable battery materials as insertion host. After initial screening the lithium based garnet molecule Li₃Nd₃W₂O₁₂ was chosen. This structure uses the tungsten redox couple at 0.8 V vs Li. This allows to create full cells that can operate in a wide potential range. The material was characterized to determine phase purity. The pristine material was reduced in size and carbon coated. The resultant electrode was tested in three setups.

- Single electrode tests: involved the testing of the carbon coated electrode with respect to a metallic Li foil which acted as both the counter electrode and the reference electrode. This test is essential to establish the feasibility of the cell as Li insertion and extraction properties are the only limiting factor in this experiment. The results of the experiments are compared with previously published results on a similar material. An increase in capacity, cycle ability and a decrease in the irreversible capacity loss is observed indicating the carbon coating is beneficial for the material. At the same time the amount of carbon was controlled so as to not reduce the volumetric capacity of the cell

- Full cell tests: the lithium stuffed garnet was coupled with a commercial cathode and tested in an organic electrolyte. The energy density of the cell is 390 Wh kg^{-1} the calculations are done on a cathode basis. The cell shows an excellent cycle ability and high energy storage capacity. Also due to the robust host structure no appreciable loss in capacity is observed at even higher current loadings
- HEC: $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ is coupled with an activated carbon electrode and tested from 0.75 to 3 V. An energy density of 33.7 Wh kg^{-1} could be obtained from this cell which is ~ 3 times of a conventional supercapacitor. The purpose of using a Lithium garnet to construct a HEC device was to develop a baseline result competitive with prevalent literature and then further build on improving material properties to enhance energy storage capabilities.

4.2 Understanding the use of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a LISICON type structure showing excellent high performance characteristics

4.2.1 Introduction

The study focusses on the use of a member of the phosphate family $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) as a potential electrode material for Li-HEC applications. Previous studies have focused on different phosphate based materials like LiFePO_4 [28-36], LiMnPO_4 [37] and LiCoPO_4 [38]. Out of these materials Lithium iron phosphate is the only one that could be commercialized. The other compounds have an extremely high insertion potential which is above the stable potential window for organic electrolytes. Lithium iron phosphate shows an extremely stable insertion potential at 3.4 V vs. Li and delivers a capacity of 170 mAh g^{-1} . But it suffers from low electronic conductivity because of increase in covalency between the metal and the phosphate group which leads to an increase in the electronic band gap making the material a semi-conductor. This has been remedied in literature by using size reduction techniques in conjunction with carbon coating. But because of its relatively low insertion potential it cannot be used successfully in HEC's to achieve a high energy density device. Also the high current performance of LiFePO_4 leaves a lot to be desired. In this section we explore the use of LVP as a potential electrode for HEC applications. LVP has been analyzed in detail by other groups to study the structural properties and the insertion and extraction [39-51]. But in this work for the first time LVP has been applied in a hybrid electrochemical capacitor. The material is studied by coupling it with AC which acts as the counter electrode and the tests are conducted in the same electrolyte as the single electrode tests. Excellent energy density and power densities were observed for the system. At the same time because of the ability of LVP to act as both an anode and a cathode, it presents us with a unique opportunity to study the dependence of electrode polarity on the energy storage capacity of HECs at a particular power density.

4.2.2 Motivation

LVP belongs to a long line of phosphates which have been tested for Li ion battery configurations. The motivation for further studying LVP as a potential Li-HEC candidate can be enumerated as follows.

- LVP operates on using the vanadium redox couple for charge compensation. In its pristine state Vanadium in LVP exists in a III state, hence the material can be cycled as an anode to insert on or two Li ions into the host structure and also as a cathode material to extract up to 2 Li atoms from the host structure. The study of LVP is hence extremely important to develop an empirical rule which can be used for similar materials to decide electrode polarity depending on the power requirements, so as to maximize the amount of energy stored in the cell.
- LVP is shown to have a Li ion conductivity of $10^{-8} \text{ cm}^2\text{s}^{-1}$ [45, 52, 53]. LVP molecules consist of a complex framework of VO_6 octahedras linked together with phosphate tetrahedras. This open cage type structure facilitates a 3D dimensional Li ion diffusion through the structure. Indicative of the fact that the material is suitable for high current applications.

4.2.3 Experimental methods

LVP-C was prepared using a fast sol gel method as initially shown in ref [54]. Li_2CO_3 (Merck, Germany), V_2O_5 (Sigma Aldrich USA, 98%), $\text{NH}_4\text{H}_2(\text{PO}_4)$ (Fischer 99.9%) were mixed in a stoichiometric ratios and dissolved in 2ml of deionized water[18]. The resulting reaction is endothermic and occurs with the simultaneous removal of carbon dioxide. Citric acid was employed as the chelating agent in the reaction, it also doubled up as the source of carbon during carbon coating. The mass of the citric acid used in the reaction depends on the amount of residual carbon left in the sample. The citric acid was then dissolved in deionized water. Both the solutions were then mixed to form a clear blue sol. Excess water in the reaction was dried at 80 °C till a dark blue gel was formed. The dried gel was then ball milled in a high energy ball mill (SPEX 8000, USA). The powder was treated at 350 °C in argon for 4 h to remove any traces of NH_3 and CO_2 . The powder was reground and pelletized to maintain good contact during sintering followed by heating at 750 °C in Argon. Structural characterization was carried out using a Bruker D8 advanced powder diffractometer using CuK_α radiation. The obtained pattern was Rietveld refined and analyzed using TOPAS V4 software. Morphological characterization was carried out using a field emission scanning electron microscope, (JEOL7600 F) and a high resolution

Transmission electron microscope JEOL- JSM 2100 F. The Raman spectra was recorded using a Witec Alpha 300 SR Raman spectrometer powered by a 480 nm Ar laser. Quantitative calculation on the amount of carbon coated on the sample were performed using TGA Q500.

Composite electrodes were formulated with a mass ratio of 8:1:1 of active mass: binder (Teflonized acetylene black): conducting carbon (Super P, TIMCAL, and China). The technique used is explained in detail in section 3.3. The electrolyte used during cell assembly is 1M LiPF_6 dissolved in a 1:1 mixture by volume of ethylene carbonate and Diethyl carbonate. Cyclic voltammetry (CV) studies were recorded at a slow scan rate 0.1 mV s^{-1} using Solartron 1470E. Galvanostatic charge discharge studies were conducted using a NEWARE battery testing system.

4.2.4 Results

LVP is known to be able to crystallize to two polymorphs, depending upon the conditions during synthesis. One of them is rhombohedral (NASICON) structure while the other is a thermodynamically stable monoclinic phase. The monoclinic phase has been shown to impart high capacities due to the ability to conduct multi-electron reactions. For the purpose of this experiment LVP was synthesized using a fast sol-gel reaction route

Figure 4. 16 Crystal structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

Figure 4. 17 Rietveld refinement of X-ray diffraction pattern of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

developed by Yuan *et al*[54]. The method employs citric acid as both a chelating agent and source for carbon coating the material *in-situ*. The carbon coating is necessary to improve the conductivity of the sample [55, 56, 30]. The structure of LVP is represented using VESTA in figure 4.16 [57]. It can be observed that the material crystallizes in a monoclinic framework (space group $\text{P2}_1/\text{n}$) consisting of Vanadium octahedras (red) connected together with PO_4 (terahedras) grey. The Li atoms are present at three distinct crystallographic locations Li(1) occupies the tetrahedral site while Li(2) and Li(3) occupy pseudo-tetrahedral sites [58]. The 3 dimensional network around the Li ions facilitates rapid Li diffusion from the structure. The recorded X-ray diffraction pattern is depicted in figure 4.17. Rietveld refinement was carried out on the materials to confirm phase purity and calculate the lattice parameters of the material. The calculated lattice parameters are summarized in table 4.2. The results are in good co-relation with previously published data on LVP-C [54, 59]. The diffraction pattern can also indexed perfectly to LVP indicating that no foreign phase is generated during the synthesis process.

Table 4. 2 Rietveld refined parameters of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

Material	$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ - C
Phase	P 2 ₁ /n
a (Å)	8.613
b (Å)	8.604
c (Å)	12.057
β (°)	90.609

Figure 4. 18(a,b) Micrographs representing the agglomerated condition of LVP, average particle size of the LVP particles;(c,d) High resolution TEM micrographs representing the layer of amorphous carbon coated on the sample.

Figure 4. 19(a) Raman spectrum of LVP; (b) TGA analysis of LVP indicating a 2.2 wt % of carbon in the sample.

Figure 4.18(a, b) illustrates the morphological profile of the prepared LVP-C it can be observed that it consists of hierarchical agglomerates of small particles ranging from 100-200 nm. Figure 4.18(c, d) are high resolution TEM micrographs indicating the crystalline nature of LVP-C. Unlike the previous section concerning carbon coating of $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ it can be observed that the *in-situ* carbon coating process in LVP results in highly non uniform carbon coating that can be observed on the boundaries of particles as shown in figure 4.18(d). The quality of carbon is important to establish the effect of carbon on the conductivity of the material. Raman spectroscopy was conducted on multiple locations on the powder sample an average of the obtained spectra is shown in figure 4.19 a. Two peaks are observed at 1350 cm^{-1} and 1589 cm^{-1} . The first peak corresponds to the presence of disordered carbon in sample and indicates the vibration of A_{1g} symmetry involving phonons near the K zone boundary. This mode is prohibited in the case of perfect graphite and can be observed in case any disorder is present in the material. The D mode is dispersive unlike the G mode and its intensity is dependent on the energy of the laser used. The G mode of vibration corresponds to E_{2g} symmetry, it involves the in plane vibration of sp^2 type carbon atoms, unlike the D mode this mode does not require the presence of six fold rings and always lies in the range of $1530\text{-}1630\text{ cm}^{-1}$ as it does in aromatic and olefinic compounds [17, 60]. The presence of both the peaks in the Raman spectra is an indication

of the presence of disordered carbon in the carbon coating at the same time the carbon does not have a high enough graphitic character to impart to the overall capacity of the material. The ratio of the intensities of the D and G peaks is directly related to the relative amounts of disordered carbon to graphitic carbon in the sample [19, 25, 61]. LVP samples displayed an I_d/I_g value of 1.007 which implies an equal distribution of both sp^2 and sp^3 carbon in the carbon coating.

Carbon coating has been known to improve conductivity in a variety of cases but it is known that excess amount of carbon leads to a decrease in the amount of tap density (percentage of active material in the electrode). TGA tests were conducted on the sample to evaluate the amount of carbon in the sample. The results of the experiment are summarized in figure 4.19 (b). As the sample is heated it can be observed that there is a reduction in the mass of the material at $\sim 410^\circ\text{C}$ the drop corresponds to decomposition of the carbon present in the sample. The weight loss is calculated to be ~ 2.2 wt. % this is indicative that ~ 2.2 wt. % of the sample is amorphous carbon. The low percentage of carbon avoids low tap densities and low volumetric capacity. A second plateau is observed in the TGA plot at $\sim 550^\circ\text{C}$ which corresponds to the decomposition of the phosphate moiety in the sample.

Because of the use of vanadium as the active redox couple in the molecule. The material can be used as both an anode (V^{3+}/V^{2+}) and a cathode (V^{3+}/V^{5+}). To determine an appropriate mass balance for HEC assembly, LVP-C is tested in a half cell configuration as both an anode and cathode. The results for the cathode testing are summarized in figure 4.20.

Figure 4.20(a) is a CV trace of LVP-C when it is used as a cathode material, the potential range for the testing was restricted to 4.5 V vs. Li in order to avoid the removal of the third Li ion from the host structure. The removal of the third Li atom from the host structure although gives extra charge storage capability to the material but it leads to irreversible crystallographic deformation of the host structure, which in turn leads to a loss in cycle ability of the material. The CV profile can be split into two major portions as shown in the figure. The separation is based on the Li site which undergoes extraction and insertion. One of the Li atoms is located at a purely tetrahedral site while the other two are located at pseudo tetrahedral sites with an extra Li-O bond. During the charge process the Lithium removal occurs according the following chemical equation [47, 59, 62].

During the charge cycle, ~ 3.6 V *vs.* Li corresponds to the first observed peak in the CV trace and the removal of the most energetic Li from the host structure. The removal occurs in two stages (i) $Li_3V_2(PO_4)_3 \rightarrow Li_{2.5}V_2(PO_4)_3$, and the (ii) $Li_{2.5}V_2(PO_4)_3 \rightarrow Li_2V_2(PO_4)_3$. This splitting occurs because of the presence of a stable phase with the composition of $Li_{2.5}V_2(PO_4)_3$. The removal of 1 Li atom from the structure is complete at 3.7 V *vs.* Li [40]. At this stage the vanadium atoms in the crystal exist as a mixture of +4 and +3 vanadium. The removal of the first Li leads to the movement of a Li atom from its original location to a tetrahedral site. As the cell is charged further the second Li atom is removed from the host structure at 4.1 V *vs.* Li *via* a two phase mechanism. At this stage all the vanadium in the sample is in a +4 state. Removal of the last Li atom from the host is kinetically the most troublesome because of the reduced ionic and electronic conductivity of the fully empty phase $V_2(PO_4)_3$ [62]. However, few reports exist which display the effect of removal of the third Lithium atom from the structure. It can be observed that the Li atom leads to extra capacity but alternatively it causes a drastic decrease in cycle life of the material [63-66]. To avoid this the system was limited to 4.3 V *vs.* Li because cycle stability is of utmost importance for HEC applications. Limiting the potential leads to a decrease in capacity but it is an acceptable tradeoff for the increased cycle ability [67-69]. During the discharge phase the mechanism reverses itself. Figure 4.20 (b) is an illustration of the charge discharge profile of LVP-C between 3-4.3 V *vs.* Li. A reversible capacity of 125 mAh g⁻¹ can be derived from the cell at a current load of 100 mA g⁻¹. On close examination the profile corroborates the lithium insertion and extraction steps observed in the CV trace. The half-cell was cycled for 100 cycles to determine the structural stability of the host material. It can be observed from figure 4.20 (c) that LVP-C retained $\sim 80\%$ of its initial charge indicating that host structure is stable after removing two Li atoms. In order to determine the performance of the materials at high current rates. Rate performance studies were conducted on the material using currents up to 10 C (1 C was assumed to be 131 mA g⁻¹ considering the removal two Li atoms), the results of the experiment are plotted in figure 4.20 (d). As expected the capacity delivered by the electrode gradually dropped as the current rate is increased. This is because the intercalation of Li through an insertion host is a diffusion limited process, and at high current rates the time period of one cycle is much

Figure 4. 20(a) Cyclic voltammetric profile of LVP-C when cycled between 3-4.5 V vs. Li.; (b) Charge discharge profile of LVP-C when used as a cathode ; (c) Capacity retention w.r.t to cycle number.(d) Rate performance of LVP-C when used as a cathode. Reproduced with permission from ref [18]

smaller than the diffusion time required for Li to intercalate into the host structure. After stressing the materials up to 10 C the current rate is relaxed to 0.1 C and it can be noted that LVP-C regains its original capacity. Indicating that the insertion host has a robust structure which does not collapse on exposure to high currents.

LVP -C was cycled as anode between 1-3 V vs. Li [70]. The results for which are summarized in Figure 4.21. The CV trace for the anode scan is shown in figure 4.21 (a), the scan was conducted at 0.1 mV s⁻¹. The trace displays three peaks corresponding to the insertion of two Li atoms into the host structure. ~1.90 V vs. Li and ~1.83 V vs. Li corresponds to the insertion of 1 Li ion into the host. The peaks are separated because of

Figure 4.21 (a) Cyclic voltammetric profile of LVP when cycled as an anode (b) Charge discharge profile of LVP when used as a anode. (c) Capacity retention of LVP for the first 100 cycles when employed as an anode material. (d) Rate performance of LVP when tested as an anode. Reproduced with permission from ref [18]

the existence of a stable phase in between with the composition of $\text{Li}_{3.5}\text{V}_2(\text{PO}_4)_3$. The peaks present at ~ 1.6 V vs. Li indicates the insertion of the second Li atom. There are certain shoulder peaks observed at ~ 1.6 V this is because of the insertion mechanism of Li atoms into the host structure. During the charge portion of the CV it can be observed that the peaks are a reflection of the discharge profile. Minimal polarization is observed when compared to previous literature indicating that carbon coating LVP leads to increased conductivity[12]. Figure 4.21(b) represents the charge discharge cycle of LVP as anode material. A reversible capacity of 92 mAh g^{-1} is observed for the system when cycled at 100 mA g^{-1} . The half-cell was cycled for 100 cycles to determine the structural stability of

the host structure during lithium insertion. Rate performance studies were conducted on the material and summarized in figure 4.21(d). As expected it can be observed that a drastic drop in capacity is observed when the current load on the cell is increased this drop is attributed to the slow nature of Lithium diffusion into the bulk, upon relaxation it can be observed that the original capacity is retrieved indicating a robust insertion host.

Commercial activated carbon is used as the counter electrode for HEC testing so that improvements made only by using LVP-C can be discerned and no artifacts due to activated carbon modifications are observed. In order to calculate the optimized mass ratio in each of testing configurations, activated carbon was tested as half-cell as both an anode and a cathode. The results are summarized in figure 4.22. It can be observed that activated carbon gives a higher capacity $\sim 45 \text{ mAh g}^{-1}$ when tested between (1-3 V vs. Li) this is attributed to the fact that in this case a smaller Li ion is adsorbed on the surface of activated carbon, when tested as a cathode (3-4.6 V vs. Li) it can be observed that a capacity of 33 mAh g^{-1} is obtained, the lower capacity is due to the charge storage by the adsorption of a much larger PF_6^- ion. In both cases the charge is stored by the formation of a double layer on the surface of the activated carbon hence the process is highly reversible and fast.

Using the capacities calculated using half-cell studies two kind of cells were assembled in a coin cell configuration using a glass fiber separator and a non-aqueous electrolyte using 1 M solution of LiPF_6 dissolved in a 1:1 by volume mixture of ethylene carbonate and Diethyl carbonate. Using the capacity profile of each of the electrodes the mass was optimized using equation 4.1.

Cell 1:

LVP-C as the cathode and AC as the anode- all cycling studied for the HEC were done at 100 mA g^{-1} . The current was calculated on the basis of the total mass of the cell (anode + cathode = 11.3 mg). The mass of LVP-C was fixed at 3 mg and the mass of AC was calculated to be 8.3 mg. The cell was cycled between 0.5 -2.75 V. The potential of the full cell is restricted to 2.75 V vs. Li to avoid the removal of more than 2 Li ions from the host structure. During the charge process Li ions are attracted towards the surface of activated carbon. The Li ions form a layer along the surface of activated leading to the formation of an electrical double which can be used to store electrical charge. The removal of Li ions from the electrolyte leads to a driving force which aids in the removal of Li ions from host structure in order to maintain the concentration of Li ions in the electrolyte solution. During

Figure 4. 22 (a) Charge discharge profile of AC when cycled as an anode; (b) Capacity vs. cycle life of activated carbon plotted for the first 500 cycles when tested as an anode.;(c) Charge discharge profile of AC when tested as a cathode between 3-4.6 V vs. Li.;(d) Capacity vs. cycle life of activated carbon when tested as a cathode. Reproduced with permission from ref [18]

the discharge process the Li ions are desorbed from the activated carbon electrode due to a reversal in polarity and Li ions present in the electrolyte are intercalated back into the host structure. The charge discharge profile of an LVP-C/AC cell is sketched in figure 4.23 (a).

Cell 2:

LVP-C as the anode and activated carbon as the cathode. The tests were conducted at 100 mA g^{-1} calculated based on the total of 15.5 mg (AC=11.5 mg and LVP-C =4 mg). In order to compare the energy density of both the cells they were cycled in the same potential range. The charge storage mechanism in cell 2 is different when compared to cell 1. During the charge phase the lithium ions are attracted towards the anode (LVP-C) and intercalate into the host structure. In a similar manner the fluorophosphates ions in the electrolyte form an electrical double layer on the surface of activated carbon. Due to the larger size of the PF_6^- it cannot effectively utilize the high surface area of the activated carbon leading to reduced energy storage properties. During the discharge process Li ions are extracted from the host material back into the electrolyte. Depending upon the nature of the anode material used,

Figure 4. 23 (a) Charge discharge profile of LVP/AC(LVP as the cathode).;(b) Charge discharge profile of AC/LVP (using LVP as the anode)

some Li might be irreversibly used for the formation of an SEI layer in order to passivate the anode against reactions with the electrolyte. Earlier studies using graphite as the anode show that pre-lithiation of the anode is necessary in order to achieve a high energy density and power density. But because of the relatively higher insertion potential of LVP-C no side reactions are expected to occur and there is no need to pre-lithiate the anode prior to

usage. This allows an essential cut down of cost and processing time for the assembly of a HEC cell. The charge discharge profiles for the first two cycles of cell 2 is illustrated in figure 4.23 b.

Initial observations indicate that there is a decrease in the area under the curve as the current loading is increased this is attributed to the fact that the limiting agent for the stored energy at high power densities is the battery electrode. Battery electrodes store energy by reversibly diffusing Li into the host structure. Solid state diffusion is kinematically sluggish

Figure 4. 24 Comparison of high rate performance depending on the choice of polarity of LVP.

when compared to charge storage *via*. the formation of an EDLC on the surface of activated carbon electrodes. Hence as the current load on the cell is increased the charge storage mechanism in the Li-HEC is a competition between charge by intercalation on the host materials or by the formation of an electrical double layer on the surface of activated carbon. At low current rates it can be observed that the profiles for both the cells are dominated by the high energy battery electrode. As the current load is increased it can be noticed the profiles adopt a linear dependence to potential similar to that observed for supercapacitor devices[71].

The energy and power densities of both cells are summarized in table 4.3. From these results it can be concluded that at the same power densities the energy density is higher when LVP-C is used as a cathode material. This can be better understood by looking at the

Li ion diffusion coefficient for LVP in either conditions summarized in table. When used as a cathode materials LVP-C exhibits a Li ion diffusion coefficient 10 times higher than when it is applied as an anode material [45, 72].

Table 4. 3 Li ion diffusion coefficient of LVP when used as cathode and anode

	Li ion Diffusion Coefficient ($\text{cm}^2 \text{s}^{-1}$)	Energy Density (Wh kg^{-1})	Power Density (W kg^{-1})
LVP-C / AC	10^{-8} - 10^{-9}	27	120
AC/LVP-C	10^{-10} - 10^{-11}	22	120

To determine the stability of the Li-HEC both cell 1 and cell 2 were cycled between 0.5 to 2.75 V for 1000 cycles. The results of the experiment are recorded in figure 4.25. It can be observed that both the cells retain almost 100 % of their original charge storage capacity

Figure 4. 25 Percentage capacity retention vs. cycle number over a period of 1000 cycles.

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even after 1000 cycles. The high stability of the HEC is due to the stability of the insertion host material at high current and also the fact that the insertion host does not need to

undergo deep charge or discharge when used in a HEC. Thus greatly improving the cycle life of the material.

A Ragone plot comparing the dependence of energy density w.r.t the power density is shown in figure 4.26. It can be observed that at lower-moderate power density requirements the LVP-C/AC displays a higher energy density. As the power density is increased to $\sim 250 \text{ W kg}^{-1}$ the AC/LVP-C displays a higher energy density. This can be attributed to an increased contribution from the supercapacitor electrode. Table 4.4 compares the energy density obtained in earlier literature with LVP-C /AC. It can be observed from the table that LVP-C performs better than all materials except $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Table 4. 4 Comparison of energy density and power density of hybrid capacitors in literature with the performance of LVP when used as the cathode and anode

S No	Anode	Cathode	E.D (Wh kg ⁻¹)	P.D (W kg ⁻¹)	Reference
1	AC	LVP-C	30 $\pm$ 10	255 $\pm$ 10	[18]
2	AC	LiMn ₂ O ₄	25 $\pm$ 5	200 $\pm$ 100	[26]
3	AC	LiVPO ₄ F			
4	LVP-C	AC	22 $\pm$ 5	120 $\pm$ 10	[18]
5	TiP ₂ O ₇	AC	13 $\pm$ 2	170	[24]
6	LiTi ₂ (PO ₄) ₃	AC	14 $\pm$ 5	180	[25]
7	Li ₄ Ti ₅ O ₁₂	AC	30 $\pm$ 10	1300 $\pm$ 500	[26]

4.2.5 Conclusion

The various scientific conclusions that can be made from section 4.2 can be summarized as follows.

- Lithium vanadium phosphates is a robust insertion type host material for HEC applications. It can be employed as either an anode or a cathode. But results from electrochemical measurements indicate that the performance of LVP-C is favorable

Figure 4. 26 Comparison of the energy density of hybrid capacitors depending on the use of LVP as an anode and cathode. Reproduced with permission from ref [18]

when employed as a cathode material when used at moderately high current rates up to 250 W kg^{-1} at higher current rates it is more favorable to use LVP-C as anode material.

- Surface modifications of LVP with carbon *in-situ* during synthesis allowed for good electronic conduction which would not have been possible for a bare phosphate base poly-anionic cathode.
- Despite excellent performance, when compared to previous literature on Li-HEC's and super capacitors. LVP is not suitable for high energy applications such as hybrid electric vehicles the relatively lower energy density when compared to Li-ion batteries is the main drawback for this type of energy storage device. Energy density can be increase in two ways, modifying the structure the of the activated carbon electrode which is dealt with in a later chapter, alternatively an expansion of the working potential range of the device can be implemented increase the net energy stored. In order to facilitate this the next section looks at the use of fluorophosphates with a high insertion potential and high capacity.

4.3 Understanding the use of a vanadium based fluorophosphate compounds as high voltage alternative Li-HEC battery electrode

4.3.1 Introduction

In this section we continue from the results obtained from the previous section and test the application of LiVPO_4F (LVPF) as a potential cathode material for hybrid capacitor applications. LVPF belongs to a class of materials called as Tavorite ($\text{LiFePO}_4\cdot\text{OH}$). Electrochemical studies on LVPF were first conducted by Barker *et al.*[73, 74] they

Figure 4. 27 Crystal structure of LiVPO_4F indicating open channels for Li ion migration.

established that LPVF can act as both a cathode and anode but the anode capacity is extremely poor and hence does not warrant further study. The structure of the material can be visualized as illustrated in figure 4.27. The material consists of VO_4F_2 octahedra linked together by a phosphate tetrahedral. The presence of F distorts the crystal such that it crystallizes to a triclinic structure. Li atoms are statistically arranged in tunnel like units as shown in figure 4.27 [75].

4.3.2 Motivation

1: LVPF has a high working potential of 4.3 V vs. Li which is 0.5 V higher than $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [76, 77]. The increase in redox potential is due to the higher ionicity of the M-F bond when compared to the M-O leading to a higher reduction potential[78].

2: From the crystal structure of the materials it can be noted that the structure is conducive to facile Lithium migration.

4.3.3 Experimental Methods

Fluorophosphates are extremely rare in nature [79] and hence we had to synthesize LiVPO_4F using carbo-thermal approach as pioneered by Barker *et al* [74]. The approach uses carbon as a reducing agent and in this case the excess carbon forms a non-uniform layer on the sample coating it with a homogenous carbon layer.

The synthesis process can be split into two parts

1: Preparation of VPO_4

V_2O_5 (Sigma Aldrich 98%), Ammonium di-hydrogen phosphate (Sigma Aldrich) and Super P (TIMCAL carbon) were mixed together in a stoichiometric ratio with 25 % excess carbon by weight, the mixture was ball milled using a SPEX high energy ball mill at 8000 rpm for 20 minutes. This was done in order to reduce the particles size and thoroughly mix the powders together. The resulting powder was pelletized under 2 tons of force and heated in a Carbolite tube furnace in the presence of Argon at 750 °C for 4 hours. So as to avoid any oxidation of carbon. The final powder obtained is a grey- black powder, VPO_4 .

2: Preparation of LiVPO_4F

VPO_4 is then further mixed with LiF in a stoichiometric ratio with 10 % of LiF because Li tends to sublime easily at high temperature. The mixture was heated to 750 °C for 15 min and then cooled rapidly. The reaction can be summarized by the equation below

4.3.4 Results

LVPF has a high insertion potential of 4.3 V vs. Li this is due to the presence of fluorine in the system. Apart from a higher insertion potential the high ionic character of fluorine leads to electronic localization near the fluorine atoms leading to a reduction of electrical conductivity of the sample. Hence a carbon assisted route is favored to create facile electron

migration pathways in the material. The method has been used successfully for the preparation of several electrochemically active species like γ - LiV_2O_5 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and LiFePO_4 [73]. The method serves a multifaceted role during the synthesis. Apart from reduction of the transition metal, it also acts as a conductive matrix and a nucleating site for the growth of LVPF. During the first step of the synthesis procedure VPO_4 is formed, VPO_4 has been known to have a monoclinic symmetry, consisting of layers of VO_6 octahedra linked together by PO_4 tetrahedras along the corners. The VPO_4 is then further reacted with lithium fluoride at 750°C for a short duration to form LVPF, due to shorter bond length between the M-F the VO_6 tetrahedra is distorted to a VO_4F_2 octahedra reducing the monoclinic symmetry to a triclinic one this is illustrated in Figure 4.28. It was noted that the reaction time, heating/cooling parameters are extremely important to obtain a pure sample. Longer heating times lead to the sublimation of LVPF into VF_3 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [80]. Till date only two reports have been published with considerable purity [77, 80]. The key is to rapidly cool the sample after formation of LVPF which occurs at ~ 10 -15 minutes. Hence for the purpose of this experiment we have adopted a similar technique and were able to develop sample with $\sim 5\%$ impurity. The impure phase is mainly $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Alternate routes for synthesis ranging from one step synthesis techniques [81] [48] and sol-gel techniques [82] have also been studied. One stop techniques show low purity levels [83, 84], whereas LVPF prepared using a sol-gel technique, display a higher degree of purity but at the same time are largely electrochemically inactive [85]. Alternate methods

Figure 4.28 Indicates the loss in symmetry of the crystal structure due to the addition of fluorine

that have been studied involve the use of r-GO as a reducing agent and conducting matrix to form graphene supported LVPF [86].

Laboratory based diffraction data was collected for LVPF and the results are summarized in figure 4.29. Rietveld refinement was carried out on the diffraction data ranging from $2\theta=10^\circ$ - 80° . The calculated lattice parameters are summarized in table 4.5. These values are in good agreement with previously reported literature[80].

From the Bragg lines in the diffraction pattern it can be noted that no significant portions of impurities are present.

Figure 4. 29 Rietveld refined X-ray diffraction pattern of LVP.

Table 4. 5 Rietveld refined parameters of LiVPO_4F

Space group		P-1 (triclinic)	
Cell volume		$174.47 \text{ \AA}^3$	
a (Å)	5.1717	α (°)	107.58

b (Å)	5.3110	$\beta(^{\circ})$	107.99
c (Å)	7.2622	$\gamma(^{\circ})$	98.35

Formation of LVPF occurs by reduction of the monoclinic symmetry of VPO_4 to a triclinic one, this is done by the modification of VO_6 octahedra to VO_4F_2 octahedras. As fluorine is known to have a higher electronegativity than O, the V-F bond (1.9797 Å) is smaller than the V-O bond (1.9848 Å). The stresses caused by such a deformed octahedra are adjusted by the molecule crystalizing as a tavorite structure. The final LVPF consists of VO_4F_2 octahedra corner shared along the c axis, the backbone of the system is supported by phosphate tetrahedras. The resulting 3 dimensional tunnel like structure can facilitate facile

Figure 4. 30(a-c) Micrographs representing the final state of the powder of synthesis, indicating a hierarchical agglomeration process during synthesis; (d) HR-TEM indicating the presence of amorphous carbon left over from the synthesis process the coating is non-uniform.

Li-ion movement even at high current rates, making LVPF a textbook candidate for hybrid capacitor applications.

Morphological studies are conducted to get an idea of the nature of particles formed during the synthesis process, HR-TEM micrographs are recorded to determine the nature and thickness of the carbon coating on the sample. The results of the above are summarized in figure 4.30. From figure 4.30(a-c) it can be noted that LVPF particles appear to be highly agglomerated with larger particles formed by hierarchical assembly of smaller particulates. Figure 4.30 (d) is an illustration of the HR-TEM micrograph, wherein the carbon layer can be easily discerned due to the lack of lattice fringes in the area. The carbon layer has been formed *in-situ* during the synthesis process. It has been shown to be a viable solution previously for poly-anionic framework materials especially phosphates [87, 25] and fluorophosphates [88]. Presence of amorphous carbon in the sample generates facile electron migration pathways through the material which facilitates good high power performance.

Although carbon coating seems like a viable option it simultaneously leads to a reduction of tap density, hence it is necessary to control the mass of the carbon deposited during the process.

Thermo-gravimetric analysis was carried on the LVPF sample in the presence of air. The experiment is designed by keeping in mind that the carbon in the sample begins to carbonize much before any thermal decomposition of LVPF. The results of the TGA experiment is illustrated in figure 4.31 (a). It can be noted that ~0.5 % of the mass is lost as the sample is heated up to 100 °C this is mainly due to any moisture that might have been absorbed on the surface of the materials. As the heating continues a sudden decrease in sample weight is observed at ~ 350 °C. At this temperature the carbon in the sample begins to react with the flowing air and forms CO₂ which is the cause of mass loss. The TGA curve plateaus again at ~ 470 °C indicating that all the carbon present in the sample has been carbonized. It can be calculated from the graph that ~ 8% by weight of the sample is carbon. The amount of carbon present in the sample is significantly greater than that shown in section 4.1 and 4.2. Hence the material does have a reduced tap density but it is an acceptable tradeoff to make the material electronically viable.

Carbon coating predominantly has two types of carbon in it.

1: Graphitic carbon: also known as ordered carbon. The carbon atoms have a sp^2 hybridization. These carbon atoms are stacked in a lamellar fashion like graphite and have free electron which allows for good electronic conductivity. Graphite is also the commercial anode material currently in use in lithium ion batteries. If the carbon coating has a large portion of graphitic carbon, the true capacity of the active material will be masked by graphite

2: Disordered carbon: This kind of carbon has a random arrangement does not interfere with the energy storage capabilities of the material and only stores minimal charge by surface adsorption techniques.

Raman spectroscopy is a convenient and non-destructive technique which can be used to

Figure 4.31 (a) TGA plot of LVPF when heated in air upto a temperature of 500 C, indicating 8 wt % of carbon in the sample; (b) Raman spectra of C-LVPF indicating clearly defined D and G peaks.

probe the type of carbon present in the sample. The Raman spectrum was collected for the LVPF sample and is illustrated in figure 4.31 (b). It can be observed that there are two main peaks of concern. The D peak at $\sim 1350\text{ cm}^{-1}$ and the G peak at $\sim 1589\text{ cm}^{-1}$. The reason for the appearance of these two Raman active modes is explained in detail in a previous section (section 4.1, 4.2). In this case it is only significant to measure the relative quantity of graphitic: disordered carbon. This can be done by measuring the individual intensities and

calculating I_d/I_g in this case $I_d/I_g = 0.99$ indicating that the carbon coating has an almost equal amount of disordered carbon and graphitic carbon.

4.3.5 Electrochemical Studies

LVPF is initially tested in a single electrode configuration in order to determine the optimum mass loading for the hybrid capacitor. The electrode is tested in an organic electrolyte 1M LiPF_6 dissolved in EC: DEC against metallic lithium. Figure 4.32 (a) represents the CV trace for the material when tested between 3-4.5 V vs. Li. A slight

Figure 4. 32: Cyclic voltammetric profile of LVPF when tested between 3-4.5 V vs. Li.; (b) Charge discharge profile of LVPF indicating a capacity of $\sim 120 \text{ mAh g}^{-1}$

anomaly is observed between 3.6 to 3.9 V vs. Li. These inflections can be attributed to the presence of small amounts of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. As the materials is charged further two split

peaks are observed at 4.28 and 4.33 V *vs.* Li. These correspond to the extraction of 1 Li atom from the structure. The splitting of the peaks has been studied by a large number of groups and the common consensus is the existence of a meta-stable state with the configuration of $\text{Li}_{0.67}\text{VPO}_4\text{F}$. Ateba *et al.* [89] was able to confirm the presence of this phase by using *in-operando* X-ray diffraction measurements. On discharge no peak splitting was observed. The reason for this behavior is unknown. The charge discharge profile of LVPF is sketched in figure 4.32 (b). A reversible capacity of $\sim 130 \text{ mAh g}^{-1}$ is obtained from the material. In the charge profile a slight inflection is observed at $\sim 3.5 \text{ V vs. Li}$ this region corresponds to the capacity contributed by $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Further on the first plateau is observed at $\sim 4.28 \text{ V vs. Li}$ and the second plateau indicating the complete removal of 1 mole of Li from the host structure is seen at $\sim 4.33 \text{ V vs. Li}$.

Preparations of Hybrid capacitor

Using the single electrode values a full Li-ion capacitor was constructed using commercial activated carbon as the counter electrode. Before the assembly process the mass on both the electrodes was balanced according to the equation specified in equation 4.1. Activated carbon is also tested as a cathode materials cycled between 1-3 V *vs.* Li. A discharge capacity of 53 mAh g^{-1} is noted for activated carbon.

The mass of the electrodes after balancing them according to their respective capacity is as follows

$$m_1 = 3 \text{ mg}$$

$$m_2 = 6.79 \text{ mg}$$

Where, m_1 is the mass of LVPF while m_2 is the mass of the activated carbon electrode. This mass balance allows for the equal distribution of charge on both the electrodes, ensuring maximum energy and appreciable power densities [8, 78]. The LVPF/AC was fabricated and tested in an organic electrolyte. The testing has been done using a current density of 100 mA g^{-1} . The charge discharge profile is illustrated in figure 4.33 (a). The current rate is calculated on the basis of total mass of the cathode and anode (9.63 mg). The mechanism of charge storage can be explained as follows. During the charge process the Li ions de-intercalate from LVPF into the electrolyte while the Li ions present in the

electrolyte are physically adsorbed on the surface of activated carbon. As the cell is discharged the Li ions are reinserted back into LVPF and desorbed from the surface of

Figure 4. 33 (a) Charge discharge profile of the LVPF/AC hybrid capacitor.;(b) Dependence of charge storage capacity on the current applied on the cell;(c) Capacity retention vs. Cycle number for the first 1000 cycles

activated carbon.

From the profile it can also be noted that the material undergoes a large IR drop. This is a characteristic observed in most hybrid capacitors. The reason for the above is not completely known and further research needs to be conducted in order to understand the phenomena. LVPF is cycled at varying current rates the results are shown in figure 4.33 (b). It can be noted that as the power is increased the nature of the profile gradually changes from that dominated by the battery electrode to that of one dominated by supercapacitor characteristics. The cell was cycled at 500 mA g^{-1} for 1000 cycles and it can be observed that there is $\sim 8\text{-}10$ percent decay in the charge storage capacity even after 1000 cycles. The high stability of the cell can be attributed to a number of factors

- The carbon coated LVPF is a robust host and is able to undergo reversible Li insertion and extraction from the host structure even at high power ratings.
- The hybrid capacitor configuration ensures that the materials does not undergo deep charge and discharge cycles thus minimizing the amount of strain acting on the host structure.

The dependence of the energy stored with respect to the power rating applied is sketched in figure 4.34. It can be observed that as expected the energy stored in the cell decreases at higher power densities. This is because the involvement of the battery electrode at high current rates is primarily limited to charge storage by surface interactions. The maximum energy density that was obtained using LVPF is $\sim 30 \text{ Wh kg}^{-1}$ at 100 W kg^{-1} at higher power densities of approximately 2000 W kg^{-1} the energy density was reduced to 2 Wh kg^{-1} .

The limitations in terms of energy density of the cell are predominantly because of the nature of activated carbon used during testing. These are not optimized for application in an organic electrolyte. In later chapters we will address this issue by the development of a highly porous, high surface area activated carbon from low cost bio-waste materials. The energy and power density of LVPF is compared with previous results in figure 1.2.

Summary

The purpose of this study was to add to the previous section which studied the dependence of hybrid capacitor performance with respect to electrode polarity. In this case we borrowed from those results (section 4.2) to test a battery material as a cathode in an HEC setup. LiVPO_4F was chosen because of its relatively high insertion potential of 4.3 V vs. Li allowing for the construction of a hybrid capacitor with a large energy storage capabilities. Also barker et al and Ateba et al successfully demonstrated that LiVPO_4F is an extremely stable insertion host.

From the results it can be observed that our assumptions in terms of electrode placement have been proved correct and using LVPF as the cathode generates a high energy density LIC.

Figure 4. 34 Ragone plot of LVPF/AC hybrid capacitor

4.3.6 Conclusion

The study of LVPF is conducted because of its open cage like structure which can be thought to be conducive to HEC applications. It is understood that the chemical

composition of LVPF leads to poor electronic conductivity. This was alleviated by using an *in-situ* carbon coating during the synthesis process. It can be noted that we have been able to achieve power densities at par with that required for PHEV vehicles with a target range of 60 miles and 120 miles respectively as illustrated in figure 1.2. But in terms of energy density further improvements are needed.

4.4 Understanding high capacity Lithium Rich layered oxides

4.4.1 Introduction

High energy cathode materials are necessary to increase the energy density of both Lithium ion batteries and HECs. Cathode materials today have been engineered to provide maximum energy and power density, a list of commercially used cathodes and their properties is listed in Table 4.6.

Table 4. 6 Intercalation compounds with their theoretical and practical capacity

Name	Theoretical Capacity (mAh g ⁻¹)	Practical Capacity (mAh g ⁻¹)
LiCoO₂	274	140
LiMn₂O₄	148	120
LiFePO₄	170	140
LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂	278	140
LiNi_{0.8}Co_{0.15}Al_{0.05}O₂	279	180

Despite their high theoretical capacity these materials are limited by their structure from delivering high practical capacities. Lithium rich layered oxides are a new class of materials that have the familiar layered structure which allows for the facile transport of the Li from the host structure. Instances have shown a capacity greater than 250 mAh g⁻¹ [90-92]. This high capacity has warranted significant research going into the following aspects of LLC's

1. Structure
2. Redox mechanism
3. Structural evolution during the cycling of the cell.

The structure of LLC's have been hypothesized to be either a nano-composite of two phases consisting of Li₂MO₃ (monoclinic) and LiMO₂ (rhombohedral) phases or a solid solution, studies including techniques such as Nuclear magnetic resonance[93], Transmission electron spectroscopy[94], X-ray absorption spectroscopy[95], Raman Spectroscopy [95], have failed to provide us with a definite answer. The main reason for

this is that the structure of LLCs is heavily dependent on the nature of the transition metal that is used[96].

LLCs also display a unique electrochemistry when compared to commercial cathodes. The common understanding of battery materials is that it compensates for the loss and gain of lithium by a redox reaction at the transition metal center. But in the case of LLCs it has been shown that the high capacity observed cannot be explained by a single redox center. Research has hypothesized that the extra charge is stored by an anionic redox reaction occurring or reductive coupling mechanism between the oxygen and the transition metal to allow for the oxygen to stay in the bulk reaction[97]. These reactions cannot be observed easily, X-ray photoelectron spectroscopy and soft X-ray absorption spectroscopy and Raman Inelastic scattering [95] have been used to establish that oxygen undergoes a transformation during the reaction and plays an integral part in charge storage but there is still no common consensus on the exact nature of this reaction. Apart from the lack of knowledge about the charge storage in LLC type compounds, voltage decay during cycling is also one of the common problems observed. This is related to local structural changes that occur irreversibly during cycling which leads to alterations in the coordination environment of the transition metal.

In this chapter we look at the synthesis techniques for LLCs aiming to modify the stacking pattern of the materials in order to be able to probe the structural properties in detail, we have restricted our studies to LLCs based on a single redox center and two redox centers, study of triple redox centers was avoided due to the many additional factors to be taken into consideration while the synthesis. We have focused on a ruthenium based family of LLCs with the general formula $\text{Li}_2\text{Ru}_{1-x}\text{M}_x\text{O}_3$ [90-92]. Initial studies were based on research conducted by Sathiya *et al.* studying the dependence of an electrochemically active element in the desired potential range (2-4.6 V vs. Li) for example substituting M with either titanium or tin. These helped to identify the nature of reaction occurring on the ruthenium redox center, but it was observed that these materials displayed an increased voltage decay during cycling and were shown to be stable not beyond 100 cycles. The reasons hypothesized for this was the gradual dislocation of the transition metal into the Li layer or the irreversible loss of oxygen from bulk which leads to side reactions with the

electrolyte. But no concrete evidence exists to confirm these hypothesis, except extremely

Figure 4. 35 Crystal structure of lithium rich layered materials. (a) Along the c axis consists of 6 TM cations surrounding a Li atom in a honeycomb like structure.;(b) Seen along b axis indicates alternating layers of Transition metal and Li atom layers.

Figure 4. 36 X-ray diffraction pattern of $\text{Li}_{2+x}\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$

localized results which cannot be considered as a representative of the bulk reaction.

The proposed structure of Lithium rich layered oxides is illustrated in figure 4.35 (a, b). It consists of alternating layers of Transition metal layers and Li layers. In each TM layer a single Li atom is coordinated with 6 TM octahedra surrounding it in a honeycomb like structure. Initially the unit cell of the crystal crystalizes in a rhombohedral phase, but as the layers stack on top of each other they tend to form a super structure [98]. A typical X-ray diffraction pattern of a lithium rich layered oxide is illustrated in figure 4.36, most of the peaks can be indexed to a rhombohedral phase (R-3m) but some of the peaks are observed to show an anomalous half width when compared to the other peaks these are attributed to the superstructure. In order to estimate the complete structure, it is hence necessary to consider the structure as a monoclinic lattice as detailed by Kalathil *et al.*[99]

The nature and symmetry of the superstructure is also highly dependent on the properties of the transition metal used. A summary of the dependence of the final structure on the nature of the transition metal used is tabulated in table 4.7

Table 4. 7 List of dopants and the possible different structures.

Elements	Space Group	Reference
Ru,Ti,Zr	C 2/c	[100-102]
Ir,Mn,Sn,Rh	C 2/m	[94, 103-105]
Mo	R-3m	[106]

The high capacity and the relatively high insertion potential of LLCs entail that their properties be studied in greater detail. An understanding of the charge storage mechanism of the material is the first step towards applying LLCs in Li-ion battery configurations and subsequently in hybrid capacitors where they could boost the energy storage capabilities of the capacitor greatly.

4.4.2 Experimental Methodology

Synthesis

All the samples prepared during the process of this experiment are labelled as listed in Table 4.8.

Table 4. 8 List of Lithium rich cathodes (LLC) studied in this section.

Serial number	Chemical composition	Starting Materials	Reference
LLC 1	Li_2RuO_3	$\text{Li}_2\text{CO}_3, \text{RuO}_2$	[100, 103]
LLC 2	$\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$	$\text{Li}_2\text{CO}_3, \text{RuO}_2, \text{TiO}_2$	[99]
LLC 3	$\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$	$\text{Li}_2\text{CO}_3, \text{RuO}_2, \text{Sn}_2\text{O}_3$	[92]
LLC 4	$\text{Li}_2\text{Ru}_{0.75}\text{Mn}_{0.25}\text{O}_3$	$\text{Li}_2\text{CO}_3, \text{RuO}_2$	[91]
LLC 5	$\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$	$\text{Li}_2\text{CO}_3, \text{RuO}_2$	

The samples were each made by mixing the raw materials stoichiometrically according to the following the chemical reaction

The reaction mixture is mixed together and ground using a mortar and pestle till a point where the mixture is uniform. The powder is pressed using a 20 mm die using a pressure of 2 tons. The green pellet is heated at 1000 °C for 24 hours at a heating & cooling rate of 2 °C/ min. the pellet is ground again and pelletized again and heated at 900 °C for 24 hours at 2 °C /min. A slow heating and cooling rate is necessary for the growth of the grain boundaries in LLCs resulting in a highly crystalline powder. This is advantageous to us while using laboratory X-ray diffraction experiments to determine structural change.

Characterization

The entire set of samples was characterized using the following techniques and instruments

- 1: X-ray diffraction – Bruker Advanced powder diffractometer.
- 2: Scanning electron microscopy- JEOL JSM 7600F
- 3: Transmission Electron Microscope – JEOL 2100
- 4: *In-situ* X-ray diffraction – Rigaku Smart X-ray Lab and Basitech Electrochemical cyclers.

5: *In- operando* X-ray Absorption Spectroscopy: Beam line 4-1 and Beam line 4-3 Stanford Synchrotron Radiation Light source at Stanford Linear accelerator.

6: Soft X-ray Absorption Spectroscopy:

7: Cyclic Voltammetry: using a Solartron 1256B

8: Galvanostatic charge discharge measurements: Using a NEWARE battery testing setup.

The electrodes for the electrochemical testing and the *in-operando* tests were constructed using the technique mentioned in section 3.4.1 (slurry coating).

A modified coin cell was design with 3mm holes covered with Kapton tape. The entire casing was then sealed in Argon to avoid any exposure to air. Aluminum tabs were used as the contact. The setup is shown in figure 4.37.

Figure 4. 37 (a) Coin cell with a 3 mm hole covered with Kapton tape to prevent leakage; (b) Coin cell sealed in a plastic pouch cell

The measurements were performed at SSRL beamline 4-1 (figure 4.39), which is equipped with a double crystal Si (220) monochromator. Before the scanning process the 2nd and third harmonics were rejected by detuning the crystals reducing the flux of the incident beam by 25% in case ruthenium. No detuning was needed in the case of Iron. Energy

calibration was monitored using metallic iron and pure ruthenium powder. The XAS

Figure 4. 38 Photograph depicting BL 4-1 used at SSRL for the conduction of X-ray absorption spectroscopy measurements.

spectra was recorded was recorded in transmission mode in 30 minute intervals. Spectra was background subtracted and normalized using ATHENA[107]. The data was then converted to the k-space in the interval of 2.5 to 10.5 ($\text{\AA}$). The fitting for the first shell was carried out using the ARTEMES software[107]. The fitting was carried by using crystallographic information file generated after the Rietveld refinement of the pristine powder pattern. The fitting was carried out on EXAFS spectra pertaining certain points in the cycling profile. The σ^2 values were calculated for each of the patterns separately and then an average σ^2 was fixed and the fitting was carried out again to avoid any co-relation among the fitting parameters.

4.4.3 Results

In this study, a range of Ruthenium based LLCs are constructed and the subsequent effect of the nature of the transition metal is studied in detail. During the initial synthesis

Figure 4.39 X-ray diffraction patterns measured for Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$, $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$, $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$, $\text{Li}_2\text{Ru}_{0.75}\text{Si}_{0.25}\text{O}_3$; (b) Is a magnified image of the peak corresponding to the 002 plane.

procedure, it was observed that single heating cycle led to an incomplete development of the superstructure peaks, following this observation it was decided to follow two long term duration heating cycles which lead to a highly crystalline sample. The ratio between Ru and the substitute TM metal was fixed at 3:1 by studying the electrochemical performance reported in previous literature, therefore all of the following results are recorded for $\text{Li}_2\text{Ru}_{0.75}\text{M}_{0.25}\text{O}_3$. The structure of these LLCs consist of alternate planes of transition metal and Li atoms as shown in Figure 4.35 and these layers follow an O3 stacking pattern implying that the oxygen layer repeats itself after every 3 layers. The transition metal layer consists of TM metal atoms arranged in a honeycomb structure around the lithium atom. The size of the transition metal controls the layered structure of the material. The X-ray diffraction pattern recorded for each of the substitutions is shown in Figure 4.39. Figure 4.39(a) is a comparison of the diffraction pattern recorded for the different substitutions. It can be deduced that Ti, Fe and Sn have been able to successfully substitute Ru in the structure to form a layered structure. Silicon on the other hand is unable to substitute Ru in the layered structure instead the silicon dioxide remains unreacted and precipitates out, leading to the formation of a bi-phasic sample containing Li_2RuO_3 and SiO_2 . Figure 4.39 (b) is magnified image of the (002) peak. It can be observed that the 002 peaks shift to a higher 2θ indicating a contraction in the c lattice parameter. The ionic radii for the transition metals used are tabulated in table 4.9. As is expected Ti having the smallest ionic radii leads to the highest shift corresponding to lesser interlayer spacing when compared to the other samples.

Table 4. 9 List of ionic radii of different transition metals

Ruthenium	0.62
Titanium	0.605
Tin	0.69
Iron	0.645

Table 4. 10 Rietveld refined lattice parameters of Sn, Ti and Fe substituted LLCs

<i>Phase</i>	<i>Li₂RuO₃</i>	<i>Li₂Ru_{0.75}Sn_{0.25}O₃</i>	<i>Li₂Ru_{0.75}Ti_{0.25}O₃</i>	<i>Li₂Ru_{0.75}Fe_{0.25}O₃</i>
<i>Space</i>	C 2/c	C 2/c	C 2/c	C 2/ c
<i>Group</i>				
<i>a</i> (Å)	4.91245(3)	5.03012(3)	5.03032(6)	5.04400(5)
<i>b</i> (Å)	8.76073(9)	8.74478(1)	8.72680(9)	8.75692(6)
<i>c</i> (Å)	9.85496(7)	9.86265(7)	9.83193(2)	9.84965(4)
<i>β</i> (°)	100.0800	99.5476	99.7969	99.8095
<i>α</i> (°)	90	90	90	90
<i>γ</i> (°)	90	90	90	90
<i>R-Bragg</i>	4.89	4.628	4.42	5.20

The Rietveld refined parameters of the samples are tabulated in Table 4.10. The parameters obtained have been compared to literature and are in good agreement with parameters reported for LLCs [92, 99, 100]. The stability of Lithium rich layered oxides is highly dependent on the stacking of the individual layers. A well-formed layered structure is facilitative towards improved long term stability and facile Li movement in/out of the structure[99]. The stacking behavior can be qualitatively analyzed by studying the individual diffraction patterns in the range of $2\theta = 20-35^\circ$. Figure 4.40 represents the comparison of the superstructure reflection for the pure sample with respect to the substituted samples. The peaks corresponding to 020 (peak 1) and 022 (peak 4) show no shift but the peaks corresponding to 111 (peak 2) and $0\bar{1}\bar{1}$ (peak 3) show a shift to a lower angle indicating an expansion of the d spacing along these orthogonal planes. The iron substituted sample shows the greatest shift among the samples. Along with the shift it can be also noted that the full width half maxima (FWHM) of the superstructure peaks is in direct correlation with the rigidity of the superstructure. The values of FWHM are elucidated for Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ and $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$, in figure 4.41(a).

Figure 4. 40 (a) Represents a magnified image of the reflections corresponding to the superstructure peaks in LLC's; (b) Comparison of the FWHM of peaks 1,2and 3.

It can be noted that the highest values are observed for the Ti substituted sample indicating that the Ti substituted sample is the most highly ordered with a well-defined stacking pattern on the other hand iron based samples display a highly ordered structure along 020 but the superstructure has a much lower rigidity when measured along the other planes. The effect of these properties on the electrochemical performance of the material is still questionable, with some reports indicating that highly disordered structure improves electrochemical performance [108, 109] and some reports suggest that highly ordered

materials provide the lowest energy barrier for Li insertion [99]. The dependence of electrochemical properties on the structural rigidity will be tested in a later section.

Figure 4.41 is an illustration of the electron micrographs collected for the samples. These were collected in order to observe any changes in morphology that might have occurred during the synthesis process. It was observed that all the samples exhibited a similar

Figure 4.41 SEM micrograph of (a) Li_2RuO_3 , (b) $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$, (c) $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$, (d) $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$.

hierarchically aggregated morphology. The size of the aggregates increases with increase in sintering time which is expected [110]. Larger particles (1-2 μm) were synthesized with future experiments such as *in-situ* X-ray diffraction in mind.

Cyclic voltammetry experiments were conducted on LLC coin cells to establish any difference in the redox behavior. These are summarized in figure 4.42. Figure 4.42(a-c) correspond to the study of a pristine Ru sample, compared to samples partially substituted

with titanium and tin respectively. It can be observed that both tin and titanium do not have any active redox couple in the testing region. As the samples are charged at 3.75 V vs. Li ruthenium undergoes an oxidation reaction from $\text{Ru}^{(\text{IV})}$ to $\text{Ru}^{(\text{V})}$. As the charge continues at 4.3 V vs. Li a sharp peak is observed. Research shows that this peak corresponds to a change occurring to the native oxygen in the structure [92, 99, 100]. There are two types of reactions occurring at this stage

1. Oxygen from the bulk and the surface is released, leading to an irreversible capacity which is lost in subsequent cycles [111].
2. Or Recently as Sathiya *et al.* [90, 92] observed the oxygen undergoes a reversible anionic redox reaction. This reaction is responsible for the extra capacity noted for Lithium rich layered cathodes.

But in this case it is observed that the peak drops intensity rapidly after the first charge indicating that the reaction type is predominantly of an irreversible nature. Also it can be

Figure 4. 42 Cyclic Voltammetry profiles for LLC's; (a) Li_2RuO_3 ; (b) $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$; (c) $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$; (d) $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$; all the tests were conducted at 0.1 mV s^{-1} .

observed that the peak corresponding to the ruthenium oxidation peak broadens. The broadening of the redox peak might be due to loss in crystallinity of the sample after the initial cycling as suggested by Sathiya *et al.*[90] . During the discharge process there are two broad peaks consistently observed for the first three cycles both of the peaks correspond to the reduction of Ruthenium to a (IV) state. Figure 4.42 d corresponds to the profile of the iron substituted sample, it can be observed that the charge scan distinctly displays three peaks, the first at ~ 3.75 V corresponds to the oxidation of ruthenium, the second peak at ~ 4.0 V vs. Li represents the oxidation of Iron (3+/4+ couple) [112, 113]. The third peak can be argued to contain the following information.

1. It is formed due irreversible oxygen evolution of Oxygen from the surface.
2. It occurs due to a mixture of a surface oxygen evolution and bulk anionic redox reaction.

During the discharge phase two peaks are observed at 3.75 V and 3.4 V vs. Li. The peaks correspond to the reduction of Ruthenium and Iron to their respective pristine state. Comparing Figure 4.43(d) with the other samples it can be observed that the redox peaks are highly reversible. Indicating that the iron substituted sample is much more robust and is able to reversibly cycle Li in and out of the host structure without large changes in crystal symmetry. Such a robust host structure makes LRFO a suitable candidate for HEC applications, although further studies are needed in order to understand the charge mechanism and improvements in electronic conductivity.

Figure 4.43 is the galvanostatic charge discharge profile of the second cycle of LLCs. It can be observed that the total capacity of LLCs are ~ 200 mAh g⁻¹ and above. The highest capacity is recorded for Li₂Ru_{0.75}Fe_{0.25}O₃ (250 mAh g⁻¹). The calculated theoretical capacities of LLC's have been tabulated in table 4.11

Figure 4.43 Galvanostatic charge/discharge profiles of Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$, $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$, $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$

Table 4. 11 Theoretical capacity of LLC's assuming the transfer of one electron transfer. The unit for the capacity reported is mAh g^{-1}

Compound	Theoretical capacity from the Ruthenium Redox couple	Theoretical capacity from the M ³⁺ Redox couple	Total Theoretical Capacity	Total observed Capacity
Li_2RuO_3	162.01	-	162.01	206.66
$\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$	132.30	-	132.30	231.33
$\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$	118.30	-	118.30	192.66
$\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$	130.56	43.52	174.08	243.88

The tabulated values indicate the fact that the capacity observed is not completely attributed to the redox reaction of the transition metal. The extra capacity can be attributed to the anionic redox reaction occurring in the bulk oxygen which allows for the removal of more than one Li atom from the host structure hence allowing for the extra capacity. The mechanism or feasibility of this reaction is still largely unknown, several scientific publications have focused on explaining it but with little success.[90, 92, 99, 114-

Figure 4. 44 In-operando X-ray diffraction patterns for the first 5 cycles. Collected between 10-60°.

117]. Towards the later part of the chapter Near edge X-ray spectroscopy is carried out on the sample in order to develop an idea about the nature of the reaction undergone at the oxygen centers.

Although lithium rich layered cathode materials exhibit a high capacity, they experience other issues such as gradual potential decay and oxygen evolution at higher potentials. In order to better understand the changes in the phase, *in-operando* X-ray diffraction measurements were carried out in a specially designed battery setup which could be used in a laboratory X-ray diffractometer while maximizing the signal to noise ratio [118]. Due

to its high capacity and higher working potential. The iron substituted LLC was a used a representative for all *in-operando* measurements.

Figure 4.44 represents the first five electrochemical cycles recorded for $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$. Due to the overlapping of the superstructure reflections with the reflections caused by teflonized acetylene black (binder) it was not possible to study the evolution of the superstructure as the cell was cycling. The cell was cycled over five cycles and diffraction patterns were collected every 11 minutes during the cycling process. It can be observed that during the charge process a change in phase is observed. The nature of the phase formed is unknown at this stage but as can be observed from the subsequent cycles the new phase slowly dissipates during the discharge process resulting in a complete reversal to the pristine phase.

Figure 4.45 illustrates the variation in the diffraction pattern during one electrochemical cycle. The cycle chosen is the second cycle as like other Lithium rich layered cathodes

Figure 4. 45 In-operando X-ray diffraction pattern of the first charge discharge cycle. Indicating the appearance of a new phase and its reversibility.

LRFO displays an unusual charge profile in the first cycle. The figure helps to confirm the reversibility of the lithium insertion and extraction behavior. From a brief literature survey it was noted that similar phase transformations have been observed from de-lithiated or de-

sodiated layered compounds based on Iron [119]. The pristine sample belongs to a monoclinic space group which arises because of the unique stacking patterns of Lithium rich layered oxides. As the sample is charged to ~ 4.25 V vs. Li it can be observed that a separated de-lithiated phase forms which can be indexed to a rhombohedral phase [119], this structural change is reversible although minor losses in intensity are observed during cycling. Figure 4.47 correlates the first charge with its corresponding diffraction pattern. The pristine electrode has a O3 type layered structure but as the material is charged up to a potential of 3.25 V vs. Li low intensity shoulder peaks are observed on the left of the (200), (202) and (204) planes simultaneously gradual reduction in area of the (004) and (131) planes are also observed (the indexed diffraction pattern can be referred from figure 4.37). Between 3.25 V and 3.6 V vs. Li the shoulder peaks show an increase in intensity while the (004) and (131) planes combine to form a single reflection. As the cell is completely charged up to 4.6 V vs. Li the new phase completely replaces the pristine material. Takeda *et al.* [120] have identified the formation of a similar phase during the charge of NaFeO_2 . The authors suggested a Jahn-Teller effect from high spin Fe^{4+} or structural compensation due to the loss of Li as the reason for distortion of the molecule.

Figure 4. 46 In-operando X-ray diffraction pattern of the first charge cycle linked with the electrochemical charge profile of $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$

Rietveld refinement based studies are necessary in order to understand structural evolution of the material in detail. But it is not practical to perform such detailed analysis on data recorded in a laboratory diffraction setup. High quality diffraction data needs to be recorded using synchrotron based radiation. Those results are reserved for future experiments.

In-operando X-ray absorption studies were conducted on modified coin cells and tested online in BL 4-1 at Stanford Synchrotron Radiation Lightsource. Figure 4.47 illustrates the charge discharge profile of $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$ and absorption spectra recorded for the material (Fe K edge) when cycled between 2-4.6 V vs. Li the grey points on the charge discharge profile indicate the points at which the absorption spectra were measured. As the cell is charged the first noticeable feature is the distortion of the Pre-edge. The pre-edge is one of the lesser studied portions of the X-ray absorption spectra but has been shown to have a wealth of information about the ligand field, spin state and Centro-symmetry of the probed atom. Metal K pre-edge absorptions arise due to a quadrupole allowed, dipole forbidden $1s \rightarrow 3d$ excitation ($\Delta l = \pm 2$ weak contribution) or due to electric dipole allowed transition ($\Delta l = \pm 1$ Intense contributions).

The XANES spectra indicates an increase of intensity of the pre edge as the cell is charged, and the shape is partially retained at the end of discharge. The low intensity in the case of the pristine material is indicative of presence of iron in a 3+ oxidation state in 6 coordinated sites. The increase in intensity on subsequent charging is indicative of change in the coordination environment of iron from 6 coordinated site, this is expected as the iron atom undergoes an oxidation reaction from $\text{Fe(III)} \rightarrow \text{Fe(IV)}$. The iron octahedral are hence changed from a perfect octahedral to a distorted structure at the end of charge [121-124].

Figure 4.47 (a) Electrochemical profile for the first charge discharge cycle; (b-c) In-operando X-ray absorption spectra of the Fe-K edge for $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$; (d) magnified section illustrating the pre edge.

Due to the relatively small shift in the XANES spectra during cycling the raw data was modified by differentiating it in order to make it easier to interpret any shift in the edge.

Figure 4.48 (a, b) represent the derivative of the mean absorption edge. The absorption edge for pristine iron lies at ~ 7123 eV. As the cell is charged both ruthenium and iron undergo oxidation reactions which should lead to a shift of the absorption edge to a higher

energy. But in this case the changes observed in the spectra were not as expected on

Figure 4. 48 (a) Derivative of normalized absorption vs Energy for the first charge cycle; (b) Derivative of normalised absorption vs. Energy for the first discharge.

charging the cell up to 3.9 V vs. Li there is a slight shift of the absorption edge to a higher energy but on further charging potentials >3.9 V vs. Li it was observed that the Iron K edge shifted towards lower intensity. This effect has never been observed for a battery material

and is counterintuitive to standard assumption. For the purpose of this experiment we hypothesize the following scenarios occurring at the TM center.

- Iron undergoes oxidation to +4 state at ~ 4 V[119].
- Oxygen at the surface begins to oxidize to form peroxo-superoxo species[115].
- Iron and oxygen undergo a reductive coupling reaction to stabilize these states.

Hence we are not able to clearly see oxidation from the absorption spectra[99].

This theory is supported factually by the fact that EXAFS fitting of the same data leads to conclude that the Fe-O bond length changes considerably during cycling which is possible only in the case of change of the formal charge on the iron atom. The results of the fitting are summarized in Table 4.12.

Table 4. 12 EXAFS fitting for Fe-K edge conducted during charge and discharge.

Potential (V vs. Li)	Fe-O bond length (Å)	σ^2
Charging		
3	2.00931	0.00359
3.5	2.00651	
3.75	1.99701	
4	1.96195	
4.1	1.90337	
4.25	1.90212	
4.4	1.90212	
4.6	1.90144	
Discharge		
4.6	1.899954	0.00359
3.7	1.89263	
3.5	1.92021	
3.3	1.92443	
2.25	1.94892	
2	1.97385	

The fitting is carried out using the ARTEMIS software [3] using starting parameters generated after the Rietveld refinement of the powder pattern in figure 4.49. The σ^2 value of 0.00359 is an indicative of a good fit. The distance of Fe from its nearest oxygen can be seen to vary from 2.00651 Å to 1.90144 Å during the charge cycle and during discharge it can be noted that the Fe-O does not completely return to its original value. This lack of complete reversibility is probable cause for the voltage fading observed in the case of Lithium rich layered oxides.

Studies regarding the Ruthenium edge are much more straightforward because of the relatively stable nature of Ru in +4 and +5 states. The XANES spectra of the Ru Kedge is illustrated in figure 4.50. Figure 4.50b shows the spectra corresponding to electrode open circuit potential, the fully charged sample and fully discharged sample. It can be noted that

Figure 4. 49 Rietveld Refinement of the X-ray diffraction pattern of $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$

as the sample is charged the spectra gradually shifts towards a higher energy by approximately ~2 eV this shift corresponds to the oxidation process of Ruthenium, subsequently on discharge to 2 V the spectra returns to a lower energy indicating the reduction of Ruthenium back to its +4 oxidation state. Further detailed fitting needs to be

carried out on the EXAFS pattern to understand changes occurring near the local structure of Ruthenium octahedras.

Figure 4.50 X-ray absorption spectra representing the changes in the Ru-K edge during one cycle; (b) Magnified image of the spectra at the pristine, fully charged and fully discharged state.

Future Work

An important part of the study on Lithium rich layered cathodes is the study of the oxygen edge using X-ray spectroscopic techniques, in order to pin-point the reaction specifics happening at the oxygen centers. The oxygen edge lies at an energy of 533 eV. It is not possible to use the earlier experimental setup to probe oxygen as the Kapton tape covering will interfere with data collection. Hence the experiment was modified so as to conduct measurements *in-situ*, wherein several electrodes were charged up to a pre-determined potential and transferred to the beamline without exposure to air for further testing. The oxygen NEXAFS analysis was done at BL 8-2 at SLAC, Stanford University. The preliminary results are plotted in figure 4.51.

As shown in figure 4.51, the spectra can be broadly divided into two parts. The low energy portion corresponds to the bonding between O (2p) and Ru (t_{2g}) and the broad high energy

Figure 4. 51 NEXAFS spectra of O-K edge during the first charge process.

spectra corresponds to the environment around oxygen. Detailed analysis of the spectra has not been carried out, but cursory examination indicates the formation of peroxide like species when the cell is fully charged.

Further studies are needed to confirm the nature of these bonds and the variation of the oxygen environment as the cell is charged.

4.4.4 Conclusion

The study on Lithium rich layered oxides is conducted, a systematic study of the various dopants used and their effect on the electrochemical properties of the LLC is considered. It was determined that substituting Ruthenium partially with Iron leads to the best electrochemical properties. We were able to improve on multiple grounds including the operating potential, the capacity and the stability of the cell. In order gain a better

perspective of the structural changes occurring in LLC's during cycling $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$ was used a representative molecule and *in-operando* X-ray diffraction and *in-operando* X-ray absorption studies are carried out on the material. The results obtained highlight important structural changes happening in the material as it is cycled. Also the results have led to invaluable insights into issues such as voltage fading. With further research into the field of Lithium Rich layered cathodes, the energy storage community will be able to apply the exceptionally high capacity of this cathodes for commercial application including technologies such as Lithium ion batteries and Li based Hybrid capacitors.

4.6 References

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Chapter 5

Development of a hierarchically porous activated carbon from waste human hair for High energy Hybrid capacitor applications

Hybrid electrochemical devices despite their varied advantages suffer from a few inherent faults of which one of the most important is that the net energy density of the device is limited by the electrode with the lower energy storage capability. Hence any amount of improvement in the energy density of the battery material will not lead to a drastic increase in the net amount of energy density. It is hence necessary to improve the energy storage capabilities of the supercapacitor electrode. Activated carbon is the material of choice because it is cheap and environmentally benign.

In this study we focus on understanding the effect of the activating agent on the activation of carbon obtained from human hair. Human hair is chosen for a variety of reasons the first being that being a common waste product it can be readily obtained from most salons and secondly the chemical composition of hair is indicative of a probably highly conducting carbon matrix. The formed carbon was analyzed using a range of techniques including X-ray diffraction, Electron microscopy, Raman spectroscopy, Adsorption/desorption studies for BET analysis. It was determined that the carbon had an impressive surface area of $1116 \text{ m}^2 \text{ g}^{-1}$ when activated with NaOH with large pore sizes ranging between 50-100 nm. The activated carbon was tested electrochemically and it was found to deliver a capacity of $\sim 60 \text{ mAh g}^{-1}$ when used between 3- 4.6 V vs. Li. As a proof of the improvement the performance of this activated carbon was compared to earlier literature on full cell hybrid capacitors and a large improvement in the net energy density is observed.³

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5.1 Introduction

Activated carbon is an integral part of hybrid capacitors. They are the most environmentally benign supercapacitor material in use today. Table 2.1 compares different kind of carbon materials for EDLC applications. Although activated carbon displays a medium gravimetric capacity and a relatively low electronic conductivity, its scalability and low price have no rival. Hence it is important to be able to improve the energy storage capacity of activated carbon this can be done keeping the following parameters in mind:

- Nature of pores: responsible for maintaining high gravimetric energy density. Pores ranging from 5-50 nm and <1 nm have been shown to increase the net capacity in a variety of instances.
- Penetration of electrolyte: depending on the nature of electrolyte used the activated carbon pores need to be tailored to achieve maximum intake. An interesting view on good interconnectivity is shown by [1], where activated carbon is designed so that outer macropores allow for maximum electrolyte penetration while the inner meso-pores act as electrolyte storage cells and catalytic channeling pathways, and the micropores contribute to the formation of a double layer.
- Functionalization of the surface: Most bio-waste materials are made of proteins during carbonization the long chain amino acids break up to form a functionalized surface, depending on the nature of the protein this functionalization can considerably increase the electronic conductivity of the sample.

The above factors can be controlled very effectively by controlling the starting material, and the activation conditions employed.

This chapter aims at understanding the effect of activation on the development of activated carbon. Most commercial activated carbon is formed by a physical activation process using CO₂ or steam. Both of these methods work by selectively burning off carbon from the surface of the material leading to formation of pores. The parameters which determine the nature of pores formed are temperature and time of activation respectively. A higher temperature and time lead to a higher mean diameter of the poles. Although physical

activation is prevalent method for activation on an industrial scale it can be noted that the during activation a large amount of carbon is lost as burn off leading to a very low yield[2]. Chemical activation includes the use of chemical reagents to modify the carbon structure, this technique offers a large variation in pore size while minimizing the carbon lost to burn off [3]. This technique is not preferred on an industrial scale because of the large amount of post processing required to wash of foreign chemical impurities from the activated carbon sample. But it is ideal for the development of high energy density activated carbon for energy storage application.

5.2 Motivation

HECs are aimed as products which can be the next generation of supercapacitors. Usage of the faradaic component allows to drastically increase the energy that can be stored at the same time leading to lighter storage installations. In order for the HEC to be of commercial value both the battery and the supercapacitor component need to be optimized. Battery electrodes have been studied in chapter 4 and optimized so as to provide a robust intercalation host for Li insertion and extraction. Unfortunately, the energy density of the HEC device is controlled by the charge storage capacity of the supercapacitor electrode. The most economically feasible supercapacitor electrode material is activated carbon. Activated carbon commercially can be obtained from a variety of petroleum products but to improve cost efficiency this chapter looks to analyze activated carbon formation from cheap bio-waste materials which show impressive electrochemical activity due to their natural morphology.

In this work we concentrate on the chemical activation of human hair. The main constituent of hair is Keratin which consists of long chains of amino acids[4]. On decomposition at high temperatures the proteins break down to the base carbon backbone. Depending on the nature of the protein it generates a surface functionalized with different elements. This functionalization leads to changes on the surface of activated carbon which influences interaction with electrolytes. The method of activation used is an amalgamation of physical and chemical activation. The agents used for the chemical activation are NaOH [5, 6], KOH [7-12] and ZnCl_2 [3, 13, 14] respectively. The chemicals have been heavily reported as

effective activating agents used in the manufacturing of activated carbon. All the above chemicals have separate activation mechanisms and lead to a different pore structure after activation, their effects have been studied through this chapter.

5.3 Experimental procedure

5.3.1 Synthesis

The activated carbon used for this experiment was obtained from human hair. The hair was sourced from a local salon at zero cost. No specific condition was placed on the procurement of the raw material, i.e. hair from all races were mixed together. The batches were initially washed with water to remove any dust from them. Then the hair strands were cut into smaller strands of length ranging from 5-10 mm. The cut hair was soaked in iso-propanol overnight to remove any organic impurities present in the hair. After which the hair was dried for 12 hours at 100 °C to get rid of any solvent left behind. The dried hair was then pre-carbonized in the presence of argon. The use of inert gas in a positive pressure environment helps us to minimize the conversion of carbon to carbon dioxide by interaction with air. The heating was carried out at 300 °C for 90 minutes. The pre-carbonized carbon was then crushed into a fine powder and divided into three batches, each batch was treated with NaOH, KOH and ZnCl₂ respectively. The mass ratio used for this mixture has been optimized earlier to 1:2 (carbon: activating agent). The mixture was dried and then reheated in argon at Temperatures ranging from 700-900 °C for 3 hours. The sample using ZnCl₂ was also alternatively carbonized in a hydrothermal bomb at 120 °C for 3 hours. The activated carbon obtained in each of the cases is washed thoroughly with warm water repeatedly to get rid of any impurities left over from the activation process.

5.3.2 Electrode Preparation

The electrodes were made by mixing with conductive additive (Super P carbon TIMCAL) and binder (Teflonized Acetylene black) in a ratio of 8:1:1. The mixture was formed into a pellet and pressed onto a 200 mm² stainless steel mesh (0.25 mm thickness, Goodfellow, UK), this acts as the current collector. All electrodes were dried in a Buchi oven at 80 °C

overnight in vacuum. The electrodes were assembled into half cells for initial electrochemical analysis in an inert argon environment. Li metal serves as both the counter and the reference electrode. Glass fiber (Whatman paper) is used as a separator between the Li electrode and the working electrode. The entire system is flooded with a 1M LiPF_6 salt solution dissolved in a 1:1 mixture of ethylene carbonate and Di-ethyl carbonate procured from Tomiyama pure chemicals, Japan.

5.3.3 Characterization

Surface morphology micrographs were collected using a JEOL 7600F (Field emission scanning electron microscope). The development of the inner pore structure was scanned using a tunneling electron microscope (JEOL JSM 2100 F). Raman spectra of the material was collected using a Witec Alpha 300 SR (480 nm). Surface area measurements were conducted using a Quantachrome NOVA 3200 BET setup. Analysis of the surface to determine the nature of functional groups on the surface was conducted using X-ray photo-electron spectroscopy. Charge discharge measurements were carried out on a NEWARE battery testing system. Cyclic voltammetry and impedance measurements were conducted on a Solartron 1470E. All electrochemical measurements were conducted at ambient temperature and pressure.

5.4 Results & Discussions

Human hair is high grade composite material consisting of two parts namely the cortex and cuticle. The outer cortex is composed of lamellar sheets held together by weak interactive forces. During the pre-carbonization process the layers achieve a high enough energy to separate from each other and form flaky entities. The introduction of this large surface area for activation is advantageous to develop a well-developed pore structure and a large surface area at the same time. Chemically human hair is composed of keratin, which is a protein molecule containing long chain amino acids. During the pre-carbonization as the sample is heated to 300 °C the proteins present in each hair fiber begin to disintegrate[15]. Leading to the production of ammonia and other sulphur and nitrogen based compounds.

The carbon present in the sample does not degrade at these low temperatures. The green sample obtained at this stage is not electrochemically active but has a high carbon content, Raman spectroscopy indicated that the sample had already started to form a separate ordered and disordered carbon phase, Electron micrographs indicate that the surface of the AC is still flaky with no visible pores present. In order to make the material electrochemically active and to promote pore formation with the increase in surface area the sample was subjected to a combination of physical and chemical activation. The process of physical activation is mainly centered on the burning off of carbon from the surface of the sample at high temperatures. When applied with chemical activation the size and distribution of the pores can be controlled. Depending on the nature of the activating agent used the pore formation can occur through the following mechanism.

- Reaction with alkali metals: Intercalation of reagent into the bulk causing expansion, and strain in the carbon matrix. But further heating is needed to remove the metal. The vigor of this process determines the nature of pores.
- Reaction with acidic reagents: the volume of pores is similar to the volume of acidic reagents use. Reaction occurs at low temperatures, leading to the formation of micropores in the sample. Higher reaction times allow for the increase on pore size to mesopores.

Table 2.1 shows the list of chemicals used for the activation process and a list of previous reports on the usage of these materials to activated carbon. The further experiments in the development of a high surface area tuned activated carbon have been divided on the basis of activation agents used.

5.4.1 Activation using NaOH/KOH

NaOH and KOH are both alkali metal based activating agents. The activation occurs through an intercalation process. The process is an electron transfer reaction, bonding occurs by transfer of electrons from the alkali metal atom to the conduction band of the host carbon, the process of intercalation is thermodynamically vigorous for K, Ru, Cs. The ionization energy of sodium is much smaller in water. In the case of this work the source of carbon is

human hair. The sample is said to have to have a partly ordered and disordered carbon structure. Hence activation is most feasible with KOH and NaOH.

The pre-carbonized human hair was mixed with NaOH or KOH in a mass ratio of 1:2 and suspended in de-ionized water for thorough mixing the water content was slowly dried off at 100 °C, the mixed solid was then heated at 750 °C for 3 hours.

Mechanism

The co-carbonization of carbon materials in the presence of chemical agents leads to the development of pores. As the carbon is mixed with NaOH, the overall reaction can be summarized as follows. The alkali atom ionizes in the water mixture prior to addition to the carbon material. Due to low ionization energy of Na it undergoes an intercalation reaction with the carbon material entering into the irregular pores of the carbon structure.

The enhancement of pores occurs at temperatures > 700 °C by explosive removal of the intercalate. Depending on the alkali content during activation and the temperature of activation the nature of the pores can be manipulated. As the temperature is increased physical activation occurs by the burning of carbon from the activated carbon matrix leading to large macro-pores. The carbon is oxidized by the hydroxide group providing

Figure 5. 1 Schematic showing the change in the microstructure of the carbon materials on activation with NaOH.

routes for the catalytic channeling of mobile Na atoms into the internal structure, leading to a well-connected porous structure. But initial approximations indicated the formation of predominantly macro and micro pores. The formation of large pores on the outside and small micropores on the inside help us to establish a pseudo-hierarchical arrangement of pores. The macro-pores allow the electrolyte to effectively wet the entire surface at the same time they allow easy mass transport of electrolyte into the bulk of the carbon. The development of pores can be illustrated in figure 5.1.

5.4.2 Activation using ZnCl_2

Figure 5. 2 Schematic showing the change in the microstructure of the carbon materials on activation with ZnCl_2

ZnCl_2 is a dehydrating agent, which influences the pyrolytic decomposition and inhibits the formation of tar during carbonization, hence increasing the carbon yield. Impregnation with ZnCl_2 is generally done using an aqueous medium and initially leads to the degradation of the protein structures. On carbonization, it results in dehydration, aromatization and evolution of pore structure of the carbon. The volume of pores is directly proportional to the ratio of ZnCl_2 added during the impregnation phase. The pore size distribution is directly proportional to the quantity of ZnCl_2 added. Meso-pores can be observed at higher concentrations with a simultaneous reduction in yield. Activation occurs at temperatures lower than $500\text{ }^\circ\text{C}$. The development of the pores can be illustrated in figure 5.2.

On comparing the final pore size of alkali activated compounds and acid activated samples it can be observed that the pore size distribution formed by both activation techniques is largely different. The alkali based mechanism leads to the formation of pores with an

average diameter of ~ 100 nm while the internal pore structure appears to be in the range of ~ 20 -50 nm. In the case of ZnCl_2 . It can be observed that the pores are as small as 1-2 nm. As a part of our initial hypothesis activated carbon needed to have a hierarchical pore size distribution with macropores or large meso-pores on the outer edge in order to facilitate the wetting of the entire surface by the electrolyte. The macropores behave as ion buffers, whereas the mesopores serve as ion transport channels. In the case of ZnCl_2 activation it is observed that although a large volume of micropores is formed these pores are largely inaccessible to the electrolyte because of the large solvation shell around the Li^+ ion and the PF_6^- in the case of an organic solvent [16, 17].

Table 5.1 (please turn over) is a summary of properties observed in the activated carbon sample depending on the activation technique.

Table 5. 1 Summary of activation results depending on the activating agent used. Lists the surface area and the half-cell capacity of the activated carbon when tested between 3-4.6 V vs. Li

	NaOH-750-2hours	KOH-750-2hours	ZnCl ₂ -750-2hours
SEM micrograph
TEM micrograph
Surface Area (m ² g ⁻¹)	1116	875	1326
Half-cell capacity (mAh g ⁻¹)	46	25	22

X-ray characterization

Since the carbon sample does not have any long range order no sharp peaks are observed in the diffraction pattern. But two broad low intensity peaks are observed at $2\theta \approx 25^\circ$ and $\approx 42^\circ$ these correspond to the partially graphitized carbon sample[18]. Dahn *et al.* [19] using empirical calculations have determined a method to calculate the degree of graphitization. The calculations use the ratio of height of the height of the (002) peak with respect to the background. A higher ratio indicates a high fraction graphitized platelets[20]. A sample measurement is illustrated in figure 5.3. In the same manner calculations were conducted for all the activating agents used during the activation process. The R value calculated for

Figure 5. 3 X-ray diffraction image collected for activated carbon activated using NaOH. Reproduced with permission from ref [15]

each of the activated carbon samples are summarized in Table 5.2. It can be observed that activation using NaOH shows the highest portion of graphitized carbon indicating that the sample is expected to have the highest electronic conductivity.

Table 5. 2 Analysis of the X-ray diffraction pattern of human hair samples.

Activating Agent	R value
Commercial Activated carbon	1.23
KOH activation	1.43
NaOH activation	1.80
ZnCl ₂ activation	1.27

Figure 5. 4 X-ray diffraction patterns collected for activated carbon activated with KOH, NaOH and ZnCl₂. Further compared with commercial steam activated carbon.

Analyzing the Raman Spectra

The nature of the carbon present in the activated carbon sample was further analyzed using Raman spectroscopy. The two main peaks of concern to us are $\sim 1350\text{ cm}^{-1}$ (D peak) and $\sim 1550\text{ cm}^{-1}$ (G peak). The G mode has an E_{2g} symmetry the eigen vector is said to involve in plane C- bond stretching in sp^2 type carbon atoms. The D mode shows an A_{1g} symmetry which involves phonons from the K zone boundary. This mode is not allowed for perfect graphite samples and can be observed only in the case of disordered carbon[21]. The ratio of the intensity of the D and G peaks has been known to be an accurate indicator of the ratio of sp^2 and sp^3 carbon in the sample[15, 22]. The position, shape and relative intensities of the D and G peaks for samples activated using NaOH, KOH and ZnCl₂ is summarized in figure 5.5 and table 5.3.

Table 5. 3 Calculated values of the ratio between the D and G peak of the Raman spectra of each of the hair samples.

Activating agent	I_d/I_g
Pre-carbonized Hair	1.0556
NaOH- @1000 C	0.9224
NaOH- @750 C	1.0610
KOH	0.9893
ZnCl ₂	1.0381

Figure 5. 5 Raman spectra of activated carbon activated using ZnCl₂, KOH and NaOH at 750 and 1000 °C

It can be noted from the results that activation using ZnCl₂ and NaOH at 750 °C leads to a higher portion of disordered carbon, at higher temperatures the carbon starts to undergo graphitization hence a higher intensity of the G peak is observed. It is necessary to optimize

the ratio of disordered to ordered carbon in the activated carbon structure. A highly ordered structure leads to a higher conductivity due to free electron present in sp^2 type carbon atoms. But at the same time graphitization reduces the available surface area on the sample and increases the chance of Li intercalation into the carbon material. On the other hand disordered structures facilitate the formation of high surface area carbon structures.

The total available surface area in the case of each of the activated carbon samples is calculated by using the BET method. It can be observed that $ZnCl_2$ displays the highest surface area but in terms of electrochemical performance lags behind NaOH (Table 5.1). This can be explained by looking at the adsorption isotherm for each sample. The adsorption isotherm for $ZnCl_2$ is a type I isotherm indicating a majority of micropores in the sample. Due to the relatively larger solvation shell observed in organic electrolytes these pores are largely inaccessible to the ions hence are electrochemically inactive. The adsorption isotherm for the NaOH activated sample on the other hand is a Type IV isotherm which is

Figure 5. 6 Comparison of the isotherm of different activating agents.

indicative of a mixture of meso-pores and micropores. Facilitating complete wetting of the

activated carbon surface with electrolyte and at the same time exploiting the full potential of a high surface area activated carbon [23].

From the above results it was concluded NaOH activation leads to a high surface area coupled with an optimum distribution of pores making it the activation method of choice for human hair. Further testing is carried out to establish the optimum carbonization temperature. The results of the test are summarized in table 5.4 (please turn over). It can be observed that at lower temperatures the pore structure is not highly developed and a maximum surface area of $856 \text{ m}^2 \text{ g}^{-1}$ can be obtained. At higher temperatures $\sim 900^\circ\text{C}$ the carbonized sample is highly porous but a significant reduction in the net yield is observed also at such high temperatures the materials can tend to start graphitizing in order to form a more ordered structure as can be observed in Figure 5.5 wherein the Raman spectra corresponding to the high temperature formation process indicates the formation of an activated carbon sample with a higher percentage of ordered carbons. Studies conducted at 750°C display a well-developed pore structure with a surface area of $1116 \text{ m}^2 \text{ g}^{-1}$. A yield of $\sim 40\%$ is observed for the process which is considerably higher when compared to higher temperature synthesis. It can be concluded from the results that the best activating agent for activating human hair is NaOH and in order to maintain a good distribution of ordered to disordered carbon while keeping the yield appreciable 750°C is the optimum activating temperature

Table 5. 4 Summary of results on activation of human hair using NaOH at varying activation temperatures

	Carbonized at 600 °C	Carbonized at 750 °C	Carbonized at 900 °C
SEM Micrographs
TEM micrograph
Surface Area	856 m ² g ⁻¹	1116 m ² g ⁻¹	983 m ² g ⁻¹
Half-cell capacity	32 mAh g ⁻¹	46 mAh g ⁻¹	38 mAh g ⁻¹
Yield	~54%	~40%	~13%

Electrochemical analysis of the optimized carbon sample

The activated carbon formed was initially tested with Li as a counter electrode in a half cell configuration. The data recorded for the CV of ACHH is illustrated in Figure 5.7. The test was carried out at a low scan rate of 1 mV s^{-1} . As the charge storage mechanism of the ACHH is purely limited to adsorption and desorption from the surface of activated carbon. No redox peaks are observed in the CV instead the curve appears to be rectangular[24, 25]. Wherein the sign of the current is immediately reversed on reversing the potential, the phenomena is purely electrostatic and is independent of the potential. The capacitance of the supercapacitor electrode was calculated using the net area under the curve which can be written as

$$C_s = \frac{1}{vw(\Delta V)} \int_{V_a}^{V_c} iVdV \quad \text{eq. 5.2}$$

Where,

C_s is the specific capacitance of the electrode in F g^{-1} ,

w is the mass of the electrode

v Indicates the scan rate.

Figure 5. 7 Cyclic voltammetric profile of ACHH. The area under the curve is used to calculate the capacitance of the material. Reproduced with permission from ref [15]

ΔV indicates the span of the CV sweep

The term under the integral is used to calculate the area under the Current vs. Potential CV curve. It can be calculated to be 136 F g^{-1} .

Figure 5. 8 Charge discharge profile of activated carbon when cycled between 3-4.6 V vs. Li ; (b) Capacity retention of activated carbon over a period of 250 cycles. Reproduced with permission from ref [15]

Figure 5.8 represents the charge discharge plot of the material using Li as the counter electrode the tests were run in an organic medium between 3-4.6 Vs. Li. A stable capacity of $\sim 46 \text{ mAh g}^{-1}$ is observed for ACHH-NaOH when tested at 100 mA g^{-1} . It can be observed that the rate of change of potential is constant further indicating the purely capacitive nature

of charge storage. The capacity obtained from this sample is able to show improvement over other activated carbons synthesized using bio-sources [11, 26, 27]. Previous reports indicate that charge storage using KOH activated carbon in an organic electrolyte is plagued with poor charge storage kinetics [11], on the other hand activation using NaOH at 750 °C leads to the formation of larger pores which can allow the percolation of the large ionic species like PF_6^- along with their solvation shell. The half-cell was cycled for 250 cycles in order to establish good cycleability of the activated carbon electrode. The result is illustrated in figure 5.8(b). It can be noted that the material undergoes ~5% capacity decay

Figure 5. 9 Survey XPS spectra of activated carbon. Reproduced with permission from ref [15]

in the first few cycles and then shows no fading which is characteristic of the physical nature of charge storage in this case. The high capacity and good high current performance is indicative of surface functionalization this was tested by conducting XPS studies. The results of the spectra were fitted using Casa XPS and summarized in figure 5.9.

The survey spectrum was collected under ultra-high vacuum. It can be noted that the carbon and oxygen were expected on the surface of the carbon. But a strong peak attributable to N_2 can also be noted on the surface. The source of this nitrogen is assumed to be keratin which was not decomposed during the carbonization process. In order to establish the nature of the N_2 molecule a high resolution spectra was gathered in the desired region the results for

which are shown in figure 5.10 (a). The N₂ spectrum could be de-convoluted into four separate spectra's corresponding to Pyrrolic nitrogen/Pyridone nitrogen, Pyridinic nitrogen, quarternary nitrogen and Pyrridine-N-oxide. They are expected because of the partial ordered nature of the carbon after activation. The N atom in these groups has a free electron

Figure 5. 10 (a) N 1s core level spectrum; (b) C 1s core level spectrum. Reproduced with permission from ref [15]

pair that it can donate easily hence it helps to conduct electrons easily at the surface of the activated carbon. For the sake of completeness, the XPS spectra of carbon is also illustrated in figure 5.10 (b). It can be noted that carbon predominantly bonded to neighboring carbon atoms but a significant portion is bonded to nitrogen. And remnants from the original protein structure can be observed in the carbonyl bond.

Table 5. 5 Summary of XPS results

N 1s core Level spectra			C1s core level spectra		
Binding (eV)	Energy	Type of Bond	Binding (eV)	Energy	Type of bond
399.0		Pyrrolic Nitrogen	284.7		C-C
396.9		Pyridinic Nitrogen	285.7		C-N
401.0		Quarternary Nitrogen	287.2		C=O
402.3		Pyrridine-N-oxide			

The properties of activated carbon generated using NaOH can be summarized as follows

- Total surface area of $1116 \text{ m}^2 \text{ g}^{-1}$.
- Large macropores on the surface with an average pore diameter of 100-200 nm. Smaller mesopores in the bulk of the carbon which can act as ion channels.
- The surface is functionalized with N which acts as an electron donating group boosting the electronic conductivity of the activating carbon.
- Half-cell capacity when tested for PF_6^- ions was observed to be 46 mAh g^{-1} . The capacitance of the carbon was recorded as 115 F g^{-1} .

Figure 5. 11 The figure depicts the nature of the surface functionalities on the surface of activated carbon. (a) Pyridine-N-oxide and Pyridinic Nitrogen;(b) Pyrrolic Nitrogen; (c) Quaternary nitrogen.

5.4.3 Symmetrical supercapacitor

A symmetrical supercapacitor is constructed using ACHH electrodes in an organic electrolyte 1M LiPF_6 dissolved in EC:DEC tested between 0-3 V. The charge discharge

profile of the symmetric capacitor is illustrated in figure 5.12 (a). The charge storage in this case is that of a pure EDLC but the electrolyte in this case acts as limited source of Li ions. It can be noted from Figure 5.12(a) that the profiles is similar to earlier reports [11] on

Figure 5. 12 Charge discharge profile of ACHH/ACHH symmetric supercapacitor; (b) Capacity retention of the supercapacitor electrode over a period of 1000 cycles ;(c) Pictorial representation of the symmetric supercapacitor. Reproduced with permission from ref [15]

symmetric capacitors but the profile displays an anomaly when charged above 2 V which is not accompanied by any loss in capacity. The deformation of the charge discharge profile can be attributed to pseudo-capacitance due to the nitrogen doped surface[27]. The cell was

cycled for more than 1000 cycles it was observed that the symmetrical cell retains 92% of the initial capacity. The high stability is indicative that the pore size is large enough for facile migration of both PF_6^- and Li^+ ions. Supercapacitors are able to charge and discharge at high rate but the energy density is an order of magnitude lesser than Li ion batteries. Hybrid capacitors combine these two technologies and can deliver an energy density 3-4 times that of normal supercapacitors even at high loads.

Figure 5. 13 Depicts the dependence of the charge storage ability with respect to the current load applied to the cell. Reproduced with permission from ref [15]

5.4.4 Hybrid capacitor

The optimized carbon from human hair is tested with a standard insertion host like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [26]. LTO is preferred as the standard because of its zero strain structure which undergoes 0 % volume change during the insertion and removal of Li ions. Also the relatively high insertion potential of 1.5 V vs. Li in the case of LTO discounts the possibility of the formation of an SEI layer.

One of the most important parameters in the case of construction of hybrid capacitors is the calculation of exact mass on each of the electrodes. This is important because excessive current loading on any of the electrodes individually will lead to a loss in the net energy density. Hence as reported in previous literature the mass in each of the electrodes is balanced [28-30] according to the following equation

$$Q = m_1 C_1 = m_2 C_2$$

Where, Q is the net charge stored by each of the electrodes. m_1 is the mass of the activated carbon electrode, C_1 is the capacity recorded for activated carbon through half-cell tests with Li. m_2 , C_2 is the mass and capacity of the faradaic component. Half-cell studies were conducted on LTO at 100 mA g^{-1} . A capacity of 160 mAh g^{-1} is recorded. Hence the parameters can be calculated as follows

$$m_2 = 3 \text{ mg (fixed quantity)}$$

$$C_2 = 160 \text{ mAh g}^{-1}$$

$$m_1 = 10.43 \text{ mg}$$

$$C_2 = 46 \text{ mAh g}^{-1}$$

Figure 5. 14 (a) Charge discharge profile of ACHH/LTO hybrid; (b) Capacity retention vs cycle life. Reproduced with permission from ref [15]

It can be observed that using this formula the mass of the activated carbon is in excess compared to the battery electrode. This allows the majority of the current to be stored in the activated electrode at high currents and prevents damage to the battery electrode. Alternate literature also indicates that reversing the mass ratio can be used to obtain good high power performance[31]. But in the case of this study the focus is to mainly establish the high energy capabilities of ACHH. Typical charge discharge profiles of ACHH/LTO is

illustrated in figure 5.14 (a). The current loading for each of the tests is calculated using the total mass of the cathode and anode =13.43 mg. It can be clearly observed that the curve is an amalgamation of battery and supercapacitor profiles. And the nature of charge storage determined by the current applied during testing. During the charge process Li ions present in electrolyte intercalate into the host structure. While the PF_6^- ions along with their solvation shell are adsorbed on the surface of activated carbon. In the case of a low current load like 50 mA g^{-1} it can be observed that there is enough time for the Li ions from the electrolyte to intercalate into the host as the current is increased the Li ions can now only be adsorbed or partially intercalate at the surface of the electrode. During the discharge the Li ions are extracted from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ host

Figure 5. 15 dependence of discharge time with respect to the current load applied on the hybrid capacitor. Reproduced with permission from ref [15]

structure and at the same time PF_6^- ions are desorbed from the surface of activated carbon

As can be observed from figure 5.15 at low currents the profile displays a higher faradaic character at higher currents the profile has a constant slope like that observed in the case of charge storage by physical adsorption on the surface of the material. This attributed to the low Li diffusion constant for battery materials leading to charge being stored only on the surface of battery materials.

Figure 5.16 compares the performance of a hybrid supercapacitor with a symmetrical supercapacitor. It can be noted that in the case of the hybrid the discharge time is increased by a factor of three. Indicating the energy stored in the hybrid is ~ 3 times that of a normal capacitor.

The hybrid device is cycled for 1000 cycles (figure 5.14 (b)) and it can be observed that it

Figure 5. 16 Comparison of the discharge time of ACHH/LTO and ACHH/ACHH.

retains 80 % of its initial capacity. The highest energy density recorded is 22.5 Wh kg^{-1} with a power density of 2 kW kg^{-1} compared to the 19.2 Wh kg^{-1} observed when commercial activated carbon was used as the cathode material. The extra energy density observed in our study is because of the distribution of pores on the surface of activated carbon. The outer surface consists of macropores which allow the electrolyte to easily flow into the carbon bulk. While the inner mesopores act as ion buffer channels and the micropores provide the large surface area for the formation of an electrical double layer. Improvements can be made to the system by modifying the electrical conductivity of the battery material so that facile electron conduction is possible even at high current rates.

5.5 Conclusion

Initial efforts are concentrated on identifying a pore structure suited to hybrid capacitors. The factors taken into consideration were surface area, pore size and surface functionalization. A hierarchical pore size distribution was found to be the best solution. The macropores on the outer surface of the carbon facilitate the entrance of the electrolyte into the pore structure while the mesopores act as both sites for energy storage and ion buffering channels which allow for fast ion transfer from the micropores. Earlier attempts at developing these kind of structures needed complex templating reactions which are both expensive and hazardous.

During the course of this chapter development of hierarchically porous structure using human hair as a source of carbon was attempted. Human hair was chosen because it is relatively inexpensive and is generally treated as waste. Activation techniques were systematically studied to identify an appropriate activating agent. Based on the mechanism of activation, final surface area of activated carbon single electrode capacity and outer pore morphology. NaOH was considered an appropriate activating agent to activate human hair. Controlling parameters such as impregnation time we were able to obtain a carbon sample with a structure similar to a hierarchical model. Electrochemical studies were conducted on the material to evaluate the effectiveness of the proposed model. The half-cell studies were able to indicate a higher charge storage capacity of 46 mAh g^{-1} and a capacitance of 115 F g^{-1} when tested in an organic electrolyte. No aberrations were found in the data unlike previous results using KOH as the activating agent which indicated that the size of the ions in the case of an organic electrolyte is detrimental to facile charge storage kinetics.

Using the success in single electrode tests the ACHH was then applied in:

- 1: Li ion symmetric capacitor
- 2: Li ion Hybrid capacitor

On comparing these two technologies it was found that the energy stored in Hybrid capacitors is 3 times that of the energy stored in a conventional supercapacitor. This opens up new pathways into research into hybrid capacitors. Further improvements can be made to hybrid capacitors by fine tuning the activated carbon further by adding additives such as

pseudocapacitive metal oxides which can increase the net amount of energy stored in the material. Although further research needs to be conducted to improve the cycle ability of the material.

5.6 References

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Chapter 6

Implications, Impact and Future work

This chapter aims at providing a summary of the results obtained during this thesis and put them into perspective so as to highlight the importance of both the faradaic and supercapacitor electrode in a HEC. Also it aims to enumerate the important conclusions drawn from the experimental results, these results can act as a rubric in a manner wherein the researcher is able to choose a material depending on the power requirements of the end usage. The results obtained are compared with previous work in the field as well as judged in terms of final target achievement. The limitations understood based on experimental results are also targeted so as to streamline further studies into hybrid capacitors.

The chapter goes on to outline studies that are still in progress such as using high capacity cathode materials for hybrid applications and also outlines the work planned for future research such as implementation of Lithium rich layered compounds as cathode materials in HECs and the use of composite activated carbon electrodes to increase the energy density of HECs.

6.1 Perspective

The purpose of this thesis is to develop advanced electrodes for hybrid capacitor applications. The initial literature survey was focused on the understanding of the working of both the faradaic component and the supercapacitor component. After an in-depth analysis of each of the mechanisms. The materials used till date were listed in order to develop a perspective on the nature of faradaic materials used for Hybrid applications. The thesis limits its studies to HECs based on organic electrolytes because they can be cycled over a wide potential range, effectively increasing the amount of energy the HEC can store.

It was noted that in order for a material to be an effective faradaic electrode it should possess the following characteristics [1-3].

- Good stability over long term cycling.
- A highly stable scaffold type structure which is able to sustain high current applications.
- An insertion potential $< 1.5 \text{ V vs. Li}$ and $> 4 \text{ V vs. Li}$. In order to maintain high working potential and in turn high energy storage capabilities.
- The materials must be stable in the presence of organic electrolytes, with the ability to form a stable SEI layer if used as an anode, and to minimize oxygen evolution when employed as the cathode.
- The material should not undergo side reactions with the current collector at any point during the cycling process.

We were able to shortlist material categories which could be applied as the battery component in hybrid capacitors

Table 6. 1: Scheme representing material classes that can act as promising electrode materials for hybrid capacitors

Structure		Reason	Reference
Layered		The structure allows for easy migration of Li ions from the material. For example LiCoO_2 ,	[4-7]
Spinel		1: Good Lithium ion mobility, 2: Minimal volume changes during electrochemical cycling. 3: Example $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiMn_2O_4	[8-14]
Garnet Structures		1: Excellent Li ion conductivity. Up to $4 \times 10^{-4} \text{ S cm}^{-1}$ 2: Low insertion potential of $\sim 0.7 \text{ V vs. Li}$. 3: Formation of stable SEI layer which promotes cycle life	[15-19]
Olivine		1: 1 D tunnels allowing for fast Li ion transport. 2: Low electronic conductivity	[20-22]
Poly-anionic compounds	Phosphates	1: Highly stable intercalation host. 2: High intercalation potential. 3: Low electronic conductivity needs carbon coating for feasible usage	[23-31]
	Fluorophosphates	1: High operating potential 2: Open Channel structure due to Fluorine distortion leading to facile Lithium migration	[23, 25, 26, 28, 29, 31-46]

Further experiments were conducted with these material types in order to judge the performance of each of the materials. The summary of results is provided below.

6.2 Summary of Results

6.2.1: Study of Lithium garnets

$\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ was successfully synthesized using a solid state synthesis process. A uniform 2 nm carbon coating was carried out on the sample using a sucrose assisted approach. The powder was characterized using diffraction, microscopy and Raman spectroscopy techniques. The powder was initially tested in half-cell configuration with metallic Li as the counter electrode. A large first cycle irreversibility is observed due to the formation of the SEI layer. It was observed approximately 25% of the irreversible capacity loss could be prevented by carbon coating the sample. Indicating that the carbon layer forms a passivating layer on the pristine materials protecting it from further interactions with the electrolyte. The material was then tested both as an HEC and a full Li ion battery. It can be noted that as expected Lithium ion batteries have a much higher energy density when compared to an HEC at low power densities. But it can be noted from table 6.2 that even at higher power ratings the Li ion battery is able to perform better than the hybrid capacitor, but care should be taken when testing Li-ion batteries at high power conditions as the host structure is known to undergo rapid disintegration on rapid cycling. Hence for high power application it is more viable to use conventional supercapacitors. But the results in this thesis indicate that HECs can effectively substitute large supercapacitor banks with installation of almost 1/3rd the size.

Table 6. 2: Comparison of Li-ion battery against a supercapacitors and a hybrid capacitor in terms of energy storage capabilities at varying power ratings. The anode material for the Li-ion battery and Hybrid capacitor is $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$

Serial Number	Configuration(materials)	Energy Density (Wh kg ⁻¹)	Power Density (W kg ⁻¹)
1	Li-Ion Battery	170	100
	(LiMn ₂ O ₄ /Li ₃ Nd ₃ W ₂ O ₁₂)	80	2000
2	Hybrid	45	100
	Capacitor(AC/Li ₃ Nd ₃ W ₂ O ₁₂)	10	2000

3	Supercapacitor(AC/AC)	20	80
		3	2000

As garnet structures have a high Li ion conductivity of the order of $4 \times 10^{-4} \text{ S cm}^{-1}$. They were considered ideal electrode materials for Li based hybrid capacitors. Hence the results obtained in Section 4.1 are considered as baseline to measure the improvements made in the subsequent sections.

6.2.2: Study of Vanadium phosphates

(a) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was successfully synthesized using a fast sol gel technique. Citric acid was used as an *in-situ* carbon coating agent which helped to carbon coat the material during sintering. In order to avoid loss of carbon the heating was carried out in argon. The material was characterized and electrochemical tests were conducted applying the material as both a cathode and an anode initially in a single electrode configuration using Li as the counter electrode. The capacity recorded was used to calculate the mass balance for the hybrid capacitor.

The aim of this experiment was to be able to develop an empirical rule to determine the polarity of the battery material depending on the power requirements of the application. The LVP electrode was tested as both a cathode and an anode and the maximum energy and power density obtained can be summarized as Table 6.3.

Table 6. 3: Compares the Energy density of the LVP depending on the polarity of the electrode and the power density applied (the values are calculated on the basis of the mass of the battery electrode used in the process)

	Energy Density(Wh kg ⁻¹)	Power Density(W kg ⁻¹)
Li₃V₂(PO₄)₃ as an anode	30±5	100
	25±5	2000
Li₃V₂(PO₄)₃ as a cathode	40±5	100
	20±5	2000

It can be observed from table 6.3 that the polarity of the faradaic component plays a pivotal role in the optimization of the energy density that can be provided by hybrid capacitors. Considering LVP as a representative compound. For high power applications it is preferable to use the faradaic component as the anode material. For low to moderate power applications it is preferred to have the faradaic component as the cathode. These observations are key to develop new chemistries for hybrid configurations with a high energy density.

- (b) LiVPO_4F was studied because of its relatively high insertion potential and open tunnel structure. The details of the experiment are discussed in section 4.3. A solid state carbon assisted route was used to synthesize the material. It was characterized to check for morphology and purity of phase. Initial tests were conducted against metallic Li. It was noted that LVPF has excellent Li conduction properties. Tests were conducted in a hybrid setup with activated carbon as the counter electrode. Because of the relatively high insertion potential and the *in-situ* carbon coating a high energy density of 55 Wh kg^{-1} at a power rating of 100 W kg^{-1} . (The calculation is based on the mass of the faradaic component). It can be seen that even when the cell is cycled at 2 kW kg^{-1} it can reversibly store 20 Wh kg^{-1} . This is about 4 times higher than that observed for commercial supercapacitors tested a similar power density.

6.2.3: Fundamental studies on Layered oxides

(a) Reconnaissance Studies

Layered materials consist of alternating layers of Li between Transition metal layers. Initial studies in this thesis involved the preparation of layered materials like $\text{H}_2\text{Ti}_3\text{O}_7$ and VO_2 . These layered oxides are known to have a high charge storage capacity but were not explored further due to their intercalation potential of 1.75 V and $\sim 2 \text{ V vs. Li}$ respectively. The details of the testing of these materials is shown in detail in Appendix – II.

(b) Detailed studies on Lithium rich layered oxides.

This class of materials have recently garnered the attention of the energy storage community. They are able to reversibly store $\sim 250 \text{ mAh g}^{-1}$ and have an operating potential

of ~ 4.2 V vs. Li. Such high capacity has not been observed for cathode materials. Hence automatically these were of interest to form high energy density Hybrid capacitor devices.

- They have been known to undergo complex redox reactions during cycling. Apart from the transition metal center oxygen based anionic redox reactions are also expected to occur. In order to apply these electrodes in a hybrid capacitor it was first necessary to develop a sound understanding of these electrodes. Ruthenium based Lithium rich layered oxides were constructed with varying dopants as shown in chapter 4, section 4.4. It was observed that the partial substitution of Ru with Fe to form the final formula $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$ is the most stable system with the highest working potential. The charge storage mechanism in these materials is still largely unknown. In order to develop the structural changes at an atomic scale various *in-operando* studies were conducted.
- In-operando X-ray diffraction experiments were designed in collaboration with Steffan *et al.*[47]. The experiments yielded never before studied details of the phase transformation undergone by lithium rich layered oxides and were able to observe the formation of monoclinic de-lithiated phase on higher potentials during charge. These results disprove an earlier hypothesis earlier by Sathiya *et al.*[48, 49] that the charge storage process leads to gradual loss in long range order. We were able to achieve reversibility of the diffraction pattern for more than 5 cycles.
- To complement *in-operando* diffraction studies *in-operando* EXAFS analysis was carried out and the results are summarized in section 4.4. In the case of the Fe K edge the shift in the near edge was too small to determine the oxidation process. Hence the extended XAS pattern was fitted and the distance between the TM and O was recorded during specific parts of the cycling process it could be observed that the M-O octahedra underwent significant changes in terms of the M-O distance indicating a change of the formal charge on the transition metal. While studying the Ru K edge no such issues were observed and a clear oxidation and reduction reaction could be observed.

- Oxygen was a challenge to observe *in-operando* because of the low absorption edge of oxygen (~530 eV). Hence we conducted *in-situ* studies to observe the nature of the oxygen edge at different parts of the electrochemical profile. At full charge we were able to observe peaks pertaining to peroxide type linkages indicating that the anionic redox also plays an important role in the energy storage mechanism.

The mechanism of Lithium rich cathodes needs to be studied further and also Ruthenium being a rare earth metal is expensive and not practical for a low cost hybrid capacitor device. Hence in order to make these materials applicable to hybrid capacitors further research is required in order to understand the structural changes in the material. This information can help to tailor the material by substituting cheaper metals instead of Ru but maintaining the high capacity.

6.2.4: Development of a high energy density supercapacitor electrode using cheap activated carbon from bio-waste sources.

In order to make the development of HECs sustainable and cost friendly it is necessary to develop a high energy density supercapacitor electrode. Activated carbon is the dominant material choice because of its relative inexpensiveness, it is environmentally benign, has a high surface area, it can be sustainable depending on the source of carbon. The source of carbon chosen for the purpose of this thesis was human hair. Initial part of the research was to identify the nature of pore distribution which can maximize the electrode electrolyte interactions and hence improve the amount of energy that can be stored by the supercapacitor. A hierarchical pore size distribution is considered to be ideal for this purpose.

- Large mesopores or macropores act as pathways to let the electrolyte enter the internal pore structure.
- Inner mesopores act as ion channeling networks and ion buffer channels which can help to make ion exchange process during the development of the EDLC faster.
- Inner micropores (<2 nm) help to enhance the net capacitance.[50]
- In the case of organic electrolytes the pore size needs to be larger than aqueous solutions because of the relatively larger size of the solvated ions.

Human hair was chosen as a cheap and easy to obtain, source of carbon. The flaky structure of human hair leads to lower activation energies. Also the presence of nitrogen in the hair helps to enhance the electronic conductivity of the sample. In order to achieve the optimum pore size distribution, studies were conducted to understand the effect of different

Figure 6. 1 Comparison of a hybrid supercapacitor with a symmetric supercapacitor and commercial supercapacitor at varying power densities

activating agents including NaOH, ZnCl_2 , KOH. It was noted that NaOH leads to the formation of the largest pores on the surface of activated carbon (100-200 nm). In order to control the degree of activation studies were conducted to calculate the optimum time and temperature which can be used to maintain significant yield and required pore structure.

The activated carbon formed was tested initially in a single electrode configuration against metallic Li as the counter electrode and 1M LiPF_6 dissolved in EC:DEC as the electrolyte. CV traces indicate a capacitance of 115 F g^{-1} . Also charge discharge profiles indicate an improvement in the charge storage capacity. This improvement can be attributed to the optimized pore size distribution in the case activated carbon from hair. Further the results

indicate the performance of the ACHH in a symmetric and asymmetric configuration. Significant improvements can be observed when compared to commercial capacitors as indicated in figure 6.1.

In the case of the commercial supercapacitor it was noted that the energy density of the symmetric hair based supercapacitor is higher than commercial activated carbon up to 200 W kg^{-1} . While the ACHH/LTO hybrid device is able to show improved energy density up to 500 W kg^{-1} . These results indicate that although activated carbon from human hair is able to display a higher energy density when compared to commercial activated carbon during low power testing it is not able to compare with commercial systems during high power testing. From our understanding the extra capacitance of the commercial systems is due to the higher fraction of micropores in these samples. Studies are still in progress in order to optimize the activation mechanism and combine activated carbon with pseudocapacitive metal oxides such as MnO_2 or RuO_2 to improve the net amount of energy stored.

6.3 Comparison of HEC results with Li-ion battery and a supercapacitor

Figure 6. 2 Ragone plot summarizing the results obtained during this thesis.

The aim of this thesis was to be able to define the field of hybrid capacitors at the same

time be able to develop sustainable and practical material chemistries which can be successfully applied in the real world to provide high energy density solutions for PHEV applications. Figure 6.2 is a summary of the results obtained during each of the carried out during the course of the thesis. The Ragone plot is used to clearly differentiate between Lithium ion batteries, supercapacitors and hybrid capacitors. It can be noted that at low power settings ($<1000 \text{ W kg}^{-1}$) the energy density follows the following trend Li-ion battery $>$ Hybrid Capacitor $>$ Supercapacitor. When tested at high power settings Hybrid capacitor $>$ Li-ion battery $>$ Supercapacitor. It is of interest to note that although Li ion batteries show higher energy densities when compared to supercapacitors during high power testing they undergo rapid capacity fading when tested for such high current loading, because of structural deformations.

6.4 Target achievement

We have been able to achieve the targets set at the start of the thesis, although further modifications are needed in the materials in order to be a PHEV energy storage solution. The extent of research carried out on hybrid capacitors coupled with the results obtained during the course of this thesis are summarized in figure 6.3. It can be observed from the figure that hybrid solutions proposed in this thesis have been able to achieve the power density that is needed to power PHEV devices.

It can be noted that although power density is achieved. The research is not able to completely reach the energy density required by PHEVs. In order to achieve this energy density, currently work is being carried out to optimize high capacity and high cycle life lithium rich layered cathodes[51, 52] coupled with composite supercapacitor electrodes and is expected to dramatically improve the properties of hybrid capacitors[11, 53-63].

Figure 6. 3 Represents previous results published on non-aqueous hybrid capacitors to compare the achieved energy and power density with the work carried out during this thesis

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6.5 Future Work

Future work in terms of improvement of the energy density of HEC's can be summarized into two experiments

6.5.1: Use of high capacity layered materials for hybrid capacitors.

Lithium rich layered materials exhibit capacities beyond 250 mAh g^{-1} . But they have been shown to a reduced cycle life when compared to other commercial layered materials. This property is attributed to the unique structure of the materials which slowly decomposes as

cycling progresses. Studies include the substitution of the major transition metal with smaller TM which stabilize the structure during cycling. Our preliminary studies include

- The synthesis of doped lithium rich layered cathodes. The parent material used is Li_2RuO_3 . It was systematically doped with Fe, Sn and Ti. These substitutions increase cycleability substantially. The best results are obtained for Fe substituted samples with the general composition $\text{Li}_{2+x}\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$.
- Further electrochemical testing was conducted and it was observed that a stable capacity of $\sim 250 \text{ mAh g}^{-1}$ was recorded. But the peculiar nature of the first charge curve was not completely understood.
- In order to develop a better understanding of structural changes corresponding to the peculiar charge curve *in-operando* studies were carried out. We were able to identify the structural changes occurring during cycling.
- Further future work needs to be conducted in order to understand the complicated anionic redox reaction occurring at oxygen centers in the material. There are two different schools of thought regarding this process one attributing the excess capacity observed to the formation of localized holes in near oxygen. And the other suggests the formation of peroxo or supeoxo type bonds in the bulk which undergo reversible redox reactions. Currently Near edge X-ray absorption fine structure studies are being carried out on $\text{Li}_2\text{Ru}_{0.75}\text{Fe}_{0.25}\text{O}_3$ at SLAC, Stanford University in order to understand the reaction occurring at oxygen centers, preliminary results obtained during these tests have been highlighted in Chapter 4
- After we are able to understand the charge storage of these compounds further optimization needs to be carried out to improve the electronic conductivity of the material. This can be achieved through a variety of techniques including the use of conductive carbon coating, or the use of conducting backbone on which the battery material is deposited. The optimized electrode then needs to be tested in a hybrid electrode configuration

6.5.2: Development of Activated carbon composites

The energy density of HECs is heavily limited by the low energy density of activated carbon. During our testing and development of an optimum sample of activated carbon, the energy density could be enhanced considerably. But as seen from figure 6.3 we have not been able to achieve the required performance. Due to this future endeavors are aimed at developing activated carbon composites with pseudo-capacitive materials like RuO_2 and

Table 6. 4 Comparing carbon based and metal oxide based supercapacitors. Evaluating the improvements possible by combining the two materials

Electrode Material	Pore Distribution	Size	Surface Area	Capacitance	Conductivity	Rate performance	Stability	Cost
Carbon	Can be tailored relatively with ease	High		Low	High	High	Excellent	Low
Metal Oxide	Cannot be tailored easily	Low	Low surface area	High	Low	Low	Poor	High
Metal oxide carbon composite	The pore size – distribution of the carbon support structure can be controlled to a high degree	High		High	Tune able depending on the carbon support	Good	Good	Medium

MnO_2 [59, 64]. These metal oxides have been shown to have a high capacitance, and good cycle life but lack in terms of good electronic conductivity. On coupling with a conductive

carbon substrate we hope to not only increase the utilization of active materials but also increase the electronic conductivity and mechanical strength of the electrode. Table 6.1 summarizes the purpose of adding a metal oxide to a carbon matrix.

A suggested approach is the development of hierarchical carbon structures from cheap carbon sources such as human hair and the same time introduce transition metal oxides into the carbon matrix as shown in the figure 6.4 reproduced from Jiang *et al.* [64]. Studies are still in progress to identify an implement such a high energy composite electrode.

Figure 6. 4 (a-d) The figure depicts the development process of a 3D aperiodic hierarchical carbon structures. (d) Ragone plot of different forms of activated carbon; (e) Improvement of capacity by the involvement of metal oxide in the 3D structure. The figure is reproduced with permission from ref [64].

6.6 Concluding Remarks

The thesis titled “Advanced electrodes for HEC application”, has successfully developed high energy and high power electrodes which are partially able to meet the targets in terms of energy and power density required to power a PHEV vehicle. The results and outcomes of this thesis apart from technological target achievement also focus on developing a fundamental understanding of the nature of materials that can be exploited as electrode materials for hybrid applications. By conducting complex characterization techniques such as *in-operando* X-ray diffraction and *in-operando* X-ray absorption studies for hybrid electrodes in order to develop a rubric which can guide future research into hybrid batteries.

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APPENDIX-I

Section 1

Study of garnets with alternative compositions

1: $\text{Li}_3\text{Y}_3\text{Mo}_2\text{O}_{12}$

2: $\text{Li}_3\text{Y}_3\text{W}_2\text{O}_{12}$

X-ray Diffraction Pattern

Appendix 1 X-ray diffraction pattern of $\text{Li}_3\text{Y}_3\text{Mo}_2\text{O}_{12}$ and $\text{Li}_3\text{Y}_3\text{W}_2\text{O}_{12}$. Both materials do not crystallize in a cubic arrangement like $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ instead form compound with a triclinic space group.

SEM Micrograph

Appendix 2 SEM micrograph of $\text{Li}_3\text{Y}_3\text{Mo}_2\text{O}_{12}$; (b) $\text{Li}_3\text{Y}_3\text{W}_2\text{O}_{12}$

Cyclic Voltammogram

Appendix 3 Cyclic voltammogram of $\text{Li}_3\text{Y}_3\text{Mo}_2\text{O}_{12}$ and $\text{Li}_3\text{Y}_3\text{W}_2\text{O}_{12}$. Both CV's indicate no electrochemical activity is observed for the Mo sample, The tungsten based sample shows a broad oxidation peak but no reduction peak.

Section 2**Thermal analysis of bare $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$**

TGA was done on the pristine sample to confirm that the sample does not undergo decomposition upto 500 °C

Appendix 4 TGA of pristine $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$

APPENDIX-II

Study of layered compounds

Section 1

1.1 Study of VO_2 layered structures as possible high power faradaic component for hybrid capacitors.

Appendix 5 Layered structure of VO_2 . The structure is indicative of good Li ion conductivity

Appendix 6 VO_2 ultra-thin platelets synthesized using a hydrothermal technique, using glucose as the reducing agent at 130 C for 3 hours.

Appendix 7 (a) Galvanostatic charge discharge profile of VO₂ when tested vs. Li. A capacity of 275 mAh g⁻¹ is observed. The insertion potential of the material is ~2.5 V making it unsuitable for HEC application. (b) The cell was cycled and observed that the system is stable for 75 cycles.

Section 1.2 Study of Hydrogen Titanate as possible layered material to be used as the cathode material in HECs

Appendix 8 X-ray diffraction pattern of $\text{H}_2\text{Ti}_3\text{O}_7$. Two sharp reflections are observed which can be indexed to the 020 and 002 plane. No clear reflections are observed in rest of X-ray diffraction pattern

Appendix 9 (a,b) Hydrogen titanate nano-platelets with an average width of 100 nm. The nano-structured Hydrogen Titanate is expected to have excellent capacity.

Appendix 10 (a) Cyclic voltammogram of Hydrogen titanate, a prominent broad oxidation and reduction peak. The difference between the peaks indicates a highly polarized sample indicating low electronic conductivity. The shape of the curve indicates pseudocapacitive type energy storage, indicating the material can be expected to have good high power performance. (b) Galvanostatic charge discharge profile of $\text{H}_2\text{Ti}_3\text{O}_7$ indicating a capacity of $\sim 160 \text{ mAh g}^{-1}$. No plateaus are observed in the GCD indicating a single phase charge transfer mechanism. The working potential of $\text{H}_2\text{Ti}_3\text{O}_7$ can be noted as 1.6 V vs. Li.

Appendix 11 Cycling performance of hydrogen titanate cycled 35 cycles it can be noted that the performance of Hydrogen titanate does not undergo capacity decay after the first cycle. Indicating good performance. But the higher active potential is not conducive to good HEC performance