RICE UNIVERSITY

Materials Compositions for Lithium Ion Batteries with Extended Thermal Stability

by

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ABSTRACT

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Advancements in portable electronics have generated a pronounced demand for rechargeable energy storage devices with superior capacity and reliability. Lithium ion batteries (LIBs) have evolved as the primary choice of portable power for several such applications. While multiple variations have been developed, safety concerns of commercial technologies limit them to atmospheric temperature operability. With several niche markets such as aerospace, defense and oil & gas demanding portable energy storage at elevated temperatures, there is a renewed interest in developing rechargeable batteries that could survive temperatures beyond 55°C. Instability of critical battery components towards extreme thermal and electrochemical conditions limit their usability at high temperatures. This study deals with developing material configurations for LIB components to stabilize them at such temperatures. Flammable organic solvent based electrolytes and low melting polymer based separators have been identified as the primary bottleneck for LIBs to survive increasing temperature. Furthermore, thermally activated degradation processes in oxide based electrodes have been identified as the reason for their limited lifetime. A quasi-solid composite comprising of room temperature ionic liquids (RTILs) and Clay was developed as an electrolyte/separator hybrid and tested
to be stable up to 120°C. These composites facilitate complete reversible Li intercalation in lithium titanate (LTO) with a stable capacity of 120 mAh g\textsuperscript{-1} for several cycles of charge and discharge while simultaneously resisting severe thermal conditions. Modified phosphate based electrodes were introduced as a reliable alternative for operability at high temperatures in this study. These systems were shown to deliver stable reversible capacity for numerous charge/discharge cycles at elevated temperatures. Higher lithium intercalation potential of the developed cathode materials makes them interesting candidates for high voltage lithium batteries, which may be dubbed as the next generation devices. Architectural engineering of battery components to amplify the device performance is also discussed. 3D electrode structures developed using CVD and electrodeposition techniques demonstrated significant enhancement in performance when compared to their 2D analogues. The study has established the prospects of LIBs at high temperatures through material tuning and engineering approaches and envisage a scope for viable devices.
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and unanticipated roadblocks. I would like to take this opportunity to name a few of them who deserve special mention. Prof. Leela Mohana Reddy Arava, who held the position of a postdoctoral fellow during the first three years of my degree would always have my endless gratitude. He introduced me to the area of Lithium Ion Batteries which I consider as one of the best things that happened to me. I am privileged to have him as a mentor who invested a lot of effort to help me become proficient in electrochemistry. He is a very dear friend along with being a great mentor. Dr. Hemtej Gullapalli, Dr. Farheen Sayed and Marco- Tulio are more than colleagues who will have my greatest acknowledgements. Their insights and backing has always helped me make a significant progress in this research. I will always hold great regards for them for all that I could learn from our day to day conversations. I would also like to extend my acknowledgements to Dr. Shaijumon Manikoth, Dr. Sanketh Gowda, Dr. Antony George, Dr. Sandeep Unnikrishnan, Dr. Soumya Vinod, Dr. Neelam Singh, Dr. Charudatta Galande and Dr. Srividya Sridhar.

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_Dedicated to my family_
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1.1 Energy Storage Devices

Portable energy storage devices can be regarded as one of the most important inventions in the history of mankind. Recently, there has been an increasing demand for portable devices with high energy density, capacity, and power output for applications extending from various sensors to electric vehicles. The spread of the usage spectrum of these devices sparked significant research interest to understand and develop newer technologies which can store more energy for longer periods of time along with shrinking the size of the devices. Based on the mechanism of energy storage, these modern day devices can be broadly categorized into two types—supercapacitors and batteries.

1.1.1. Supercapacitors

Supercapacitors are the common name for ElectricDouble Layer Capacitor (EDLC) capable of delivering high power outputs. In a dielectric capacitor, the ions in the dielectric medium separate during charge and get accumulated at each of the
conductors and the charges recombine during discharge releasing stored potential energy in the form of electrical energy. The rate of recombination of charges during discharge is extremely high, leading to a large discharge of energy in a short interval of time. Supercapacitors store energy by the formation of an electrical double layer by the accumulation of charges onto active surface areas. Unlike that of a dielectric capacitor, a supercapacitor has an electrolyte consisting of movable ions. A schematic of the charge and discharge mechanisms in a supercapacitor is represented in Figure 1-1.

![Figure 1-1- Schematic of the mechanism of charge and discharge in an EDLC showing the charge separation and recombination during charging and discharging process leading to the formation of double layer at the electrode.](image)

Figure 1-1- Schematic of the mechanism of charge and discharge in an EDLC showing the charge separation and recombination during charging and discharging process leading to the formation of double layer at the electrode.
1.1.2. Batteries

The mechanism of energy storage in a battery involves electrochemical redox reaction during the processes of charge and discharge. A battery consists of two electrodes- a positive electrode (cathode) and a negative electrode (anode) separated by a Li-ion containing electrolyte. The mechanism of energy storage in a battery involves electrochemical redox reactions at the electrodes, forcing electron flow through the external circuit. The electric current from a battery is dependent on the rate of charge transfer at an electrode which is proportional to the number of ions undergoing electrochemical reaction per unit time.

1.1.2.1. History of battery development

The discovery of the first voltaic cell by Alessandro Volta in 1800, wherein he demonstrated that two dissimilar metals, zinc and copper, when separated as electrodes (the anode and cathode, respectively) by an acidic electrolyte, produced an electric current. This initiated the research in electrical energy generation and storage. Subsequently, the laws of electrochemistry by Michael Faraday provided a deeper understanding of the electrochemical reactions which paved the path for development of primary and secondary battery chemistries. The developments of lead-acid (Gaston Planté, 1859), nickel-cadmium (Waldemar Jungner, 1899), and nickel-iron (Thomas Edison, 1901) systems can be regarded as a few note-worthy milestones in this direction which have been commercially used till date.
The first generation of batteries known as the primary batteries could not be recharged due to the irreversible nature of the electrochemical reaction. Examples of such cell systems include alkaline batteries, Ni-Cd, Zn-Carbon, Ni-MH, etc. Such primary batteries have the obvious disadvantages of lower lifetime and the cost associated with replacing them. Thus, as an alternative, rechargeable battery technologies have been explored.

The second generation of batteries, also known as secondary batteries, are of the rechargeable type. The first successful rechargeable battery was the lead acid battery with lead oxide as one of the electrode and metallic lead as the other electrode and concentrated sulfuric acid as the electrolyte. It has been proven to be a source of high energy among all the available technologies in rechargeable batteries and is being used, commercially, in automotive engines. Albeit, there have been many problems relating to packaging, power density and safety.

With the aim of achieving better power density, not compromising on the energy density, other chemistries such as lithium ion, lithium-air, Zinc-air, etc. have been explored. Table 1.1 lists different rechargeable battery chemistries being explored currently with their specific advantages and disadvantages. There has been a great interest in LIBs due to their high reversible energy densities and volumetric capacities compared to other rechargeable and non-rechargeable devices. Lithium metal with low density (0.53 g cm\(^{-3}\)), high specific capacity (3862 mAh/g), and highest operation voltage (-3.04 V versus Standard Hydrogen Electrode)[1] can diffuse
through the electrolyte and the electrodes with great ease, which makes it the most preferred choice.

**Table 1.1- Different types of rechargeable battery chemistries**

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Features</th>
<th>Environmental impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-MH (established)</td>
<td>Low voltage, moderate energy density, high power density, Applications: portable, large-scale</td>
<td>Nickel not green (difficult extraction/unsustainable), toxic. Not rare but limited Recyclable</td>
</tr>
<tr>
<td>Lead-acid (established)</td>
<td>Poor energy density, moderate power rate, low cost, Applications: large-scale, start-up power, stationary</td>
<td>High-temperature cyclability limited Lead is toxic but recycling is efficient to 95%</td>
</tr>
<tr>
<td>Lithium ion (established)</td>
<td>High energy density, power rate, cycle life, costly Applications: portable, possibly large-scale</td>
<td>Depletable elements (cobalt) in most applications; replacements manganese and iron are green (abundant and sustainable) Lithium chemistry relatively green (abundant but the chemistry needs to be improved) Recycling feasible but at an extra energy cost</td>
</tr>
<tr>
<td>Zinc-air (established)</td>
<td>Medium energy density, high power density Applications: large-scale</td>
<td>Mostly primary or mechanically rechargeable Zinc smelting not green, especially if primary Easily recyclable</td>
</tr>
<tr>
<td>Lithium-organic (future)</td>
<td>High capacity and energy density but limited power rate. Technology amenable to a low cost Applications: medium- and large-scale, with the exception of power tools</td>
<td>Rechargeable Excellent carbon footprint Renewable electrodes Easy recycling</td>
</tr>
<tr>
<td>Lithium-air (future)</td>
<td>High energy density but poor energy efficiency and rate capability Technology amenable to a low cost Applications: large-scale, preferably stationary</td>
<td>Rechargeability to be proven Excellent carbon footprint Renewable electrodes Easy recycling</td>
</tr>
<tr>
<td>Magnesium-sulphur (future)</td>
<td>Predicted: high energy density, power density unknown, cycle life unknown</td>
<td>Magnesium and sulphur are green Recyclable Small carbon footprint</td>
</tr>
<tr>
<td>Al-CF₆ (future)</td>
<td>Predicted: moderate energy density, power density unknown</td>
<td>Aluminium and fluorine are green but industries are not Recyclable</td>
</tr>
<tr>
<td>Proton battery (future)</td>
<td>Predicted: all organic, low voltage, moderate energy density, power density unknown</td>
<td>Green, biodegradable</td>
</tr>
</tbody>
</table>
1.1.2.2. Mechanism of charge transfer in a LIB

During the charge of a battery, Li- ions from the cathode are released into the electrolyte while the Li- ions in the electrolyte are incorporated into the anode as shown in Figure 1-2. While during the discharge, the intercalated Li- ions from the anode dissolve back into the electrolyte and Li- ions are intercalated into the cathode. The electrons released as a result of the delithiation at the anode travel through the load in the external circuit which is seen as the current. The flow of electrons continues until complete delithiation.

The half-cell reactions involved in a commercial LCO/graphite cell is given as

*Cathode half-cell:*

\[ LiCoO_2 \leftrightarrow xLi^+ + Li_{(1-x)}CoO_2 + xe^- \quad (1-1) \]

*Anode half-cell:*

\[ xLi^+ + 6C + xe^- \leftrightarrow Li_xC_6 \quad (1-2) \]
1.1.2.3. Performance metrics in a LIB

Capacity, C-rate, power density and energy density are some specific metrics that are used to gauge the performance of a battery.

1. Capacity is the amount of charge transferred during the charge/discharge of a battery represented as Ah units.
2. C-rate is the rate at which the nominal capacity of the electrode is achieved. For example, 1C indicates the charge to 100% SOC or discharge to 0% SOC of a battery.

3. Energy and Power density is the amount of energy and power that can be extracted from a battery w.r.t the mass (gravimetric) or volume (volumetric) of the device and is represented as Wh kg\(^{-1}\) or Wh L\(^{-1}\) and W kg\(^{-1}\) or W L\(^{-1}\).

The metrics can be measured from various techniques such as cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge experiments. Figure 1-3 shows the process that occurs in a simple electrode reaction. During reduction, the species capable of receiving electrons diffuses to the surface and then away from the surface after reduction. Current at the surface is generated by the transfer of electrons from the electrode to the redox species. In the absence of a redox species, the interface will behave as a capacitor in which the charge and voltage are dependent on a proportionality constant C known as the capacitance of the medium. Capacitance is an important parameter in electrochemical system which defines the current of the device.
1.1.2.3.1. **Cyclic Voltammetry**

In a cyclic voltammetry (CV) the exchange current during charge and discharge are plotted as a function of the voltage at a constant voltage rate. A typical CV profile is represented in Figure 1-4. The voltage applied to the working electrode is scanned linearly from an initial value to a pre-determined cut-off where the scan is reversed. In a LIB, the exchange current is plot against the voltage applied and the peak current represents the exchange current involved in a redox reaction.
Figure 1-4- A typical cyclic voltammetry curve indicating reversible charge and discharge redox peaks [2]

The positive peak represents an anodic reaction and the negative peak represents the cathodic reaction. The voltage at which the redox reaction occurs is determined by the Nernst equation.

\[ E = E^{o'} - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right) ; X = 0 \]  

(1-3)

Where \( O \) is the oxidized form and \( R \) is the reduced form. A reversible half-cell reaction typically occurs at the same cathodic and anodic potentials where the
oxidation and reduction reactions take place during charge and discharge reactions. The height of the peak currents can be used to determine the concentration of the reactant in the bulk solution which varies as the square root of the scan rate.

1.1.2.3.2. **Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique that is used to analyze the changes in the reactive elements in the device during the electrochemical redox reactions. The charge transfer during the electrochemical reactions leads to both faradaic and non-faradaic components. A small perturbation of the electrode state can induce close to linear behavior that can be modeled using solutions of relevant mathematical equations. The reactions can be represented as an electrochemical equivalent circuit (EEC) as shown in Figure 1-5 (a), where the faradaic component arises from the electron transfer across the interface overcoming an appropriate activation barrier [3]. The schematic shows an electrode electrolyte interface in which the electrode is negatively charged and the corresponding EEC corresponding to the elements in the electrical circuit wherein the activation barrier also known as the polarization resistance ($R_p$), uncompensated solution resistance ($R_s$) and the non-faradaic double-layer capacitor component ($C_d$) is shown. Mass transports of reactant and product during charge transfer at the interface results in Warburg impedance ($Z_w$). The reactance of the system to electrical signals is plotted as the imaginary component ($-Z''(\omega)$) vs the real component ($Z'(\omega)$) as shown as a Nyquist plot in Figure 1-5 (b) [4]. The plot appears as a semicircle with a radius of
$R_p/2$, with a high frequency intercept of $R_s$ and a low frequency intercept of $(R_s + R_p)$ on the $Z'(\omega)$.

![Image of double layer formation and equivalent circuit]

Figure 1-5- (a) Schematic showing the formation of double layer at the electrode/electrolyte interface and the equivalent circuit, (b) Typical impedance curve showing the semicircle and the real constants. [Inset: equivalent circuit of the corresponding EIS curve] [4]

When an electrode is in contact with an electrolyte containing ions, the ions align themselves at the interface forming the Inner Helmholtz Plane (IHP) and Outer Helmholtz plane (OHP). These planes create the electronic barrier forming a double layer.
1.1.2.3.3. **Cycle Life Measurements**

The charge and discharge measurements are conducted to measure the capacity and to understand the cyclic stability of the device. There are two types of charge-discharge measurements -

(i) **Constant current (CC) mode**

(ii) **Constant Voltage (CVolt) mode**

Under CC mode, a device is charged with a constant current rate or a C-rate between a voltage window encompassing the lithiation and de-lithiation potentials of the cell. A small over-charge and over-discharge are applied to ensure complete lithiation and de-lithiation and the voltage vs capacity are plotted to understand the contribution of each voltage towards the total capacity of the device under a constant current. Under ideal conditions, there is a linear drop in voltage representing a capacitive behavior until it reaches the redox potential of Li in the lattice at which, there is a voltage plateau. The plateau is an indicative of the onset of the redox reaction, end of which marks the completion of the reaction. Subsequent charge or discharge follows a capacitive behavior since there is no redox reaction at those potentials. Thus, it can be inferred that each voltage plateau in a charge-discharge profile corresponds to a redox reaction at those potentials which appear as peaks in CV plot. A cell is charged or discharged at the lithiation voltage in the CVolt mode until 100% SOC. A cell discharged under constant voltage ensures constant current output and a current vs capacity was plotted. Under practical conditions of battery use, most of the electronic applications apply a constant voltage discharge. The
voltage output from a cell is the potential corresponding to the redox reaction and the voltage drops at the end of the reaction.

Continuous cycling within the voltage window for over large number of cycles helps to understand the cyclic stability of the cell which is understood from coulombic efficiency (CE) of the cycle. Coulombic efficiency is defined as the ratio of the amount of energy extracted from the cell during discharge to the amount of energy supplied to the cell during the charge process. A 100% CE implies a complete reversibility of the redox process and a 100% CE for large number of cycles indicates long term stability of the cell. Figure 1-6 [5] shows an example cyclic stability plot of Lithium iron phosphate (LFP) based lithium battery indicating the capacity vs cycle number. The black plot is the capacity as a function of the cycle number and the red plot is the CE when charged at a C-rate of C/2 corresponding to a current density of 0.25 mA cm$^{-2}$. The inset shows the voltage profile of the same cell at 1$^{st}$, 10$^{th}$, 100$^{th}$ and 150$^{th}$ cycles.
1.2 Materials for Components of LIBs

Most of the commercial LIBs comprise of an anode (carbonaceous, Li based compounds or Li metal)[6]–[14] and lithium infused metal oxides as cathode[15]–[26] with a solution of lithium salt in an organic solvent as the electrolyte (1M LiPF₆ in 1:1 v/v ethyl and methyl carbonates)[27]–[38]. On the basis of the anode chosen, the rechargeable systems are called as Lithium battery consisting of Li metal as anode and as LIB consisting of other materials as anodes. Figure 1-7 shows various classes.
of materials that have been explored as cathodes and anodes for LIBs and their respective intercalation potentials vs Li/Li$^+$ and their capacities.

Figure 1-7- Voltage versus capacity for positive- and negative-electrode materials presently used or under serious considerations for the next generation of rechargeable Li-based cells. [1]

1.2.1. Anodes for LIBs-

Commercially adopted anodes such as graphite and silicon have been reported[39] to provide capacities of ~300 to 4200 mAh g$^{-1}$ respectively. Apart from graphite, other structures of carbon such as carbon nanotubes, carbon nanofibers and graphene and many other organic materials have been reported as potential anode materials. There have also been reports of synthesis of hybrid structures of carbon nanotubes and graphene which have been predicted to demonstrate better
electrochemical performance. But, carbon is known to undergo irreversible reaction with lithium during the first discharge forming a layer of the SEI. This results in decrease in the number of active sites on the surface of the electrode and a drop in the capacity is observed.

Alternatives to carbon anodes have been explored in parallel with the hope of finding materials with better capacities and stability (electrochemical and thermal). Several lithium based nitrides[40] and intermetallics [8], [41]–[44] have been reported to have good electrochemical performance (up to 600 mAh g\(^{-1}\)). But, poor cyclic stability resulting from large volume changes remains a major challenge in such electrodes. Tailoring spinel or olivine structures by the selection of appropriate Curetransition metal oxides have resulted in a new class of electrochemically active materials which can provide constant potential. One such example is lithium titanium oxide, Li\(_4\)Ti\(_5\)O\(_{12}\) (LTO) which provides a constant voltage of 1.5 V vs Li/Li\(^{+}\). LTO undergoes transition from spinel to rock-salt structure upon intercalation of lithium, resulting in Li\(_7\)Ti\(_5\)O\(_{12}\) [45]–[47].

1.2.2. Cathodes for LIBs-

Cathodes are a source of the lithium ions in the cell and materials with large amount of reversible Li in the lattice provide larger capacities and greater energy. A few early efforts in developing cathodes for LIBs began with the development of fluoride based (CF)\(_n\) systems[48], [49], followed by transition metal oxides such as silver vanadium oxide Ag\(_2\)V\(_4\)O\(_{11}\) which was widely used in implant devices[50]–[52].
In spite of high cell potential of 3V, electrochemical reaction using this system was irreversible which limits them for primary battery applications.

The current generation cathode material must fulfil the following properties for successful operation in a LIB:

1. Presence of a transition metal which can readily undergo redox reactions.
2. High free energy of reaction with Li and at high electrochemical potential.
3. High capacity with one or more exchangeable lithium per transition metal.
4. Structural stability of lattice upon reversible insertion and extraction of Li.
5. Low cost and environmentally benign

In spite of high voltages corresponding to high energy densities, LIBs are sought after for their high power densities which is the rate at which energy can be extracted from a battery. Albeit high lithiation potential, cathodes need to be extremely resistant to the large structural changes that occur during fast lithiation and de-lithiation dynamics. Further, safety of a battery is the most important criteria during its entire lifetime. A safe LIB cathode does not undergo structural decomposition releasing hazardous by products or gases which may potentially lead to explosions or fires.

Cathodes can be broadly categorized into three groups as shown in Figure 1-8

(i) Structures which have a transition metal oxide framework with metal cations ordered in all the layers (layered and spinel) and
(ii) Materials with open structures like tunnel compounds, olivine based with poly-anion framework, etc.

Figure 1-8- Li-ion battery cathodes: important formulae, structures, and potential profiles during discharge[53]

1.2.2.1. Layered Structures

The progress in cathode development incorporating intercalation chemistry [56]-[61] established layered chalcogenides as stable systems. TiS$_2$ was widely sought after owing to its favorable layered structure, high capacities and intercalation potentials (~3V). In spite of successful operation, limited cycle life, large volume changes resulting in breakdown of structural integrity and dendrite formations due
to Li plating causing safety hazards were few of the major challenges which prompted for an alternative to the chalcogenides systems[62]. Transition metal based layered oxides such as V$_6$O$_{13}$ [63] and Li$_x$MO$_2$ (M= Co, Ni, Mn) were reported to demonstrate higher capacities and voltages owing to more pronounced ionic character of the M-O bond and have gained significant interest[16], [64]. Several years of optimization of challenges pertaining to electrodes and the electrolytes resulted in the commercialization of the LiCoO$_2$ (LCO)/C based LIBs in 1991 with a potential of 3.6V. Following the commercial success of LCO, a large number of analogues and other oxide based layered structures have been investigated[65]–[69]. Lithiated oxides which can act as a source of Li are typically used in LIBs, while oxides such as V$_2$O$_5$ can be used only in Li batteries.

1.2.2.1.1. Vanadium based oxides

The structure of layered V$_2$O$_5$ consists of VO$_6$ octahedra sharing edges with each other. The characteristic distortion in the VO$_6$ octahedra is the reason for the assembly into large number of layered structures[70]. Figure 1-9- Schematic showing atomic arrangement in V2O5 and the stacking of the layers [71].show the schematic of a unit cell of α- V$_2$O$_5$ which exists as orthorhombic structure with space group $Pmnn$. [71]
1.2.2.1.2. Electrochemistry of V$_2$O$_5$

Intercalation of electron donating cations induce electronic conductivity into the structure, known as mixed conductors, which is ideal for use as electrodes in LIBs [72], [73]. V$_2$O$_5$, devoid of exchangeable Li, was subjected to an initial discharge to saturate the lattice with Li atoms for further electrochemical redox reactions. The process of lithiation of V$_2$O$_5$ begins with the formation of $\alpha$- Li$_x$V$_2$O$_5$ for up to 1% of Li in the lattice. Subsequent intercalation of Li transforms $\alpha$- V$_2$O$_5$ phase to $\varepsilon$- phase for $0.35 < x < 0.7$. The $\delta$- phase forms for $x = 1$ by gliding of layers in the b- direction. An efficient reversibility can be achieved for $x = 0.5$ Li which corresponds to a specific capacity of 147 mAh g$^{-1}$. Irreversible transformations can be observed under over-charge or deep- discharge conditions where in, more than 1 Li atom is intercalated.
into the crystal resulting in a severely puckered γ-phase. The α/ε, ε/δ and δ/γ transformations can be observed in a lithiation profile of V₂O₅ as potential plateaus at 3.4 V, 3.2 V and 2.3 V respectively as shown in Figure 1-10. The reversible half-cell reactions showing the formation of different phases at different stages of lithiation[74]–[76].

\[
\begin{align*}
\alpha V_2O_5 + 0.5 Li^+ + 0.5 e^- & \leftrightarrow \epsilon Li_{0.5}V_2O_5 & (1-4) \\
\epsilon Li_{0.5}V_2O_5 + 0.5 Li^+ + 0.5 e^- & \leftrightarrow \delta LiV_2O_5 & (1-5) \\
\delta LiV_2O_5 + 1 Li^+ + 1 e^- & \leftrightarrow \gamma Li_2V_2O_5 & (1-6)
\end{align*}
\]

In α-, ε-, and δ-phases the VO₅ square pyramids are arranged in rows with the apexes ordered up, up, down. In the highly puckered gamma-phase, these are organized up, down, up, down. Further attempts to lithiate the γ-phase results in the formation of a tetragonal ω-phase at 1.9 V which is preserved upon reversible cycling within 0.4 < x < 2.65 [77]. This omega-phase cycles in a single solid-solution phase with the last lithium coming out at over 4 V. The omega-material has a tetragonal structure, which on extended cycling becomes a simple rock-salt structure with a = 4.1 Å with the formula Li₀.₆V₀.₄O. These structural modifications can be attributes the high OCV at low lithium content to the meta-stability of the defective rock-salt lattice which can contain up to 60% vacancies on the cation sub-lattice.
Figure 1-10- First cycle discharge profile of V$_2$O$_5$ plotted as voltage (vs Li/Li$^+$) vs capacity showing various phase transformations during the discharge.

Development of gel structures have resulted in improvement in the performance of the V$_2$O$_5$ and several methods of synthesis of gels have been proposed [78]–[81]. Subsequently, it was realized that further improvement in the performance can be achieved by oxygen annealing of the gels to form nano-
crystalline $V_2O_5$ [71], [80], [82]. Nano-crystalline structures offer facile strain relaxation, shorter Li diffusion distances and higher surface area.

Recent research interest is targeted towards other layered oxides of V among which $V_6O_{13}$ and VO$_2$ have gained attention for their comparable electrochemical properties. $V_6O_{13}$ consists of alternate single and double vanadium oxide layers with an average 4.33 oxidation state of V. The maximum uptake of Li corresponds to the complete reduction of V to +3 state which is equivalent to a theoretical energy density of about 900 Wh kg$^{-1}$ [83]. Detailed investigation of the structural transformation of $V_6O_{13}$ concludes a lithiation capacity of 4.5 Li per formula unit of the compound by chemical lithiation methods and a capacity of 8 Li per formula unit during electrochemical lithiation. Similar to $V_2O_5$, $V_6O_{13}$ also undergoes several phase transformations during the lithiation process resulting in an overall expansion of 7.6% at the end of complete lithiation[83]–[95]. Multiple phase transitions involving decrease in electronic conductivity and lack of structural stability owing to large volume changes render it unviable for commercial application.

On the other hand, the monoclinic rutile form of VO$_2$ is an electrochemically active polymorph with a stable capacity of 120 mAh g$^{-1}$ at a voltage cut off of 2V [96]. The metastable VO$_2$ (B) intercalates Li at a potential of 2.5 V and exhibits good capacity retention of 250 mAh g$^{-1}$ from an initial capacity of 300 mAh g$^{-1}$ making it suitable for application as cathodes in LIBs [97]–[102].
1.2.2.1.3. **LiₓMO₂ type and its derivatives**

Lithium cobalt oxide (LCO) is the most common material of this type of Li containing layered transition metal oxides consisting of rhombohedral symmetry with the space group $R3m$ and is suited to accommodate large changes in Li concentration. This crystal structure of closed-packed oxygen layers stacked in an ABC sequence with Co and Li ions residing in octahedral sites in alternating layers between the oxygen planes as shown in Figure 1-11. The cubic close-packed lattice of LCO facilitates electrochemical removal of Li which transforms to hexagonal CoO₂ on complete de-lithiation.

![Figure 1-11- Schematic of LiCoO₂ unit cell drawn with lithium ions horizontally between CoO₂ octahedra. Lattice parameters $a_{hex.} = b_{hex.} = 2.8138$ Å and $c_{hex.} = 14.0516$ Å, and the figure on the right is the projection along the [110] zone axis showing lithium, cobalt and oxygen atoms in columns [103].](image)
1.2.2.1.4. Electrochemistry of LiCoO$_2$

The Li ions undergo unobstructed reversible de-intercalation in two dimensional pathways resulting in electrostatic repulsions of CoO$_2$ sheets and expansion in hexagonal lattice along the c axis leading to instability in the lattice.

Figure 1-12 shows the typical charge-discharge profile for LixCoO$_2$ between 3.6-4.85V vs Li/Li$^+$. The sequential formation of several phases is indicated as the x varies between 1 and 0.05. Efficient reversible cycling of LCO can be achieved for de-lithiation only up to Li$_{0.5}$CoO$_2$ corresponding to a capacity of 140 mAh g$^{-1}$ beyond which, the structural integrity of the lattice is compromised. The upper cutoff voltage of LCO of 4.2 V, corresponds to extraction and insertion 0.5 Li per LCO via a three stage process which is shown as three voltage plateaus in. The first plateau relates to the first order metal-insulator transition between two hexagonal phases with a variation in Li fraction (x) between 0.75 < x < 0.95. Subsequent phase transitions around x = 0.5 are order/disorder transitions which are reflected as two voltage plateaus at 4.1 V. Such changes in concentration in the lattice leads to several anisotropic strain changes, induced by the Jahn-Teller-Distortion, which greatly affect the rate constants of the electrochemical intercalation and de-intercalation [103], [104].
Figure 1-12- Charge-discharge curves $\text{Li}_x\text{CoO}_2$ at C/24 rate in the range 3.6–4.85 V vs. Li$^0$/Li$^+$. The sequence of the several phases is indicated as $x$ varies from 1.0–0.05 [105].

A higher cutoff of 4.5V results in a faster fade in capacity and Co deposition on the Li anode. Extensive research has been conducted to understand the mechanism for dissolution of Co into the electrolyte and the subsequent occurrence on the
negative electrode [106], [107]. XAS studies by Nakai et al. and others predicted that changes in oxidation state of Co through the formation of holes (Co) as the possible compensation mechanism [108]–[113]. Alternatively, *ab initio* calculations [114]–[118] and EELS [119], [120] measurements hypothesize the formation of oxygen holes (O). Surface investigations of LCO through XANES [121] reveal occurrences of both the mechanisms which may not be a representation of the bulk of the electrode. While a vast understanding of the structural changes in LCO can be gained, the *ex-situ* nature of all these measurements could not shed light on the dynamic changes during the process of charge and discharge. Alamgir et al. have conducted *in-situ* study of Li(1-x)CoO2 based battery to identify the fundamental and transition phases during cycling [122]. It was found that the charge compensation in LCO occurs by the formation of both oxygen and cobalt holes up to removal of 25% of lithium. Further removal results in formation of Co holes alone. The ferroelectric coupling between Co4+ rich CoO2 sheets causes drop in c parameter beyond 4.2V. Similar to LiNiO2, transition of Co3+ into the octahedral sites within the Van der Waals layer through the adjacent tetrahedral sites may be a potential route for the dissolution [123], [124].

The structural changes coupled with the removal of Li atoms binding the layers lead to micro-cracks coupled with the release of Li and Co into the solution [125], [126].

The results and the predicted hypotheses agree well with the several other predictions for each of the characterization measurements [127]–[132].

Doping with trivalent cations such as Ni, Mn, Cr, etc. at Co3+ sites or coating with metal oxides or phosphates have been sought as alternatives to curb metal dissolution and improve electrochemical performance [39], [131], [133]–[138].
Efforts to stabilize the crystal structure has led to the development of several newer stoichiometry such as Li(CoNiMn)\(_{1/3}\)O\(_2\) referred to as NMC [139]–[146] and Li rich layered oxides such as \(x\)Li\(_2\)MnO\(_3\)-(1-\(x\))LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) composite [147]–[153] which exhibit higher lithiation potentials and theoretical capacities. The power densities of electrodes, on the other hand, depend on their morphological characteristics and higher power densities can be obtained by tailoring the design through control of hierarchical architecture assembly [153]–[159]. Such agglomeration of nanoparticles results in a porous microstructure increasing the effective contact area of the electrode and electrolyte. In spite of thorough understanding of the electrochemistry of the layered oxides, problems such as limited cycle life owing to Mn dissolution and the power density owing to sluggish kinetics increased cost and toxicity could not be fully overcome [148].

1.2.2.2. Spinel Structures

The quest for fabricating cathodes with higher operating potentials lead to the development of a new class of structures known as the “spinel” structures by Thackeray et al. in 1983 [64], [160], [161]. Spinels are characterized by the formula LiM\(_2\)O\(_4\) with the oxygen framework similar to that of the layered structures. The robust 3D framework of the oxygen anion facilitates faster cycling rates with enhanced structural stability during charge and discharge cycles. Thus, these structures are considered suitable for high power applications of LIBs.
1.2.2.2.1. Lithium Manganese oxide (LiMn$_2$O$_4$ or LMO)

LiMn$_2$O$_4$ or LMO belongs to the A[B$_2$]O$_4$, type spinel which crystallizes in a space group of Fd3m and a lattice parameter of 8.239 Å [64], [162]–[167]. Figure 1-13 shows a schematic of the crystal structure of a typical spinel compound. Unlike the layered structure, 3/4 of the transition metal ions occupy the octahedral positions and the remaining are located in the Li sites. Li$^+$ and Mn$^{2+}$ cations in the lattice are present on the 16d and 8a sites respectively, and the oxygen ions are located on the 32e sites. Half of the Mn atoms occupy octahedral positions and the other half are found in the tetrahedral positions forming an edge sharing network of MnO$_6$ octahedra. The nearly cubic close pack nature of the lattice provides a compact three-dimensional network for Li transport during intercalation and de-intercalation. The three-dimensional network favors use of the compound in high charge and discharge rates.
1.2.2.2.2. Electrochemistry of LMO

The de-lithiation of LMO proceeds in two voltage steps, one around 4V and another around 3V. The first voltage step corresponds to the insertion of Li ions into the smaller oxygen tetrahedral sites of Li$_x$Mn$_2$O$_4$ up to $x \leq 1$ following which the intercalation proceeds by Li ions occupying the large oxygen octahedron positions for $x \geq 1$ [64], [169], [170]. Figure 1-14 is a schematic of the typical discharge profile of LMO. Electrochemical redox reaction in spinel structures occur at constant electrochemical potential unlike the sloping profile of the layered structures indicating unaltered site energies. Larger lattice distortions upon Li intercalation and
de-intercalation affect the site energies which is minimized in spinels due to the close packed oxygen sub-lattice. In spite of intercalation in layered structures at the same lattice site for all the concentrations of Li, partial oxidation and migration of Mn into Li sites at lower potential results in two plateaus in LiMnO$_2$. However, the origin of two plateaus in spinel structures can be attributed to the intercalation of Li into tetrahedral sites for $x < 1$ and into octahedral sites for $x > 1$ [67], [171], [172].

**Figure 1-14- Profile of discharge curve in spinel lithium manganate [53]**

During the charge of a spinel lattice as shown in Figure 1-14, the Li atoms in the octahedral sites experience stronger repulsive forces from the local environment facilitating easier removal at lower potentials. Subsequent removal of Li from the tetrahedral sites, which have lower site energies, require higher energies and are extracted at higher potentials [173]–[177]. The higher potential plateau is a
combination of two plateaus each at 4.1V and 4V respectively attributed to reversible extraction/ intercalation of Li from tetrahedral sites. For large fractions \(x > 1\) of Li in the lattice \(\text{Li}_x\text{Mn}_2\text{O}_4\), the cubic spinel undergoes transformation to tetragonal spinel with vertex sharing between \(\text{MnO}_6\) octahedrons and \(\text{LiO}_6\) octahedrons and face sharing \(\text{LiO}_4\) tetrahedrons and \(\text{MnO}_6\) octahedrons. The phase transformations are associated with Jahn- Teller distortions of up to 6.5% in the unit- cell volume arising from the interactions between nonbonding electrons in the p orbital of the oxygen anions and the d orbitals of the octahedral Mn. In cubic phase, the 3d electrons in \(\text{Mn}^{2+}\) are present in the \(t_{2g}\) orbitals and the empty \(e_g\) orbitals interact strongly with the p-orbital electrons of oxygen atoms. Further lithiation adds electrons into the \(e_g\) orbitals which repel the p electrons resulting in cubic to tetragonal transformation. The reduced gap between the \(e_g\) state and the fermi level explains the abrupt drop in the plateau potential and the origin of two stage lithiation [178]–[180].

Albeit good electrochemical properties of Mn based spinels, a gradual capacity fade is observed over long term cycling. Localized anisotropy in lithiation of different particles creates non- uniform phase transformations resulting in the co-existence of cubic and tetragonal phases. This mixed phase composition has been predicted to be the cause of capacity loss due to the disproportionation reaction [181], [182].

\[
2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}
\]  

(1-7)
1.2.2.3. Polyanion structures- NASICON and Olivine type

Polyanion structures (NaSICON or olivine type) built from corner sharing MO$_6$ octahedra and XO$_4$ tetrahedra anions have gained recent interest owing to their excellent structural stabilities due to strong nature of the M-O bonds. Phosphate based olivine structures (Pnma) with Fe$^{3+}$/Fe$^{2+}$ and V$^{4+}$/V$^{3+}$ have been demonstrated to have higher redox potentials than their oxide counterparts and hence can deliver higher energy densities with good cyclic stability. Poor electronic conductivity, however, have limited their use in commercial systems as compared to the oxides which can be improved to a certain extent through physical, chemical and morphological modifications. Surface coatings, alternative synthesis routes to produce large surface area structures, chemical doping, mechanical grinding, etc. were some of the proposed approaches to tailor particles for desired properties.

1.2.2.3.1. Lithium Iron Phosphate (LiFePO$_4$) (LFP)

The most common phosphate based system, LiFePO$_4$ known as LFP, consists of phosphorous atoms occupies the tetrahedral sites and iron atoms occupy the octahedral sites as shown in Figure 1-15. The lattice parameters of an ordered phase of LFP consists of a = 10.333 Å, b = 6.011 Å, and c = 4.696 Å, while those synthesized at higher temperatures may contain iron atoms in the lithium site, which is reflected in the lattice parameters of a = 10.381 Å, b = 6.013 Å, and c = 4.716 Å blocking diffusion of the lithium ions [183], [184].
1.2.2.3.2. Electrochemistry of LFP

The de-lithiation mechanism of LFP involves oxidation of Fe$^{2+}$ to Fe$^{3+}$ to form FePO$_4$ which is immiscible into LFP forming a two phase mixture [185]–[192]. Electronic conduction in LFP occurs by polaron hopping [193] and is low ($10^{-9}$ S cm$^{-1}$) for pure LFP [15].

Figure 1-15- Schematic of atomic arrangement in Lithium Iron Phosphate [183], [184]
Several methods have been reported to improve the conductivity of LFP by heat treating to increase hole conductivity [194], addition of conductive phase [195], [196], doping of other transition metals such as Mn [197], [198], Co [199], [200], V [191], Ti [201], Zn [202], Al, Mg [203]–[206], change of morphology and microstructure [207]–[211], etc. Most of the dopants induce p-type conductivity limiting the possibility of increase in the number of holes. Such induced positive defects can be compensated with a negative charge which may be created by positive cation vacancies or oxygen interstitials. High free energies of formation of negative compensation does not favor the oxygen vacancies or the phosphorous removal and the charge compensation by the removal of Li or Fe would lead to an increase in the number of electrons in the conduction band. The most plausible conduction mechanism is the creation of holes to compensate for the Li vacancies.

The voltage profile during the electrochemical charge discharge of LFP half-cell at constant current is depicted in Figure 1-16. The strong P–O covalence stabilizes the anti-bonding Fe3+/Fe2+ state through this Fe–O–P inductive effect justifying a high lithium intercalation voltage of 3.4V versus Li/Li+. 
Electrolytes for LIBs

The electrolyte may be considered as the inert component of the battery compatible with both the cathode and the anode surfaces. Li ions in the electrolyte migrate from one electrode to another during the process of charge and discharge while maintaining the electrical neutrality of the system. A good electrolyte in a LIB must possess the following criteria:
(i) High ionic conductivity and low electronic conductivity

(ii) Large electrochemical stability- No decomposition until high potentials

(iii) Chemical inertness with all other components of the battery

(iv) High thermal stability

(v) Low toxicity and environmental benignity

Based on the solvent used to fabricate the electrolytes, they may be categorized as aqueous, non-aqueous, polymer gel, solid polymer, hybrid, electrolytes, etc. A few most common electrolyte types have been elaborated in this section.

1.2.3.1. Organic electrolytes

These are most common non-aqueous type of electrolytes that was first to be commercialized in early 1990s. Commercial LIBs contain Lithium hexafluorophosphate (LiPF₆) salt dissolved in organic carbonates in particular, mixtures of ethylene carbonate(EC) with dimethyl carbonate (DMC), propylene carbonate (PC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC). These solutions fall into the category of polar aprotic solvents which include ethers, esters, alkyl carbonates, nitriles and sulfones. The inset in Figure 1-17 shows the cathodic and anodic stabilities of various organic solvent based electrolytes and the changes in the stability limits with the addition of various Li salts. Alkyl carbonate solutions consisting of C atoms at 4+ oxidation state have high anodic and low
cathodic stability and are considered apt for high voltage LIB applications. However, the anodic stability of the electrolytes is defined by the catalytic oxidation of the anions on the electrode in contact and varies with surface.

Figure 1-17- The anodic behavior of Al foils (CC for cathodes) in various Li salt solutions (alkyl carbonates). The anodic stability of Li battery systems depends on passivation phenomena of Al CC. The inset includes schematic potnetio-dynamic behaviors of various families of non-aqueous solutions, containing tetra-alkyl ammonium salts (e.g. (C₄H₉)₄NClO₄), with inert electrodes (Pt, glassy carbon) [212].

The Figure 1-17 depicts the potentio- dynamic current response of Al foil for LIB cathodes in various alkyl carbonate solutions. Al foils reach most passivation with
LiPF$_6$ due to the formation of insoluble species such as AlF$_3$ and Al (PF$_6$)$_3$ that block any dissolution of Al ions into the solution. On the other hand, despite low cathodic stability of alkyl carbonates attributed to the cations can reach very stable passivation on Li- graphite anodes [213]–[215].

In spite of commercial success of the alkyl carbonate electrolytes, the passivation of the electrodes are not complete. There are several other inevitable problems which eventually result in detrimental failures, especially at elevated temperatures. Further, deposition of transition metals onto anode surfaces affect the passivation properties of the current collectors which considerable worsen the performance leading to capacity fade [216], [217]. The stability of the passivation layer can be enhanced by pre- surface treatments by use of solution additives that react on electrodes to form surface films. Following the extensive research, a variety of organo- boron compounds and functional groups such as sulfones [218], [219], amide [220], carbonates [221], [222], etc. have been proven as effective film- forming additives. Additives containing electron withdrawing groups such as –CN, Cl or F facilitate reduction of the electrolyte and stabilize the passivation layer. Organic additives result in polymeric SEI formation initiated by the organic groups. Yong et al. demonstrated polymeric SEI formation using allyl cyanide (AC) on graphite electrode in which the polymerization is initiated by the double bond of AC. In other cases containing electron withdrawing groups, the polymerization proceeds through a radical formation mechanism [223]–[231]. A recent research in compounds containing halogen functional groups have seen improved electrochemical performance. Halogens aid in surface modification of electrode materials increasing
the electronic conductivity of the electrode. McMillan et al. have reported the use of halogens in electrolyte as additives such as chloro-ethylene carbonate and fluoro-ethylene carbonate with organic solvents, propylene carbonate (PC) or ethylene carbonate (EC) showed increased cycle life [232]–[236]. Beyond the anode additives, cathode additives have also been developed to suppress many side reactions which are involved during the cycling of a cathode. Transition metal dissolution causing of capacity fade is a common challenge with cathodes. Addition of film forming additives which are expected to oxidize prior to the solvents have been explored. Abe et al. [225], [237] reported organic additives having lower oxidation potential than the organic electrolytes to improve the cycle performance of LCO at high voltage. Several similar attempts to suppress the oxidative decomposition of LCO and their derived compositions have been explored for high voltage applications [238]–[249]. Mn based spinel structures also have serious problems of Mn dissolution, Jahn- Teller distortion, HF attack leading to structural decomposition. Hexamethyldisilazane in the electrolyte prevents the formation of HF by dehydration and acid neutralization and suppresses capacity fading after storage at high temperatures [250]–[252]. Similarly, additives containing boron, silane and phosphorous functional groups have been shown to have great improvement in cyclic performance [253]–[256].

1.2.3.2. Polymer electrolytes

The study of polymers as electrolytes for energy storage devices was initiated by Fenton et al. in 1973, but gained interest after the research by Armand et al. investigating technological significance [257]. Inspired by this work, several new
systems were developed and structural and electrochemical properties were investigated through experimental and theoretical modeling methods [258]–[260]. The main motive behind the development of polymer electrolytes was to overcome the low mechanical strength and safety issue of liquid electrolytes by suppression of dendritic Li deposition. Though broadly classified into solid electrolytes, the mechanism of ionic conduction through these systems occurs via polymer matrix unlike ion hopping in case of other solid electrolytes. Conventional polymer electrolytes possess ionic conductivities in the range $10^{-3}$ to $10^{-2}$ S cm$^{-1}$, Li ion transference number of 0.5[261]–[263], chemical, mechanical and thermal stabilities.

Although a large number of polymer electrolyte systems have been prepared and characterized, it is possible and convenient to group all the polymer systems into two broad categories, i.e., pure solid polymer electrolyte (SPE) and plasticized or gelled polymer electrolyte (GPE) systems. The most common polymer matrices that have been used as SPEs are (poly) Ethylene Oxide (PEO) [264]–[270], (poly) Acrylo Nitrile (PAN) [271]–[276], (poly) Methyl Methacrylate (PMMA) [277]–[279], (poly Vinyledene Fluoride (pVdF) [280]–[282], etc. Among these, poly (ethylene oxide), PEO which have the inherent advantages of dimensional stability, safety and the ability to prevent dendritic Li growth have been explored for commercial applications. In spite of good ionic conductivities of PEO systems, higher values are essential for room temperature LIB applications which can be achieved by adding plasticizers [278], [283], [284] or by addition of room temperature ionic liquids (RTILs) as additives [285]. Modified PEO electrolytes have been efficiently demonstrated in LIBs consisting of LiMn$_2$O$_4$ [286] and LiFePO$_4$ [287].
Gel electrolytes are usually obtained by incorporating a larger quantity of liquid plasticizer and/or solvents to a polymer matrix that is capable of forming a stable gel with the polymer host structure. The conduction mechanism in polymer gels is similar to that in the liquid electrolytes, but a gel has improved safety and shape flexibility over a liquid. The most commonly used polymer gel electrolyte is poly(vinylidene fluoride) (PVdF) to which hexafluoropropylene (HFP) is typically added to reduce the crystallinity of the polymer [288]–[291]. Variations such as incorporation of small amounts (up to 7 wt%) of ceramic fillers such as alumina [292], silica [293], titania [294], BaTiO3 [295], etc. into the GPEs was also explored to tailor the porosity, ionic conductivity and to enhance mechanical properties of the gel electrolyte. Attempts to increase the conductivities by addition of RTILs and ceramic particles have resulted in positive effects and have also shown improved performance of LIBs [296]–[300].

1.2.3.3. Solid ceramic electrolytes

Ceramic electrolytes are the most suitable materials for high temperature applications and other extreme conditions. Unlike molten salt electrolytes these systems provide workable Li-ion conduction in the solid state and also eliminate the need for containment of the otherwise used liquid electrolytes and have been used in LIBs [301]–[303]. The solid ceramic electrolytes, however, exhibit ionic conductivities between $10^{-6}$ to $10^{-4}$ mS cm$^{-1}$ with increase in temperatures which is still very less compared to organic or polymer gel electrolytes at room temperature (10 mS cm$^{-1}$) due to large interfacial resistances. Oxides [304]–[308], sulfides [309]–
[311] and phosphate[312]–[316] based compounds have been reported as the most common systems.

Inability of solid electrolytes to access interior of the electrodes (poor electrolyte diffusion) limit their use only to thin-film based LIB technology. Several attempts to increase areal energy density of such thin-film LIB by increasing active electrode thickness, led to significant loss in both power and energy density of the cell due to unutilized active electrode material [317]–[321]. Thus, it is necessary for a high temperature electrolyte system to possess good wetting properties with the electrode and high Li-ion conductivity over the entire operating temperature range to realize a working LIB in the desired thermal window.

1.3 Current state of LIBs at High temperature

In spite of excellent energy storage and delivery capabilities of LIBs, the commercial technologies are still plagued with severe safety challenges. Continuous reversible charge and discharge of a LIB was found to demonstrate fires as a result of short circuits and battery failure. Dendritic mossy growth on lithium surfaces due to uneven Li plating leads to short circuiting of the electrodes and a large tunneling of electrical energy between the electrodes leads to internal heating of the cell. Boiling and combustion of the organic electrolyte and subsequent rise in internal pressure due to evolution of combustion gases cause explosion and fires. Many earlier commercial technologies have been discontinued for safety reasons. Figure 1-18
shows some examples of fires in commercial battery packs used in iPhones, Dell laptops and the cockpit of Boeing Dreamliner.

$\beta$-$\text{Al}_2\text{O}_3$ ($11\text{Al}_2\text{O}_3\cdot x\text{Na}_2\text{O}$) was first proposed by Ford Motor Company in 1967 as a solid electrolyte as an alternative to aqueous electrolytes which demonstrated high Na ion conductivity at elevated temperatures. The decline of the oil market in 1970s and the promise of higher voltages and energy densities have garnered tremendous interest to developed high-temperature Na ion batteries using non-aqueous electrolyte systems. As a result, Na-S and Na-$\text{NiCl}_2$ batteries with operating temperatures beyond 350°C have been commercialized [322]. On the other hand, the Na-$\text{NiCl}_2$ (“Zebra”) battery employs a molten salt NaAlCl$_4$ electrolyte Moderate specific energies of about 100 Wh kg$^{-1}$ and concerns about the possibility of a violent uncontained reaction between molten Na and molten S in Na-S systems and the reduction of the electrolyte in Na-$\text{NiCl}_2$ system to Al metal and NaCl in the event of $\beta$-$\text{Al}_2\text{O}_3$ rupture limit these systems for stationary applications. At present, Na–$\text{NiCl}_2$ batteries are being marketed for stationary, back-up energy storage as well as niche mobile applications, such as demanding submarine applications (Rolls Royce), hybrid diesel–electric locomotives (General Electric), and bus fleets (Fiamm Sonik/MES-DEA).
Figure 1-18- Real time pictures showing battery fires in iphone, Dell laptops and Boeing Dreamliner cockpits showing disastrous consequences of heating of comercial LIBs.

Realizing high temperature rechargeable LIBs has been unsuccessful due to unavailability of safe operating ceramic electrolyte for a long time. High temperature resistant polymer electrolyte LIBs were developed for stationary storage applications
as preliminary alternative that could operate well between $80^\circ$C and $120^\circ$C. However, problems of dendritic deposition and short circuiting were inevitable in such systems which led to the discontinuation of the commercial production of these devices [323], [324]. The challenge of developing LIBs which can operate at high temperatures persists owing to lack of safe electrolytes and degrading electrode reactions.

### 1.4 Improving power density of LIBs

In spite of several advantages, low power densities of the state of the art LIBs limits their use in applications such as mobile phone batteries, mobile electronic devices etc. Slow diffusion kinetics of lithium in the electrode causes underutilization of the electrode when cycled at high rates. This results in high over potential and excessive internal heating of the cell leading to explosion or fire. Development of LIBs with high power capability is a major challenge which, if accomplished, can greatly expand the horizon of the applicability of LIBs to applications from camera flashes to micro sensors. Figure 1-19 shows a plot of power density versus the energy density of various energy storage devices and their relative comparison. It can be seen that supercapacitors deliver the highest power densities with very low energy densities while LIBs possess high energy densities with moderate power densities.
Figure 1.19 - Ragone plot comparing the volumetric power density versus volumetric energy density of various energy storage technologies [325]

For conventional lithium ion batteries, typical volumetric energy and power densities are around $10–60 \, \mu W \, h \, cm^{-2} \, \mu m^{-1}$ and $1–100 \, \mu W \, cm^{-2} \, \mu m^{-1}$. It is possible to achieve higher power density, up to $1,000 \, \mu W \, cm^{-2} \, \mu m^{-1}$, by using porous battery electrodes that reduce ion diffusion through the active anode and cathode materials, as well as designs that reduce ion diffusion time in the electrolyte and decrease electrical resistance in the electrodes [326]–[330].

The most preferred approach to improve the power density is to architecture the electrodes in 3D, thereby, reducing the lithium diffusion distances by increasing the effective contact surface area with the electrolyte. This facilitates excess lithium
uptake from the electrolyte in a very short time. Several reports have been published explaining various approaches to obtain 3D electrodes and stable cycling data has been obtained. [9], [12], [331]–[333]. Further, reducing the feature size of the microstructure of the active material shortens the diffusion distances in the solid. A combination of larger electrode/electrolyte interface area and short mean path within the solid lattice enhances the power density of the cell.

1.4.1. Nano structuring electrodes

Nano structuring of battery materials into several morphologies have been intensely explored and have been reported to achieve orders of magnitude increase in power densities. The power density in a LIB is limited by the size of the poorly conducting ceramic cathode particles which do not provide sufficient electronic and Li ion conductivity for fast charge and discharges. Coating active particles with conducting phases such as graphitic carbons was suggested as a reliable approach for increasing the electronic conductivity between the particles. However, poor Li diffusivity within the solid crystal lattice and the unstable anion framework to structural changes during Li intercalation and de-intercalation restrict the use of cells at high C-rates. Although most of the C based anodes demonstrate high electronic conductivity and the layered structure facilitates easy diffusion of Li ions, large structural and volumetric changes in large particles result in stress related cracking and failure of the electrode. Reducing the particle or flake sizes reduces the absolute volume changes and related stresses and have been shown to increase the cyclic stability of the electrodes.
1.4.2. Conformal deposition

Albeit fabricating electrodes with 3D architecture, effective conduction of electrons generated as a result of redox reactions is achieved through good contact with the current collectors. Specifically, high rates of charge and discharge demands faster conduction of electrons which otherwise, results in charge build up over the surface of the electrode. This leads to over potential effects and subsequently loss in energy density. There have been several reports on fabricating various 3D current collector architectures and their specific applications [334]–[336]. A summary of the most common architectures have been depicted in Figure 1-20.
The most common methods of deposition of electrode materials onto current collectors is by slurry coating, spraying, sputtering, etc. Although commercially applied, these methods are viable for large area bulk electrodes with thicknesses about 20-30 µm. However, they do not offer conformal coatings on to 3D electrodes, thereby, obstructing the access of the electrolytes to the interior of the electrode by filling up the entire pore volume. Several other techniques such as chemical vapor
deposition (CVD), electrodeposition, atomic layer deposition (ALD), etc. have been developed in the recent times which provide highly controlled layers. [337]–[339]

1.4.2.1. Chemical Vapor Deposition

Chemical vapor deposition (CVD) has been identified as the most effective technique to grow or deposit high quality high performing materials. Often used in the semiconductor industry, a wide range of materials from polycrystalline to amorphous can be grown in a single step through a bottom up approach. The process offers a great control over the quality and the quantity of the film and can be easily scaled to commercial volumes. Depending on the deposition conditions, CVD can be classified into several categories. However, Atmospheric CVD using liquid precursors is the most common laboratory scale method adopted for the growth of most of the materials. Figure x shows a schematic of a typical CVD process setup for the growth of carbon nanostructures and mechanism using a liquid precursor.

Figure 1-21: Schematic diagram of the chemical vapor deposition apparatus for growth of carbon nanostructures [340].
Since the discovery of CNTs, there has been a great interest to grow carbon nanostructures and numerous CVD processes have been developed for different morphologies [341]-[344]. Graphene has been among the most widely explored structures and CVD stands as a one-step process to achieve impurity free graphene and its modified analogues with high reproducibility to tailor specific properties for different applications. In spite of increased theoretical capacity and superior electronic properties, application of graphene as an active material in energy storage devices is difficult as graphene nano-sheets produced by wet exfoliation tend to aggregate during the preparation and application processes causing discontinuous pathways that limit fast ion transport. Recent advancements in CVD techniques had facilitated growth of graphene on various metallic substrates such as Ni,[345], Cu [346], Pd [347], Ru [348] and Ir [349]. Mattevi et al. (2010) [350] has done a comprehensive review of various reported variations. Other methods such as doping CVD graphene lattice to improve the electronic conductivity were explored [351], [352], among which nitrogen doped demonstrated good rate capabilities of LIBs with capacities of about 1500 mAh g⁻¹. Chemical doping combined with microstructural modifications have proven to improve the performance significantly owing to advantages of high surface area and modified conductivity by the presence of hetero atom. Recent attempts have successfully resulted in the development of CVD grown graphite networks onto prefabricated metallic templates with controlled geometries for large scale energy storage electrodes [353]-[355].

Beyond carbon, CVD of semiconducting TMDCs have attracted a lot of recent attention because of their wide tunability in structure and properties via tuning layer
numbers, chemical compositions, strains of the materials, etc. Few materials widely explored are MoS$_2$, MoSe$_2$, WS$_2$, etc. [356].

1.4.2.2. Electrodeposition

The process of electrodeposition has been well established for deposition of conducting coatings onto various substrates at low temperatures. Close control of morphology and quality of the films without high temperature treatment makes this technique unique. Precise control over the deposition parameters such as voltage, time and crystallinity of the substrate surface can yield layer by layer deposition. Unlike CVD or sputtering, this facilitates conformal and selective coating onto patterned surfaces suitable necessary for realization of nanoscale architectures. Initially, the technique has been adopted for the development of nanostructured 3D metallic current collectors. Template assisted depositons of Al and Cu were widely studied and several morphological variations have been reported [357]–[359]. Subsequently, the technique has been extended to the deposition of electrodes of a LIB. Electrodeposition of MoS$_2$ from a solution of ammonium thiomolybdate as precursor has been demonstrated as bulk LIB electrodes which triggered research in exploring several other unconventional 2D systems for conformal deposition onto 3D architectures [319], [360]. Similarly, CuS using ethylenediaminetetraacetic acid-disodium–copper [361] and MnO$_2$ [9] were other systems that have been reported.
1.4.2.3. Atomic layer deposition

ALD has been sought as an important tool for obtaining highly homogeneous thin films of various materials. The technique has basic characteristics of self-assembly; in other words, in contrast to other deposition techniques, ALD proceeds through self-limitation in reactions between chemicals and substrates. It provides a great control over the thickness of the deposited layer with the precision of one atomic layer per cycle. The deposition process consists of four essential steps:

1) Precursor exposure

2) Purging of precursors and byproducts from the chamber

3) Exposure of the reactant species, typically oxidants or reagents, and

4) Purging of the reactants and byproduct molecules from the chamber

A detailed description of the process has been illustrated in the schematic in Figure 1-22. Although there are many similarities between ALD and chemical vapor deposition (CVD), the clear and distinctive feature of ALD lies in the self-limitation for precursor adsorption and alternate, sequential exposure of precursors and reactants. ALD was utilized only for limited applications in the early stage of development due to its low growth rate, but it soon evolved to be used in a wide variety of applications due to great progress in nanoscale semiconductor device fabrication such as nanotechnology, the environment and energy (lithium batteries, fuel cells and photovoltaics). [362]–[364]. Due to the benefits of ALD such as excellent conformity,
precise thickness controllability, and good film properties at low growth temperatures, its applications are expanding more rapidly than ever.

![Schematic showing the stages of deposition in one cycle of conventional ALD process](image)

**Figure 1-22- Schematic showing the stages of deposition in one cycle of conventional ALD process [365]**

In spite of large control over the film quality and the conformality, slow growth rates are still a limiting factor to adopt the technique for roll-to-roll processing of substrates rendering it economically unviable. The layer growth during such a cycle, or growth per cycle (GPC), is typically ~0.1 nm per cycle [366], [367]. In the recent times, the technique of Spatial ALD (s-ALD) was developed to enable growth of thin
conformal layers on large surface areas at extremely fast rates (1 nm/s) thereby, facilitating roll to roll process (Figure 1-23) [368]-[371]. s-ALD combines the advantages of the conventional ALD, i.e., growth of uniform, pinhole free and highly conformal thin films on large area and flexible substrates, with high deposition rates (~nm/s). For this reason, spatial ALD has been proposed as an innovative technique for the growth of thin films in the electronics and solar cell industry [372], [373]. This enables growth of large thicknesses in a very short time, which could be advantageous for 3D architectures.

In conventional ALD, the deposition reaction is divided in two time-sequenced self-limiting half-reactions, each one being separated by purge steps. In the case of Al₂O₃, one deposition cycle includes a dose of an aluminum precursor (mostly trimethyl aluminum, TMA), followed by a purge step to remove excess precursor and reactants, a subsequent oxidation step by dosing H₂O, O₂ or O₃ and, finally, another purge step. The entire process mostly takes place at elevated temperatures (thermal ALD) and at low reactor pressure, but one or more cycle steps may also be facilitated by, e.g., a plasma (plasma enhanced ALD). Thus to obtain thicker films, the cycles have to be repeated many times. As each cycle step can take up to several seconds, the overall deposition rates are of the order of hundredths of nanometers per second. One way to speed up the process is by batch processing, but this is not always compatible with industrial needs.

s-ALD concept based on the spatial separation of the half-reactions, instead of temporal, combined with gas-bearing technology. In this concept, illustrated
schematically in Figure 1-23, the reactor has separate zones exposing the precursors one by one to a substrate that moves underneath the reactor. Between and around the reaction zones, shields of inert gas separate the precursor flows. When operated properly, these gas shields can act as gas bearings, facilitating virtually frictionless movement between reactor and substrate.

**Figure 1-23- Schematic showing a roll to roll spatial ALD process and the wafer level spatial ALD fabrication by rotating head setup.**

### 1.5 Scope of Thesis

Although several applications demand the need for a rechargeable LIB stable at high temperatures, thermal instability of critical battery components impede their safe operability beyond 55°C. The ultimate goal of this thesis is to identify those vulnerable components, investigate the failure mechanisms of commercial materials at high temperatures and develop alternate materials configurations for facilitating safe operation of LIB at extreme temperatures. Chapter 1 recognizes the niche of the market for high temperature stable LIBs, provides an elaborate literature research on
different classes of materials for individual components of a LIB and a comprehensive understanding of their influence on several electrochemical parameters. Since the organic solvent based electrolytes have been identified as the bottleneck for high temperature operability of LIBs, chapter 2 deals with the development of a composite quasi-solid system as an alternative electrolyte. Several structural and electrochemical characterizations have been performed to gather thorough understanding of the mechanism of charge transfer of the system and optimizations have been made to achieve successful working of a lithium battery at 120°C. The failure mechanisms of commercial oxide based cathodes at high temperatures have been investigated in chapter 3. Subsequently, in pursuit of a material with high intercalation voltage and structural stability, phosphate based cathode composition was designed. Several chemical configurations of the composition were tested and optimized in chapter 4 to achieve a desired stoichiometry and has been demonstrated as a potential high voltage cathode in lithium battery with stable cyclability at 60°C and at 90°C. High power densities in a battery can be achieved through 3D electrode architectures current collectors and electrodes and several techniques for 3D structuring of graphene as a current collector were developed in chapter 5. CVD grown graphene was used as a substrate to deposit TMDC based high energy electrodes and have been reported to exhibit increased rate capabilities when employed as electrodes in LIBs. Chapter 6 summarizes the key findings in this thesis.
Chapter 2

Quasi solid Electrolytes for HT LIBs

2.1 Introduction

The growing demand for LIBs at extreme thermal conditions in areas such as space, defense, oil and gas exploration, etc. have created a need for development of devices which can not only withstand severe conditions but demonstrate high energy and power densities, both gravimetrically and volumetrically. Although several technologies have been developed and commercialized to cater a vast market, high temperature application has still been a challenge owing to the instability of the components in the battery assembly. For example, most of the commercial LIBs consist of organic solvent based electrolytes, as discussed in section 1.2.3, which limit their operation at high temperatures above 80°C. Other solid ceramic electrolytes which can withstand high temperatures possess poor ionic conductivities and limited wettability with the electrodes, which limit their application to thin film technologies. Applications such as sensors mounted onto drill bits for oil exploration or gas turbines demand a wide range of temperature stability (between room temperature
to 150°C) and require rechargeable energy storage devices operating at temperatures above 100°C.

The earliest technologies of portable energy storage devices were primary type which operated at temperatures only beyond 300°C [374]–[376]. Subsequently, rechargeable lithium ion batteries using organic solvent based electrolytes were first demonstrated by Sony Corporation. Several other proposed electrolyte chemistries which were polymer based or gel type had limited thermal stability owing to their low melting or softening temperatures. A stable electrolyte must satisfy the following requirements to be able to apply at high temperatures:

1. Non-toxicity, non-flammability and high boiling point
2. High thermal and mechanical stability
3. Electrochemical properties comparable to organic electrolytes
4. Reduced degradation reactions

2.1.1. Room Temperature Ionic Liquids

Room-temperature ionic liquids (RTILs) have been considered as a potential alternative to address the issue of high temperature stability. RTILs have several advantages such as low vapor pressure, non-flammability, thermal stability, low toxicity and large electrochemical potential window [296], [377]–[379]. High thermal stability and negligible vapor pressure make these systems a safe option for operation at high temperatures. There have been numerous reports of room temperature ionic
liquids being used as electrolytes in lithium half cells and have been reported to have a very high stable voltage window. These RTILs are composed of a cation like quaternary ammonium, alkylpyridinium, alkylpyrrolidinium, alkylpyrazolium and alkylimidazolium [380]–[384] combined with a variety of large anions having a delocalized charge (PF$_6^-$, BF$_4^-$ and TFSI$^-$), as shown in Figure 2-1.

![Common Cations and Anions for Room Temperature Ionic Liquids](image)

**Figure 2-1 Common cations and anions for room temperature ionic liquids [385]**

Sakaeb and Matsumoto recently proposed a novel RTIL, N-methyl- N-propylpiperidinium bis(trifluoromethanesulfonyl)imide as electrolyte base, which exhibited excellent properties in Li/LiCoO2 cell [379]. In case of the commercial graphite electrode system, RTILs undergo decomposition at voltages where lithiation occurs in graphite [references for graphite and RTILs]. The formation of an unstable
SEI layer by the reductive decomposition of the ionic liquid on an anode surface, restricts the application of ionic liquids. Therefore, an appropriate SEI-forming additive is necessary to guarantee the electrochemical performances of ionic liquid-containing electrolytes [386]–[390]. Though imidazolium and piperidinium based RTILs are both used widely as electrolytes, the major difference between imidazolium and piperidinium salts is that the positive charge is delocalized in the aromatic ring of the imidazolium salt and localized on the nitrogen atom of the piperidinium salt due to which the aromatic imidazolium core is much more readily reduced than the piperidinium system, which contain no vacant orbital. Recently, there have been reports for the use of piperidinium based ILs for high voltage super capacitors and lithium batteries [391]–[393].

2.1.2. Separators

Although RTILs can withstand much higher temperatures, another component of the energy storage device, the separator, which encapsulates the electrolyte and acts as the ion-permeable membrane separating the electrodes limits the temperature stability. Use of polymer matrices for this purpose has been proposed and resulted in the development of gel polymer electrolytes (GPE) with RTILs. In spite of good electrochemical properties of GPEs, significant expansion and shrinkage during operation causing buildup of internal stresses and structural instability and melting of most of the polymer hosts at temperatures above 100°C results in cell failure.
The electrolyte-separator bottleneck at high temperature can be resolved by eliminating the low melting polymer component and formulating an RTIL-infused ceramic composite electrolyte. Initial test of the concept for supercapacitor application [295] yielded excellent structural stability and electrochemical performance. A similar approach has been investigated in this chapter to understand the behavior of the quasi solid composite in a LIB [394]. A ceramic was mixed with an RTIL consisting of Li salt as a source of Li ions to form a quasi- solid system that can be sandwiched between the two electrodes in a LIB. The ceramic part provides the structural stability and the ionic liquids aid in the transfer of Li ions.

2.2 Experimental Details

2.2.1. Synthesis of the Quasi- solid electrolyte

The quasi- solid electrolytes used in this study were the composites fabricated using naturally occurring bentonite clay obtained from Southern Clay Products Inc or h-BN procured from Sigma Aldrich Inc., along with a solution of 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (PP13-TFSI) ionic liquid from IoLiTec and Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) from Sigma Aldrich Inc.

Most of the naturally occurring clays contain large amount of intrinsic moisture which reacts with the lithium ions resulting in the decomposition of the electrolyte or aids formation of HF, which corrodes the battery components. Hence, removal of the moisture without decomposing the layered structure of clay is essential for the stable performance of LIBs. The moisture trapped in bentonite clay is known to exist in two forms:
(i) Adsorbed moisture which is trapped within the layers of clay and

(ii) Lattice moisture which solvates the clay ions

The adsorbed moisture makes up for the greater fraction (98%) of the total amount of moisture present. However, the weak interaction of the water molecules with the clay lattice facilitates easy removal by low temperature (200°C) heat treatment. However, the strong solvation interactions of the lattice moisture requires severe and controlled thermal conditions to keep the clay structure intact.

Pre-heating of the clay at 200°C in air, followed by heating in a vacuum furnace at 650°C for 1 hour under inert atmosphere helps removal of 99.99% of moisture and is stored in an argon filled glove box. The hydrophobic nature of h-BN, on the other hand, renders it moisture free and does not require extreme thermal pre-treatment. The powders were dried at 200°C for overnight to ensure removal of traces of adsorbed moisture and stored in an argon filled glovebox. A measured volume of the PP13- TFSI was taken in a vial and heated on a hot plate under constant stirring at 120°C for 12 hours inside the glove box prior to the addition of the Li salt. A stoichiometric amount of LiTFSI was then added to PP13- TFSI and further stirred for 12 hours to obtain a homogeneous solution of desired molarity. Dried ceramic and the LiTFSI- PP13- TFSI solution were mixed in appropriate weight ratio and mechanically ground in a mortar to obtain the quasi-solid slurry. The composite with clay consisted of 1:1 (w/w) of clay and LiTFSI- PP13- TFSI. The fabricated quasi solid electrolytes were characterized for their structural and electrochemical properties.
2.2.2. Morphology and Thermal Stability Determination

The structural and physical properties of the composites was estimated using scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman Spectroscopy and Thermo-gravimetric analysis (TGA). The conditions of the measurements have been elaborated below.

2.2.2.1. Scanning Electron Microscopy (SEM)

SEM images of the dried clay powder and as-prepared composite was taken with 20 keV of electron beam under high vacuum mode (working pressure $5 \times 10^{-5}$ torr) at a working distance of 10 mm. Low (1000x) and high (100000x) magnification images were recorded to understand the changes in morphology of the particles at the macro and micro scales respectively.

2.2.2.2. X-ray Diffraction (XRD)

Cu- Kα radiation source was used to produce X-ray diffraction pattern on a Rigaku D/Max Ultima II goniometer. The spectra was recorded between 10 and 90 degrees at a sampling rate of $2^\circ \text{ min}^{-1}$ for both dried ceramic powder and the quasi solid composite.

2.2.2.3. Raman Spectroscopy

Raman spectroscopy was performed to understand the interaction between various species in the composite system. The spectra was recorded with a laser of wavelength 514 nm between 500 and 2000 cm$^{-1}$. 
2.2.2.4. Thermo-gravimetric Analysis (TGA)

The TGA was performed to understand the thermal stability of the composites to be able to use them for high temperature applications. The measurement was performed on pure clay powder and the composite system in an argon atmosphere. The samples were heated at a constant ramp rate of $10^\circ\text{C min}^{-1}$ from room temperature (25$^\circ\text{C}$) to 1000$^\circ\text{C}$ and the fraction of weight was plot as a function of the temperature. The system was allowed to cool under air.

2.2.3. Electrochemical Characterization

2.2.3.1. Voltage Stability Determination

The voltage stability of the composite electrolyte was measured using a three electrode setup using Li metal as reference and the counter electrode and stainless steel as the working electrode. The electrodes were dipped into the composite and a linear anodic sweep of voltage was performed from the open circuit voltage (OCV) to 5V and a cathodic sweep from the OCV to 0.1V at a rate of 0.1 mV s$^{-1}$. The experiment was repeated at different temperatures by heating the setup on a hot plate inside an argon filled glovebox. The current was plotted as a function of the voltage and the change in the slope indicates a redox reaction.

2.2.3.2. Ionic Conductivity Measurements

The ionic conductivity measurements were made using a 2 electrode 2032 type coin cell setup using a Potentiostat/Galvanostat with a frequency response
analysis capabilities (AUTOLAB PGSTAT 302 N ECOCHEMIE). The quasi solid composite was sandwiched and pressed up to a known thickness between 2 stainless steel foils of known diameter. Electrochemical impedance spectra was recorded with a voltage amplitude of 5 mV s\(^{-1}\) between 10 mHz and 10 kHz. The ionic conductivity of the system was calculated from the charge transfer resistance obtained using the following Vogel- Tammann- Fulcher (VTF) equation as given by equation

\[
\sigma = \frac{A}{\sqrt{T}} \exp \left[ \frac{-B}{k(T-T_o)} \right]
\]  

(2-1)

Where A, B and T\(_o\) are the fitting parameters, \(\sigma\) is the conductivity, k is the Boltzman constant and T is the temperature.

### 2.2.3.3. Lithium transport measurement

Lithium ion transference numbers were calculated following the method proposed by Vincent et al. [261], based on the current relaxation after application of a constant bias corrected by changes in the interfacial resistance of the passivation layer formed on top of lithium electrodes. Measurements were made using symmetric cells containing two lithium metal electrodes and the electrolyte, with the interfacial resistance evaluated by electrochemical impedance spectroscopy (100 kHz to 100 Hz, 5 mV amplitude with respect to the open-circuit potential). The current relaxation was performed by applying and holding a constant bias, with magnitude chosen to assure that the ohmic drop in the passivation layer is not much larger than the effective potential within the electrolyte. Lithium ion transference numbers were
calculated correcting for changes in the electrolyte conductivity, as described by Abraham et al. [395].

2.2.4. Lithium Battery Performance

2.2.4.1. Assembly

For the assembly of LIB, LTO electrodes were prepared by spray casting a slurry consisting of LTO (80 % w/w), Poly-vinylidenefluoride (10 % w/w) binder, carbon black (10 % w/w) in a 1-methyl- 2-pyrrolidone (NMP) solvent on to copper current collectors. The electrodes were then hot rolled to a thickness of 40µm. The electrolyte slurry was spread onto the lithium foil and sandwiched with the LTO electrode, and packed into a 2032 type coin cell.

2.2.4.2. Cyclic voltammetry

The cyclic voltammetry (CV) is performed on an Autolab potentiostat/glvanostat at a constant voltage ramp rate or the scan rate. The lithium battery with LTO working electrode was cycled reversibly between 1- 2 V and a plot of the current vs voltage was plotted. The measurements were repeated at different scan rates of 0.1, 0.5 and 1 mV s$^{-1}$ at a constant temperature of 120$^\circ$C and at various temperatures of 25, 60 and 120$^\circ$C at a constant scan rate of 0.1 mV s$^{-1}$.

2.2.4.3. Charge Discharge measurements

The Galvanostatic charge-discharge measurements were conducted using a battery test station from (Arbin Instruments) between the same between the same
voltage limits as that of the CV measurements and were cycled for several cycles at constant current density.

### 2.3 Results and Discussion

#### 2.3.1. Analysis of Structural and Physical properties

##### 2.3.1.1. Bentonite Clay

Bentonites are naturally occurring class of clays which are typically categorized into cationic type of clays. Most clays are composed of aluminosilicate layers consisting of one to two Si-O tetrahedral sheets and one Al-O octahedral sheet. In spite of electrostatic and hydrogen bonds between the layers, clays are known to exhibit high thermal and mechanical stability. Excess negative surface charges develop on the layer surfaces due to substitutions in central atoms which react with the cations maintaining crystallographic integrity during structural expansion and contraction. Extensive research by Pinnavaia et al. and many others have provided deep understanding of catalytic and electrochemical properties of different types of clays [396]–[400]. It was concluded that the layered structure aids in intercalation of various cations and promotes ionic conduction which is necessary for electrochemical applications. Figure 2-2 is a schematic showing the arrangement of various atoms and layers in the bentonite clay structure.
2.3.1.2. Composite electrolyte

Figure 2-3 is a schematic representation of the clay-RTIL quasi solid composite and the structure of the LIB as envisioned. The composite was fabricated as mentioned in the section 1.2.1. Absorbent properties of clay due to presence of interlayer and surface charges provide good affinity to ions in RTIL forming a homogeneous mixture upon manual mechanical grinding.
The left figure of the schematic shows a full LIB indicating the presence of the quasi-solid composite and a possible distribution of clay layers and the RTIL. A real-time image of the spread composite slurry is shown. The photographs to the right are the individual components of the composite which were mixed to form the composite. The dissolved Li salt into the RTIL provides the necessary Li ions for conduction during electrochemical cycling of the cell. Exfoliation of clay platelets by RTIL were reported earlier [402], [403] and similar phenomenon was observed upon mixing the components.

Figure 2-3- A schematic representation of the components employed for synthesis of clay–RTIL quasi-solid-state electrolyte along with the envisioned structure of the LIB.
Figure 2-4- Scanning electron microscope image of dried bentonite clay

Figure 2-5- Scanning electron microscope image of Clay-LiTFSI-PP13-TFSI
2.3.1.2.1. **Ionic conductivity**

The physical, thermal and electrochemical properties of the composite depends on the concentrations or fractions of individual components. Several weight ratios of the liquid and solid components were tested for the mechanical rigidity and a weight ratio of 1:1 was identified an optimum ratio for a stable cell assembly. Ionic conductivity measurements with varying Li ion concentration in the system provides understanding of the conduction kinetics and information relating to the relative efficiency of the electrolyte in cycling. Figure 2-6 show Arrhenius plots of the ionic conductivity vs temperature for different Li salt concentrations. 0.2 M, 0.6 M and 1.0 M molar concentrations of the Li salt were studied and their variation in ionic conductivities were plotted at different temperatures from room temperature to 120°C. Although the conductivities for a specific concentration was found to increase with temperature as predicted by the decrease in viscosity of the RTIL, the system followed a VTF type of behavior as shown in

The pre- exponential factor A is proportional to the number of charge carriers in the electrolyte. Addition of Li salt into the electrolyte increases the viscosity of the electrolyte reducing the overall mobility of the charges in the composite. Hence, a decreased conductivity was observed for higher concentrations at room temperature. However, as the temperature was increased to temperatures beyond 80°C, the composite with 1.0 M concentration of the Li salt was found to have the highest ionic conductivity indicating enhanced ionic mobility owing to reduced viscosity. A high
conductivity of 3.35 mS cm\(^{-1}\) was observed for the system with 1.0 M concentration at 120°C.

**Figure 2-6** - Arrhenius plots of varying molar concentrations of LiTFSI in clay/PPMI composite

The non-linear behavior of the ionic conductivities were hypothesized of possible increased interactions between the components of the composite. A Raman spectra of (Figure 2-7) the composite and the pure RTIL shows an increase in the high frequency component of the band at 745 cm\(^{-1}\) which corresponds to the interactions of the TFSI\(^-\). The red line is the original Raman peak which is de-convoluted and fitted.
into the peaks corresponding to the bound and free TFSI\(^-\) as shown by the blue and the green curves. The increased intensity of the green curve and the suppression of the blue curve upon addition of clay is indicative of increased TFSI\(^-\) interactions which get aggravated at higher temperatures. The interactions can, however, not be fully understood due to the complex nature of the components.

![Raman spectra](image)

**Figure 2-7**- Raman spectra of (a) LiTFSI- PP13- TFSI and (b) Clay- LiTFSI- PP13- TFSI showing increased interaction of TFSI\(^-\) on addition of clay

However, increased conductivity at high temperatures and increased TFSI\(^-\) interactions do not necessarily correspond to high Li ion transfer in the electrolyte.
Ionic conductivity is a measure of the summation of conductivities of all the cations and anions including the cations of the clay layers. Li ions transference number (T_{Li+}) is a quantitative measure of the transfer properties of the Li ions in the electrolyte and can be directly translated to the electrochemical performance of the electrolyte. Conventional organic electrolytes and other RTILs in literature typically have a T_{Li+} of about 0.1 and the clay- LiTFSI- PP13- TFSI was measured to have 0.06 at 25°C and 0.08 ± 0.02 at 120°C. The reduced Li ion transfer in the clay based systems can be because of the exfoliation of the ceramic particles releasing metal cations while trapping the piperidinium cations to balance the negative charges.

2.3.1.2.2. Thermal stability

Measurements of thermal stability of the composite have been performed using the TGA and the weight vs the temperature was plotted. The TGA plot as shown in figure x indicates excellent thermal stability of the composite up to 355°C against 370°C for the LiTFSI- PP13- TFSI alone. It can understood that the weight loss of the composite at 355°C is entirely because of the decomposition the RTIL while the ceramic stands stable. Hence, 50% weight change was observed beyond 355°C corresponding to the 50% weight fraction of the RTIL in the electrolyte composite beyond which the weight begins to stabilize again.
2.3.2. Electrochemical Characterization

2.3.2.1. Electrochemical Stability

Linear sweep voltammetry (LSV) measurements to determine the electrochemical stability of the electrolytes revealed an anodic stability of 5V for the Clay-LiTFSI-PP13-TFSI at room temperature as indicated by the blue line in Figure 2-9. The curve represented by the black line corresponds to the stability of the liquid.
LiTFSI- \textit{PP13- TFSI} solution at 120°C which also had no signs of degradation until 5V. This implies the addition of clay does not induce any side reactions at room temperature and the composite retains the stability of pure LiTFSI- \textit{PP13- TFSI} solution. However, a sudden spike in the current was seen beyond 3.1V in the red curve, corresponding the stability plot for Clay- LiTFSI- \textit{PP13- TFSI} at 120°C, implying decomposition reactions. This observation could be attributed to a thermally activated interaction between the components of the composite as indicated by the increased TFSI$^-$ interactions shown in Raman spectra, limiting the operation voltage of the composite to 3.1V. The cathodic sweep had no decomposition reactions until 0.1V for both the pure LiTFSI- \textit{PP13- TFSI} and the Clay- LiTFSI- \textit{PP13- TFSI} composite up to 120°C. From the understanding garnered from structural, thermal and electrochemical stability measurements, a 3V LIB can be developed with this electrolyte and operated successfully at 120°C. However, no conclusive evidence could be obtained from the stability plots on the type of interactions between the clay and LiTFSI- \textit{PP13- TFSI} in the system. LTO with lithiation/ de-lithiation voltages (1.5V) under 3V was used as a model electrode system to understand the performance of the Clay- LiTFSI- \textit{PP13- TFSI} quasi solid system in a lithium battery at 120°C. The non-SEI forming property of LTO in addition to its thermal and structural stability was considered compatible for use with the quasi solid composite. The cell was assembled as mentioned in section 2.2.4.1 using Li metal as anode and LTO as cathode and tested for CV and charge discharge behavior.
2.3.2.2. Cyclic Voltammetry

Comparative CV scans of the LTO/Li battery were taken between 1 and 3 V at a scan rate of 0.1 mV s\(^{-1}\) for different temperatures (25, 60 and 120\(^{\circ}\)C) and were plotted in Figure 2-10 (a). Complying with the expected behavior, the CV curves show a single redox peak at \(\sim 1.5\) V corresponding to Li intercalation and de-intercalation in LTO for all the temperatures. A broad redox peak was observed at 1.74/1.28 V for the cell at room temperature (25\(^{\circ}\)C) and the separation between the charge and
discharge can be attributed to the sluggish kinetics (reduced Li ion mobility) at room temperature. As the temperature increases, the peaks move closer to each other and the redox potentials were recorded as 1.64/1.45 V at 120°C i.e., an over-potential of 200mV. The decreased separation is due to the increased ionic mobility of Li ions in the electrolyte which reduce the activation barrier for the redox process. The respective peak positions have been labeled in the figure for scan at each temperature. Further, upon increasing the temperature to 120°C, a second delithiation peak was observed at 1.4 V which indicates a non-reversible reaction. The non-reversible nature of this peak implies consumption of Li ion by LTO reducing the coulombic efficiency (CE) of the system. Also, the degradation of the electrolyte was seen initiate beyond 2.7 V at 120°C, whereas, there is no change in current for the curves at 25°C and 60°C at 2.7V. An increase in peak currents was observed with increase in temperature indicating increased redox reactions in the device and more charge transfer. This is again related to the Li ion mobility in the electrolyte.

Figure 2-10(b) is the representative CV plots at 120°C taken at varying scan rates- 0.1, 0.5 and 1 mV s⁻¹. It can be observed that in spite of increased peak currents at higher scan rates, the lithiation peak get broader at faster scans implying that the lithiation reaction does not reach completion at 1V. Further, although there are no additional degradation reactions between 1 and 3 V, the non-reversible peak can be observed for the scan at 0.5 mV s⁻¹, which is suppressed for scan at 1 mV s⁻¹. Thus, the reaction can be hypothesized as having a slower rate constant compared to the lithiation reaction.
A comparison of the redox peak currents versus the scan rates at all the temperatures have been plotted in Figure 2-10 (c) and the values for the measurement at 120°C have been quantitatively reported in the table 1 (Table 2.1). A ratio of the anodic to the cathodic peak currents is an indicative of the efficiency of the reversibility of the reaction and a value close to 1 indicates complete reversibility. It can be seen from the table that there is complete reversibility at slow scan rates while the efficiency is compromised at faster voltage rates. The high ratios could be because of reduced intercalated Li ions during the discharge process resulting in loss of exchange current or because of unanticipated anodic reactions which contribute to additional exchange currents at the same potential. The anodic reactions could be dissolution of transitional metals or cationic exchange reactions which were not fully understood.
Figure 2-10- CV measurements of LTO half-cell using Clay- LiTFSI- PP13-LiTFSI composite electrolyte at (a) various temperatures at a scan rate of 0.1
mV s\(^{-1}\) and (b) various scan rates at 120 °C. (c) Plot of peak currents versus scan rates and different temperatures during charge and discharge cycles.

Table 2.1- Table showing the anodic and cathodic voltages at each scan rate at 120°C and the ratio of peak currents

<table>
<thead>
<tr>
<th>Scan rate (mV s(^{-1}))</th>
<th>(E_{pa}) (V)</th>
<th>(E_{pc}) (V)</th>
<th>(E_{1/2}) (V)</th>
<th>(\Delta E) (V)</th>
<th>(I_{pa}/I_{pc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.65</td>
<td>1.45</td>
<td>1.55</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.73</td>
<td>1.36</td>
<td>1.54</td>
<td>0.37</td>
<td>1.56</td>
</tr>
<tr>
<td>1.0</td>
<td>1.81</td>
<td>1.28</td>
<td>1.54</td>
<td>0.53</td>
<td>1.57</td>
</tr>
</tbody>
</table>

2.3.2.3. Cyclic stability

The long term stability of the electrolyte to several cycles of charge and discharge was estimated by charging and discharging of the LTO/Li cell with the Clay-LiTFSI-PP13-TFSI quasi-solid system. Figure 2-11 (a) is a voltage profile with the capacity stored of the Li battery cycled with a C-rate of C/3 at 120°C. The black curve corresponds to the first cycle and profiles of few other cycles up to 100 cycles were compared. Since LTO is devoid of reversible Li, the electrode must be lithiated first by discharging the cell to 1V. Subsequently, the charge discharge cycling is continued. At C/3 the first discharge profile indicates two closely related plateaus corresponding to the two discharge peaks in the CV profile while the charge profile indicates one plateau at ~ 1.5V. The two discharge plateaus could be attributed to additional
reactions in the discharge step. The reactions also occur in the charge step but are merged into one another and is shown as one plateau. However, this secondary reaction is consistent and contributes the same amount of capacity for all the cycles which is directly translated into a capacity of 65 mAh g\(^{-1}\). A reduced capacity as compared to the theoretical capacity of 150 mAh g\(^{-1}\) may be because of the increased interactions of the electrolyte components. Figure 2-11 (b) is the cyclic stability plot of capacity of the cell against the number of cycles. It can be seen that the capacity remained stable for over 100 cycles of charge-discharge as indicated by the blue and red curves corresponding to the charge and discharge capacities respectively at a C-rate of C/3 with a coulombic efficiency (CE) of about 99% for all the cycles indicating complete reversibility of the redox process.
A probe into slower and faster scans to understand the stability of the system to current fluctuations is performed. Figure 2-12 is a cyclic stability plot with a C-rate of 1C and Figure 2-13 is a cyclic stability plot with a C-rate of C/8. It can be observed that the system demonstrated a stable capacity for more than 140 cycles at 1C and more than 40 cycles at C/8 indicating high structural stability of the composite electrolyte at 120°C and resistance to current rates. An increased capacity of 80 mAh g⁻¹ was obtained for the cell cycled at C/8 since slow scan allows sufficient time for lithiation and de-lithiation process. This indicates that the cell can regain the entire capacity at a specific C-rate after subjecting it to current fluctuations as a proof of versatility of the system.
Figure 2-12- Cyclic stability plot of LTO half-cells cycled at 120°C at 1C
2.3.2.4. Thermal fluctuation test

The robustness of the system to temperature fluctuations was tested by subjecting the cell to different thermal conditions at different stages of charging. A charge discharge profile of the tests and the response of the cell is represented in Figure 2-14. The red curve corresponds to the temperature variation. It can be seen that the cell was exposed to 120°C for 15 hours until it finishes one cycle of discharge and charge after which it was cooled down to room temperature (25°C) and held at that temperature for 24 hours. Later, the cell was again heated to 120°C and the
cycling was continued. The blue curve corresponds to the current variation that was supplied during charge and discharge. The cell was cycled with a constant current of 30 µA, corresponding to a current density of 20 mA g\(^{-1}\). However, no current was applied as long as the cell was stored at 25°C. The black curve corresponds to the voltage profile of the cell showing plateaus at 1.5V corresponding to redox intercalation of Li. Although the electrolyte underwent severe viscosity changes due to cooling and heating cycles, there is a complete regain of ionic conductivity and a 100% retention in capacity.

Figure 2-14- Plot of thermal fluctuation tests of LTO half-cells with the composite electrolyte
2.3.2.5. Self- Discharge test

Self- discharge of a storage device is a very important parameter to gauge the efficiency and life of a device. It is a measure of the amount of loss that occurs from a system at a specific state of charge or discharge. Generally, LIBs are known to have negligible self- discharge since the loss of charge occurs by an electrochemical redox reaction. However, the rate of loss of charge is higher at high temperatures owing to faster kinetics facilitated by increased temperatures. An LTO/Li lithium battery containing the Clay- LiTFSI- PP13- TFSI quasi solid electrolyte was cycled for three cycles and then lithiated before the initiation of self- discharge as represented in Figure 2-15. The red curve corresponds to the temperature isotherm indicating the cell temperature at 120°C. The black curve corresponds to the voltage profile of the cell plotted as a function of time (in hours). As shown in the figure, the cell was allowed to undergo self- discharge by supplying zero current (0A) for a period of 24 hours after being cycled for 3 cycles at 120°C with a current density of 20 mA g⁻¹. Later the cell was subjected to cycling at the same current density and the stable capacity before ageing and after ageing were calculated. The cell exhibited a high capacity retention of 98% after ageing for 24 hours at 120°C implying limited self- discharge at extreme temperatures. The voltage of the cell stabilizes to the OCV value and thus contains potential greater than 1V, the point where it was discharged to.
Figure 2-15- Self discharge measurements on LTO half-cells using quasi-solid Clay-LiTFSI-PP13-TFSI electrolyte

2.4 Conclusions

A stable quasi-solid electrolyte system that can facilitate operating a LIB at high temperatures has been developed. These composites have been found to demonstrate high thermal stability up to 350°C compared to other conventional polymer based systems which can withstand no more than 100°C. In spite of sustaining high temperatures, the quasi-solid systems have a wide electrochemical stability window of up to 3V. Since these systems are based on RTILs which exhibit...
negligible vapor pressures, the compositions are extremely safe until a very high operation temperature rendering robust use of LIBs at extreme conditions. Albeit low ionic conductivities at room temperatures resulting in reduced electrochemical performance, the ionic conductivity follows a VTF behavior reaching values comparable to organic electrolytes at slightly elevated temperatures. This facilitates complete utilization of the electrolytes without having the need to heat them to very high temperatures to achieve electrochemical activity unlike molten salt systems. The synthesized electrolyte composites have been tested using LTO as the active electrode at various temperatures up to 120°C. The use of lithiated composite of clay infused with RTIL as an electrolyte/separator demonstrated good cyclic stability implying their structural integrity at high temperatures even at long exposures and constant diffusion of lithium ions. A high reversible capacity of 80 mAh g⁻¹ could be obtained at a cycling rate of C/3 for 30 cycles due to the increased wetting of the interior surfaces of the electrode by the infused RTIL. Thus, a new class of quasi-solid electrolyte composition was demonstrated as an apt electrolyte for LiBs operating at high temperatures. These electrolyte systems offer two fold advantage of both thermal stability of solid state electrolytes and good wetting properties of liquid electrolytes with high electrochemical stability window enabling the application of these electrolytes over a wide temperature range unlike conventional solid electrolyte systems operable only at high temperatures.
Chapter 3

Conventional Cathodes at High Temperature

The choice of suitable cathodes with large specific capacities and higher voltages facilitate fabrication of LIBs with greater energy densities to cater the increasing demand for applications ranging from consumer electronics to electric vehicles (EV). A recent interest in utilizing LIBs under extreme conditions has created a need for developing cathodes with higher structural, thermal and electrochemical stability at elevated temperatures. As mentioned in chapter 1, most of the commercially used cathodes undergo various secondary reactions which may be more pronounced when cycled at higher temperatures. Figure 3-1 shows a schematic of the possible secondary reactions which may be occurring at the cathode. However, there have been no attempts to study the performance of common cathode materials at high temperatures.
As seen from the figure, structural cracking associated with transition metal dissolution is one of the major factors for capacity losses in high voltage cathode systems. The challenge of metal dissolution is significant even at room temperatures which becomes highly pronounced at elevated temperatures. These metal ions migrate to the negative electrodes and deposit there after reduction, forming layers of metal on the anode surface. The non-reversible nature of the metal dissolution results in the loss of active mass of the cathodes which translates to severe fade in capacity. Several simultaneous reactions such as current collector corrosion, anodic electrolyte decomposition, formation of precipitation phases post electrolyte decomposition, etc. become more distinct at elevated temperatures. This study
reports behavior of commonly used commercial cathode systems, specially, layered (Lithium cobalt oxide (LCO), Vanadium pentoxide (V2O5)) and olivine type (Lithium iron phosphate (LFP)), under high temperatures and attempts to understand the degradation mechanisms of common cathodes at high temperatures in presence of PP13-TFSI electrolyte were made.

| 3.1 General experimental methods |

3.1.1. Structural and Morphological Characterization

Scanning Electron Microscopy (SEM)

SEM images of the powder and electrode was taken with 20 keV of electron beam under high vacuum mode (working pressure 5 × 10^{-5} torr) at a working distance of 10 mm.

X- ray Diffraction (XRD)

Cu- Kα radiation source was used to produce X- ray diffraction pattern on a Rigaku D/Max Ultima II goniometer. The spectra was recorded between 10 and 90 degrees at a sampling rate of 2° min^{-1} for both dried ceramic powder and the quasi solid composite.
3.1.2. Lithium Battery Measurements

3.1.2.1. Assembly

For the assembly of LIB, electrodes were prepared by spray casting a slurry consisting of active material (70 % w/w), Poly-vinyledenefluoride (10 % w/w) binder, carbon black (20 % w/w) in a 1-methyl-2-pyrrolidone (NMP) solvent on to aluminum current collectors. The process of spray casting was adopted from a previous research [404] and a similar approach was followed for fabricating all the positive and negative electrode used in this study. The electrodes were then hot rolled to a thickness of 40µm. The cast and dried electrodes were punched into circular disks and the active material weight was measured. The disks were then packed into a 2032 type coin cell using quartz microfiber membranes as separators and 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) and LiTFSI-PP13-TFSI as the electrolyte.

3.1.2.2. Cyclic voltammetry

The cyclic voltammetry (CV) is performed on the Autolab potentiostat/glavanostat (AUTOLAB PGSTAT 302 N ECOCHEMIE) at a constant voltage ramp rate or the scan rate of 0.1 mV s$^{-1}$ and a plot of the current vs voltage was plotted.

3.1.2.3. Charge Discharge measurements

The galvanostatic charge-discharge measurements were conducted using a battery test station from (Arbin Instruments) between the same voltage limits as that
of the CV measurements and were cycled for several cycles at constant current density. The current density was chosen according to the C-rates.

3.2 Investigating electrochemical behavior of layered oxides at high temperature

Layered oxides have been materials of interest owing to their ease of lithiation within the inter layers and high lithiation potentials. While the electrochemical properties of layered oxides have been thoroughly studied for their room temperature performance and elaborated in chapter 1. However, not much efforts have been made towards understanding the behavior at elevated temperatures. Fundamental understanding of the electrode reactions and degradation mechanisms of such batteries will lead to improvements in operational life, which are necessary for the widespread commercialization of LIB-powered electric vehicles and also application in several other areas. Among the several investigated layered oxides, LCO and V$_2$O$_5$ have demonstrated extraordinary electrochemical properties and have been commercialized. In this section, the electrochemical performance of LCO and V$_2$O$_5$ at high temperatures have been investigated.

3.2.1. Lithium cobalt oxide (LCO)

3.2.1.1. Experimental

The pure LCO powders were obtained from Sigma Aldrich and the LCO slurries were made according to the method mention in the 3.1.2. The pure powders and the
cast electrodes were characterized for the structural and morphological properties using SEM and XRD.

2032 coin cells were assembled using quartz microfiber membranes as separators and 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) and LiTFSI-PP13-TPSI as the electrolytes and were subjected to cyclic voltammetry and galvanostatic charge discharge at room temperature and 120°C at a constant current density of 20 mA g$^{-1}$.

3.2.1.2. Results and discussion

Lithium battery measurements with 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) were shown in Figure 3-2. It can be seen that the cell demonstrated good cyclic performance with a total discharge capacity of $\sim$100 mAh g$^{-1}$ during charge and discharge. However, there is some inherent capacity fade, the reason for which has been discussed earlier in section 1.2.2.
Figure 3-2: Cyclic stability plots of LCO half-cell with 1M LiPF$_6$ in EC/DMC (1:1 v/v) as electrolyte at 25°C

Figure 3-3 shows the voltage profile of the LCO half-cell during charge-discharge process at 25°C using quartz microfiber separator and LiTFSI-PP13-TFSI as the electrolyte. The profile shows a sloping plateau which is characteristic of the layered structures with oxygen framework. On the other hand, voltage profile of the LCO half-cell cycled at 120°C as a function of exposure time to 120°C indicates not more than one cycle of charge and discharge as observed from Figure 3-4. The voltage does not reach the designated charge cutoff and begins to drop much before the final value.
Figure 3-3- Voltage profile of the LCO half-cell during charge-discharge process at 25°C using quartz microfiber separator and LiTFSI-PP13-TFSI as the electrolyte.
Several hypothesis predicting charge compensation mechanisms as the possible reason for the capacity fade have been discussed. In Li$_x$CoO$_2$, there is no coupling between the $e_g$ states of Co and the 2s states of Li and the lowest-energy is reached in the interplanar stacking. This leads to as many equivalent Co sites as possible which is consistent with Co$^{3+/4+}$ tendency for charge delocalization at $x = 0.5$. In Li$_{0.5}$CoO$_2$, Co tends to have an intermediate oxidation state of +3.5 that induces a
transition to a monoclinic structure. Further, dissolution of the metal ion in the electrolyte induces oxygen release, which becomes more important upon increasing the temperature. This further results in increased interfacial impedance at high voltages due to oxidative decomposition of the electrolyte forming passivation films on the surface and release of oxygen forming Li/O2 deficient oxide phase [405]–[409]. These degradation reactions are time dependent which increases the charge transfer resistance at the cathode surface due to formation of an organic low conducting SEI layer [410], [411].

Nicholas et al. have extensively studied the entropy profiles and measured performance degradation at various stages in their cycle life [412]. Several others have also explored the entropy changes in LCO based half cells and full cells. Reynier et al. [413] have identified three distinct regions of LCO from an entropy profile of the uncycled LCO half-cell which has a relatively flat zone from 0.95< x< 0.83 (corresponding to about 20-50 mAh g⁻¹) representing first order metallic to semiconductor phases. The increase in \( \frac{dE}{dT} \) for 0.83 < x < 0.6 (corresponding to 55 to 120 mAh g⁻¹) follows a lattice gas model and further de-lithiation (0.6 < x < 0.49 corresponding to 120 to 15 mAh g⁻¹) results in hexagonal to monoclinic transformation represented by a local minimum. The entropy profile of the LCO half-cell cycled at a C-rate of C/2 reports of an unchanged shape and magnitude of the curve from the uncycled system indicating kinetic nature of the capacity losses in LCO electrode and not fundamental structural or thermodynamic changes.
3.2.2. Vanadium Pentoxide ($V_2O_5$)

3.2.2.1. Experimental

The pure $V_2O_5$ powders were obtained from Sigma Aldrich and the slurries were made according to the method mention in the section 3.1.2. 2032 coin cells were assembled using quartz microfiber membranes as separators and 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) and LiTFSI- $PP13$- TFSI as the electrolytes and were subjected to cyclic voltammetry and galvanostatic charge discharge at room temperature and 120°C at a constant current density of 20 mA g$^{-1}$.

3.2.2.2. Results and discussion

A typical measurement of cyclic stability of $V_2O_5$ is represented as Figure 3-5 using 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) as the electrolyte and quartz microfiber membranes as separator between 2-3 V vs Li/Li$^+$. The electrodes demonstrate excellent cyclic stability with a capacity of ~120 mAh g$^{-1}$ for 50 cycles of charge and discharge. Cycling between 2-3 V results in transformation between the $\delta$ to $\gamma$ phases which correspond to 1 Li exchange and about half the total theoretical capacity (~250 mAh g$^{-1}$).
Figure 3-5- Cyclic stability plot of $\text{V}_2\text{O}_5$ using 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) as the electrolyte and quartz microfiber membranes as separator cycled between 2-3 V vs Li/Li$^+$. High temperature performance of $\text{V}_2\text{O}_5$ has been probed using LiTFSI- $\text{PP13}$-TFSI as electrolytes and the lithium battery measurements were performed at 120°C. Coin cells were tested with a current density of 20 mA g$^{-1}$, corresponding to a C-rate of C/5, and the voltage versus the test time plot of the cells cycled between 2-4V vs Li/Li$^+$ is shown in Figure 3-6. Albeit a high OCV of 3.4 V, the cell suffers a catastrophic failure after 3 cycles of charge and discharge. Further, the voltage profile for the first three cycles do not represent any distinct lithiation plateaus indicating no significant
lithiation kinetics. This can be attributed to the significant transition metal dissolution as discussed in the lithiation mechanism in section 1.2.2.1. The cell undergoes a sudden failure during the fourth charge and begins to discharge prior to reaching 4V, which does not recover after discharge to 2V. This indicates a temperature induced kinetic effect which may be similar to that observed for LCO.

Braithwaite et al. [414] have reported that the deep discharge of V$_2$O$_5$ for conditions under 2V often results in the formation of the irreversible ω-phase.
where the intercalated Li is strongly bonded to the host oxide which cannot be electrochemically removed. A deeper investigation into the first discharge at 120°C (Figure 3-7) shows the formation of irreversible and non-electrochemically active ω-phase which may be detrimental for the battery performance. The strong bond energy of the Li with the host lattice is the reason for the irreversible nature of this plateau.

Figure 3-7- First discharge voltage profile of a V$_2$O$_5$ half-cell with LiTFSI-PP13-TFSI as the electrolyte, quartz microfiber membrane as the separator cycled to 2V
3.2.3. Lithium Iron Phosphate (LFP)

3.2.3.1. Experimental

The pure LFP powders were obtained from MTI Inc. and the slurries were made according to the method mentioned in the section 3.1.2. 2032 coin cells were assembled using quartz microfiber membranes as separators and 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) and LiTFSI- PP13- TFSI as the electrolytes and were subjected to cyclic voltammetry and galvanostatic charge discharge at room temperature and 120°C at a constant current density.

3.2.3.2. Results and discussion

Structural stability of poly-anion frameworks have attracted attention of researchers for their application as cathodes in LiBs. Among the several poly-anion cathodes that have been reported LFP has been investigated thoroughly and has been commercialized. As discussed in section 1.2.2.3, LFP has been known for its structural stability at room temperature, moderate lithiation potential (3.4V) and its robustness to electrochemical cycling at high C- rates. Figure 3-8 is a cyclic stability plot of LFP half-cell using 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) as the electrolyte cycled at 20 mAg$^{-1}$ corresponding to a C-rate of C/8. Unlike the layered cathodes, LFP shows excellent cyclic stability with a capacity of 125 mAh g$^{-1}$ for over 45 cycles of charge and discharge with a coulombic efficiency of more than 99%. A high coulombic efficiency indicates complete reversibility of the redox process with minimum undesired reactions which is highly essential for the stable performance of a battery.
The electrochemical stability of the lattice can be attributed to the rigid PO$_4^{3-}$ framework which can resist any structural deformations induced due to Li intercalation or extraction. The 3D nature of the structure provides intercalation pathways along all the directions which renders LFP stable at high C-rates. Section 1.2.2.3 elaborates on the lithiation mechanism in LFP as via the formation of a two-phase solid state mixture. However, the dissolution of transition metal is reduced due to the oxidation of Fe to Fe$^{3+}$ which is more stable.

Figure 3-8- Cyclic stability plot of LFP half-cell using 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) as the electrolyte cycled at 20 mAg$^{-1}$ at 25$^\circ$C.
In spite of excellent electrochemical properties and rigid crystal structure, high temperature performance of LFP was minimally explored. Figure 3-9 provides a cyclic stability plot of LFP half-cell using LiTFSI-PP13-TFSI as the electrolyte and cycled at 120°C at a current rate of C/5. At elevated temperatures of 120°C, the LFP cathode provides nearly stable capacity of about 125 mAh g⁻¹ for over 200 cycles of charge and discharge. The coulombic efficiency is consistent at about 99% for all the cycles implying insignificant parallel reactions. However, such long term exposure to high temperatures results in a capacity fade of 12% at the end of 100 cycles and about 20% at the end of 200 cycles.

Figure 3-9- Cyclic stability plot of LFP half-cell using LiTFSI-PP13-TFSI as the electrolyte cycled at 20 mAg⁻¹ at 120°C.
Maccario et al. [415] investigated the structural and electrochemical changes of LFP at RT, 40°C and 60°C. While charging the cell between 2- 4.5V, the cell cycled with good cyclic stability for over 100 cycles at RT and at 40°C, a reduced capacity of 155 mAh g⁻¹ was observed for the cell at 40°C. Faster loss in capacity was observed for cell cycling at 60°C which were hypothesized to faster kinetics of parasitic reaction beyond 4.1V vs Li/Li⁺. However, no significant structural changes were observed at all temperatures. Yu et al. [416] and Vaknin et al. [417] have observed temperature dependence of Li ion conductivity through the three crystallographic directions in a single crystal of LFP through AC EIS measurements. Their results indicate that ionic conductivity along the [010] direction is much higher than that in both [100] and [001] directions. Slow diffusion kinetics present a large barriers for surface diffusion and the anti-site defects obstruct the bulk vacancy diffusion of Li ions in LFP. Kurita et al. [418] have performed Li battery measurements with LFP as the positive electrode using 1M LiBOB in EC as the electrolyte up to 115°C. Following several charge discharge and AC EIS measurements, they hypothesized that the increase in temperature may induce formation of resistive layers at electrode/electrolyte interfaces. The nature of the surface layer, including chemical species and the formation temperature, will depend on the electrolyte used. Amine et al.[419] also report of a significant capacity fade in LFP/C full cells at slightly elevated temperatures of 37°C. A systematic analysis of the Fe²⁺ using inductively coupled plasma (ICP) technique revealed amounts of about 640 ppm in the electrolyte solution. However, this dissolution was identified as not a major reason for the capacity fade observed. A deeper probe into the capacity fade revealed deposition of
Fe metal at the surface of the negative electrode which comes from the dissolved Fe$^{2+}$ from the LFP and not the Fe$^{2+}$ already present in the electrolyte. A weak acidic environment has been identified to suppress the dissolution.

### 3.3 Summary

Commercial layered structures, LCO and V$_2$O$_5$ have been investigated for their electrochemical behavior at room temperature and at $120^\circ$C. In spite of their well-known good performance at room temperature using organic electrolytes, the redox capabilities of these systems have been extremely poignant at elevated temperatures along with ionic liquid electrolytes. Layered structures have a fragile oxygen anion framework which combined with increased kinetics of transition metal dissolution can be deleterious for the cell. The thermodynamic understanding of the transition metal dissolution reveals a kinetic induced increment in the reaction rates and no structural modifications resulting in loss of active material upon continued ageing under high temperatures. The heated cells undergo faster activation of metal dissolution reactions with no additional phase transformations and subsequently deposit onto the negative electrode which may eventually lead to micro-shorting and to catastrophic failure. Although the mechanism of metal loss reactions are different for each of LCO and V$_2$O$_5$, such as the charge compensation mechanism in LCO and the formation of reversible $\omega$- phase in V$_2$O$_5$, it can be derived that the oxygen skeleton and the layered nature of these systems render it unemployable for high temperature applications. Further, owing to the structural stability of the polyanion framework, commercial LFP structures were investigated for their resilience to high
temperatures. In spite of certain degree of capacity fade, LFP cells survived more than 100 cycles at temperatures beyond 100°C making polyanions structures promising for high temperature applications. Albeit good resistance to thermal and electrochemical stresses, the LFP cathodes have limited energy densities owing to their low intercalation voltages (3.4V vs Li/Li⁺). Further, the LFP was also found to undergo trace yet thermally induced transition metal dissolution resulting in capacity fade over extended cycling which otherwise is not significant at room temperature. The necessity for higher energy densities at high temperatures still remains a challenge.
Chapter 4

Stablizing $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ for High Temperature Operation

Increased demand for high power and high energy Li-ion batteries (LIBs) has sparked tremendous interest to achieve better performing devices through tailored materials for positive electrodes. The commercial success of LiCoO$_2$ (LCO) with an intercalation voltage of 3.7 V has prompted development of various other layered oxides with higher intercalation voltages and capacity values as positive materials for LIBs. Layered materials have been demonstrated to have limited electrochemical stability under extreme thermal conditions because to their fragile oxygen anion framework. This unstable network results in severe transition metal loss at higher voltages limiting the total working potential of the system. Spinel structures based on Mn consisting of three dimensional network of anion network report of higher lithiation voltages but have been notorious for poor electronic conductivities and much severe dissolution issues due to disproportionation reactions in Mn. A large gap of about 1V between the removals of both the Li atoms from the unit cell puts a constraint on the reversible capacities and the voltages. In order to use the higher voltage plateau, the structure is subjected to a raster through the entire voltage range
during the first charge creating an instability in the system due to the loss of both the Li. A first charge involves loss of all the Li from the structure and the subsequent cycling within the high voltage range of about 4.2V incorporates only one Li per unit cell. The empty Li sites for the second Li creates a lattice strain resulting in the enhancement of degradation kinetics. Cycling within the lower potential plateau (2.9V) limits the energy density of the electrode and subsequently, the cell. Alternatively, the successful operation of LFP at 120°C have prompted the development of several polyanion structures, predominantly with phosphate framework owing to the strong nature of the M-O bonds in these systems. Monoclinic Li3V2(PO4)3, (LVP), with intercalation voltages over 4.5 V (vs Li/Li+) and energy densities over 600 Wh kg-1 has been the focus among the phosphate class of materials for superior structural stability and rate capability. However, in spite of high energy and power densities, intercalation at high voltage beyond 4 V pristine LVP is associated with several structural and morphological challenges which affects the energy retention significantly. Low electronic conductivity, extensive particle agglomeration and loss of transition metal which modifies the atomic arrangements as a consequence of altering lattice entropy are the major bottlenecks for commercial application. This study is a deliberate attempt to understand the underlying mechanism of capacity fade in LVP structures and tailor the stoichiometry to stabilize the structure for temperatures as high as 90°C.
4.1 General experimental methods

4.1.1. Structural and Morphological Characterization

Scanning Electron Microscopy (SEM)

SEM images of the powder and electrode was taken with 20 keV of electron beam under high vacuum mode (working pressure 5x 10^{-5} torr) at a working distance of 10 mm.

X-ray Diffraction (XRD)

Cu- Kα radiation source was used to produce X-ray diffraction pattern on a Rigaku D/Max Ultima II goniometer. The spectra was recorded between 10 and 90 degrees at a sampling rate of 2° min^{-1} for both dried ceramic powder and the quasi solid composite.

4.1.2. Lithium Battery Measurements

4.1.2.1. Assembly

For the assembly of LIB, electrodes were prepared by spray casting a slurry consisting of active material (70 % w/w), Poly-vinylidenefluoride (10 % w/w) binder, carbon black (20 % w/w) in a 1-methyl- 2-pyrrolidone (NMP) solvent on to aluminum current collectors. The process of spray casting was adopted from a previous research [404] and a similar approach was followed for fabricating all the positive and negative electrode used in this study. The electrodes were then hot rolled
to a thickness of 40µm. The cast and dried electrodes were punched into circular disks and the active material weight was measured. The disks were then packed into a 2032 type coin cell using quartz microfiber membranes as separators and 1M LiPF$_6$ in a solution of EC/DMC (1:1 v/v) for tests up to 60°C and LiTFSI-PP13-TFSI as the electrolyte for cells operating beyond 60°C.

4.1.2.2. Cyclic voltammetry

The cyclic voltammetry (CV) is performed on the Autolab potentiostat/glvanostat (AUTOLAB PGSTAT 302 N ECOCHEMIE) at a constant voltage ramp rate or the scan rate of 0.1 mV s$^{-1}$ and a plot of the current vs voltage was plotted.

4.1.2.3. Charge Discharge measurements

The galvanostatic charge-discharge measurements were conducted using a battery test station from (Arbin Instruments) between the same voltage limits as that of the CV measurements and were cycled for several cycles at constant current density. The current density was chosen according to the C-rates.

4.2 Lithium Vanadium Phosphate (LVP)

The structural stability of LFP towards electrochemical cycling at high temperatures has motivated the development to achieve higher lithiation potential (> 4V) cathode materials which can perform with similar stability while providing increased energy densities. Among several poly-anion structures that have been
proposed, V based systems with Li$_3$X$_2$ (PO$_4$)$_3$ type arrangement [420] [421], have been of recent interest owing to superior structural, thermal and mechanical stabilities. Figure 4-1 is a schematic of the atomic arrangement in different electrochemical active phases of LVP indicating the positions of constituent atoms.

Figure 4-1- Schematic of the atomic arrangement in rhombohedral and monoclinic phases of LVP indicating the positions of constituent atoms

On the basis of the structural interconnects between the [V$_2$ (PO$_4$)$_3$] units, LVP exists in rhombohedral or NASICON (sodium superionic conductor) framework and the thermodynamically more stable monoclinic structure. The monoclinic phase crystallizes with P21/n, with the constituent atoms distributed over distinct co-ordinates at the crystallographic 4e site, including the three lithium atoms. The
The arrangement of Li atoms into the monoclinic phase is such that Li1 sites experience a five-fold coordination while the Li2 and Li3 experience a four-fold coordination inducing a minor monoclinic distortion [422]. The transition metal (V) is distributed over two independent positions. The atypical distribution causes anisotropy in ionic conduction promoting ionic conduction along the [001] [423], [424].

4.2.1. Experimental

4.2.2. Synthesis of LVP powders

The pristine LVP powders were synthesized using analytical grade LiNO3 (reagent plus, Sigma Aldrich), NH₄VO₃ (99%, Sigma Aldrich), NH₄H₂PO₄ (99.99%, Aldrich) and NH₂CH₂COOH (99%, Alfa Aesar) as reagents.

The powder samples were synthesized by auto-gel combustion method. The net oxidizing valences of respective nitrates as well as the reducing valence of the fuel (glycine) were calculated. For this system, the stoichiometric ratio of the amounts of metal nitrates to that of glycine was found to be 1:5. However, a 50% fuel deficient ratio was taken which is known to give soft agglomerated nano-powders, further facilitating kinetic for formation of product. To synthesize parent LVP, the required amounts of NH₄VO₃ was first dissolved in pre-heated deionized water. Subsequently, weighed NH₄H₂PO₄, LiNO₃ and NH₂CH₂COOH were added one after another while ensuring complete dissolution. Finally, glycine was added, which on thermal dehydration gave highly viscous green liquid. The temperature of the hot plate kept constant for slow heating. The gel precursor swelled and auto ignited with slow
evolution of large volume of gases to produce voluminous powders. The as obtained product was ground to powder to ensure further homogenization. This powder sample was subjected to heat treatment in two steps. To ensure removal of carbonaceous product the sample was first heated at 350 °C in Ar/H₂ atmosphere for 4 h. Followed by heating at 800 °C for 10 h.

4.2.3. Results and Discussion

4.2.3.1. Structural characterization

In present study the XRD pattern obtained was subjected to Rietveld refinement using Fullprof package in the standard setting space group P21/n (Figure 4-2). The background of the observed diffraction data was fitted using a fifth order polynomial function and the diffraction profile was modeled using pseudo-Voigt profile function. The initial cycles of the Rietveld refinement were carried with the scale, background, and profile parameters along with the unit cell parameters. The overall temperature coefficient was also varied. To get the information about the lattice constant, the dopants were equally distributed at available two host cation sites. The observed parameters; a = 8.5904 Å (7), b= 8.5880 Å (7), c= 12.0132 Å (10) and β₀ = 90.5040 (90) show a close agreement with the values reported earlier (Nazar et al) [424]. With an intercalation voltage over 4V and higher energy density of 600 Wh kg⁻¹, LVP can be a prospective alternative and shall be explored as a suitable material for high temperature performance.
An investigation of morphology of the electrode particles reveals nearly spherical particles between 0.5 and 5 µm agglomerated to form a dense porous network as seen in the SEM image in Figure 4-3. The agglomeration of particles occur during the gel combustion process when the localized temperatures reach to as high as 1000°C. Although this increases the mean free path of Li ions within the particle, the porous network facilitates increased wetting of the particles with electrolyte to the interior of the electrode enabling Li intercalation from several sites on the surface. The rigid network offers good mechanical strength to the electrode resisting the stresses due to volume changes during charge and discharge cycles.
4.2.3.2. Electrochemical performance of LVP

During the charge process in a Li battery, the Li ions are extracted from the crystal structure and the deficiency of the positive charge is compensated by the changes in oxidation state of the transition metal in the cathode. LVP has three stages of de-lithiation at corresponding to each of the Li atoms in the structure. The lithiation and de-lithiation mechanism can be represented according to the equations. Several reports suggesting different mechanisms of Li extraction in LVP when charged to 4.3V have hypothesized partial oxidation of $V^{3+}$ to $V^{4+}$ for each of the Li to reveal a structure.
with one Li atom \((\text{LiV}_2(\text{PO}_4)_3)\) consisting of Li atoms in position 1 with four fold coordination. Charging to higher voltages with a cutoff of 4.5 V removes the third Li atom at 4.35 V oxidizing \(V^{4+}\) to \(V^{5+}\). Although there is no structural irreversibility associated with extraction of the third Li, progressive V dissolution and electrolyte decomposition contribute to faster capacity fade. [425]–[428].

Figure 4-4 is a cyclic voltammetry plot of LVP half-cell with 1M LiPF\(_6\) in a 1:1 (v/v) ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC) measured between 3 to 4.3 V at a scan rate of 0.1 mV s\(^{-1}\) at room temperature. The de-lithiation peaks were observed at 3.65V, 3.75V and 4.15V and the corresponding lithiation peaks were observed at 3.55V, 3.65V and 3.95V respectively. The first two peaks in the CV plot at 3.6 V and 3.7 V correspond to the removal of the first Li ion, Li1. During the process, V at position 2 (indicated as V2 in the schematic in Figure 4-1) undergoes transition from \(V^{+3}\) to \(V^{+4}\) resulting in a structure consisting of V atoms with mixed oxidation states. At 3.6 V, half the V2 atoms change oxidation states and the rest of the V2 atoms undergo oxidation at 3.7 V. The capacity output of the cell at this stage is about 70 mAh g\(^{-1}\). The second stage of de-lithiation corresponding to the removal of the second Li ion, as indicated in equation occurs at 4.1 V. The peak at 4.1 V represents the de-lithiation and the subsequent oxidation of V atoms at V1, from \(V^{+3}\) to \(V^{+4}\). The second stage of Li removal is associated with a capacity output of 132 mAh g\(^{-1}\). Further charging of the battery results in the loss of third Li ion, with the change in oxidation state of all the V atoms from \(V^{+4}\) to \(V^{+5}\). This change is irreversible as seen from the absence of the corresponding discharge peak which may lead to collapse of the crystal structure and loss in electrochemical stability. Although, the theoretical
capacity of LVP is 197 mAh g\(^{-1}\) for 3 Li ions, a reversible capacity of 132 mAh g\(^{-1}\) can be extracted by cycling two Li ions for good electrochemical stability.

Figure 4-4- Cyclic voltammetry plot of LVP half-cell with 1M LiPF\(_6\) in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) measured between 3 to 4.3 V at a scan rate of 0.1 mV s\(^{-1}\) at room temperature

The cyclic stability of a material to several cycles of charge and discharge is evaluated from the plot of the specific output capacity from the cell during charge and discharge vs the number of cycles. The voltage range chosen corresponds to two Li ions and the charge and discharge capacities were measured a C rate of C/10 for each
cycle as shown in Figure 4-5. The red plot corresponds to the discharge capacities and the blue plot corresponds to the charge capacities. At capacity of ~ 125 mAh g$^{-1}$ was observed in the first cycle. However, the capacity decreases over subsequent cycles with a capacity of ~ 75 mAh g$^{-1}$ at the end of 150 cycles. A high capacity in the first cycle can be attributed to several side reactions associated with the formation of passivation layers over the electrodes and the current collectors resulting from the reaction of the electrolyte with the surfaces of the electrodes. The coulombic efficiency of the cell, represented by the green plot, was calculated for each cycle as the ratio of the discharge capacity to the charge capacity in that cycle. An efficiency of less than 97% was observed indicating irreversible loss of Li ions in each cycle. The capacity loss can be due to several reasons including large particle size leading to polarization overpotential, dissolution of V atoms due to the parasitic reaction with electrolyte during the de-lithiation process, etc. The dissolution process leads to higher voltage hysteresis and larger charge transfer resistance [429]–[432].
The performance of LVP at high temperatures was evaluated by assembling a 2032 coin cell lithium battery using 1M solution of LiTFSI in PP13- TFSI as the electrolyte and quartz microfiber membrane as the separator as mentioned in section 3.1.2.1. Figure 4-6 is the CV plot of the cell recorded at 90°C for 30 cycles. The peak positions were observed to be consistent with the cell using conventional organic electrolyte indicating no significant over- potentials due to reduced ionic...
conductivities in ionic liquids. However, there is a decrease in intensity of the peak currents over cycling. A reduction in the fraction of the active monoclinic phase can be directly inferred from the decrease in the intensity of the peak currents suggesting phase transformation reactions at high temperatures. Further, first two peaks at 3.65V and 3.75V tend to merge during the de-lithiation stage over a long cycling at 90°C. The shape of the curve in cycle 30 indicates incomplete de-lithiation of both Li1 and Li2. The lithiation peak of Li2 at 3.9V was observed to be broader than the peak in cycle 1. The discrepancy in the lithiation and de-lithiation suggests changes in mechanism of intercalation which may be attributed to changes in active phase and the decrease in intensity of lithiation peaks at 3.55 V and 3.65 V support the proposed hypothesis.

A deeper resolution of the peaks at 4.1V reveals origin of a second peak from the primary peak and a gradual suppression of the primary peak after the 5th cycle, resulting in a positive shift of the de-lithiation peak and a negative shift of the lithiation peak. This implies an increase in the over-potential and thus, greater energy exchange in lithiating or de-lithiating the structure.
Figure 4-6- CV plot of the LVP half-cell recorded for 30 cycles at 90°C using 1M LiTFSI in PP13-TFSI as the electrolyte and quartz microfiber membrane as separator.
The formation of new phases during cycling has a direct effect on the cyclic stability of the lithium half-cell as seen from the plot of charge and discharge capacity with cycles in Figure 4-7. The capacities were measured at a slow current rate of C/10 corresponding to a current density of 14 mA g\(^{-1}\). In spite of high charge and discharge capacities of 180 mAh g\(^{-1}\) and 150 mAh g\(^{-1}\) respectively in the first cycle, significant loss in capacity during subsequent cycling with a capacity of about 60 mAh g\(^{-1}\) after 25 cycles and a coulombic efficiency of only 91% was observed. The fade in the capacities support the claim of formation of a new phase until the 15\(^{th}\) cycle, beyond which, the capacities tend to stabilize. This indicates that the new phase has reduced electrochemical capacity as compared to the monoclinic phase.

Figure 4-7- Cyclic stability plot of LVP half-cell at 90\(^{o}\)C using 1M LiTFSI in PP13- TFSI as the electrolyte and quartz microfiber membrane as separator
4.3 Modification of V based poly-anion materials for stable high voltage cathodes at high temperatures.

Albeit excellent structural stability of the poly-anion framework of LVP at room temperature, the instability of the crystal structure to electrochemical redox reactions at high temperature have paralyzed its application in lithium batteries at extreme thermal conditions. Owing to the limitations of oxide based spinel and layered structures as described earlier, stabilizing the structure to render it resistant to phase transformations was attempted by doping with a suitable atom. The dopant atom must fulfill the following properties:

1. Comparable ionic radius to $V^{3+}$ to minimize the strain in the lattice.

2. Oxidation potential greater than $V^{3+/4+}$ to prevent the preferential oxidation of doping element to $V$. This limits the efficacy of the dopant to stabilize the structure during charge and discharge.

3. No effect on specific capacity and energy density. Atoms with comparable ionic radius are substituted in the $V$ sites and do not occupy Li sites.

Liu et al. have summarized all the possible elements that were extensively explored as dopants in several structures to alleviate or tailor specific electrochemical properties and their influence on the specific capacity and energy density at various oxidation states [53]. Figure 4-8 shows the average intercalation potential in phosphates versus maximum gravimetric capacity achievable. Energy density curves at 600 and 800 Wh/kg are drawn in the figure (blue dashed lines). The
red dashed line indicates the upper potential, which is considered safe against the decomposition of the normal electrolyte. Different colors and markers are used to distinguish different elements. The green dashed rectangle shows the potential tendency of phosphates in the third period.

![Diagram showing the effect of dopants on intercalation potential and specific capacity of phosphate-based electrodes.](image)

**Figure 4-8- Effect of various dopants on the intercalation potential and the specific capacity of phosphate based electrodes [53].**

From the plethora of dopant elements, $\text{Ti}^{3+/4+}$, $\text{Mn}^{3+/4+}$, $\text{Cr}^{3+/4+}$, $\text{Fe}^{3+/4+}$, $\text{Ni}^{3+/4+}$ and $\text{Co}^{3+/4+}$ have no significant influence on the specific capacity. $\text{Fe}^{3+/4+}$ has been shown to increase the electrical conductivity and the structural stability while $\text{Ti}^{3+/4+}$ enhances the ionic conductivity up to three orders of magnitude. Elements beyond these such as $\text{Cr}^{2+/3+}$, $\text{Fe}^{2+/3+}$, etc. although facilitate enhancement in specific capacity,
are notorious for unstable crystal structures owing to their dissolution into the electrolyte because of low oxidation potentials. The red dotted line in the chart at 4.5V indicates the typical stability limit of the conventional organic electrolytes. LVP electrodes are cycled up to 4.3V which is well below the stability limits of the electrolytes. As it can be seen, V undergoes $V^{4+/5+}$ transition at potential close to 4.5V, which agrees with the de-lithiation mechanism elaborated above. This transformation promotes V dissolution into the electrolyte and renders the structure unstable. However, doping the structure with an element with oxidation potential less than 4.5V activates preferential oxidation of the dopant resulting in the dissolution of the doped atom. Hence, elements with oxidation potential higher than 4.5V undergo no redox transformation and aid in effective stabilization of the structure. Among the list of elements with potentials greater than 4.5V, Cr$^{3+}$ has the ionic radius comparable to that of V$^{3+}$ and has been chosen as the dopant element.

Theoretical calculations predict 6% (mol) of doping in LVP structure as the limit to retain the monoclinic crystal structure. Compositions with dopant concentration from 1% to 6% (mol) were prepared using the gel combustion method.

**4.3.1. Experimental methods**

The Cr$^{3+}$ substituted LVP powders were synthesized following the same procedure as adopted for synthesizing pure LVP powders. However, the reagent solution was mixed with stoichiometric amounts of Cr(NO$_3$)$_3$.9H$_2$O (99.99%, Sigma Aldrich), as the source of Cr in the lattice. For substituted LVP samples, calculated
amount of substituent precursors were added before addition of NH$_2$CH$_2$COOH. The further process was same as that for parent composition.

The annealing conditions for higher Cr$^{3+}$ substituted samples (6, 8 and 10 mol%), was slightly modified and the final heating temperature was decreased to 700 °C, as higher Cr$^{3+}$ lowered the decomposition temperature of LVP.

4.3.2. Results and Discussion

4.3.2.1. Structural Characterization of Cr doped LVP

In order to explore the effect of substitution of Cr$^{3+}$ the samples were similarly subjected to XRD analysis. Figure 4-9 shows the XRD patterns of substituted samples. The ionic radii of Cr$^{3+}$ (0.61Å) is close to that of V$^{3+}$ (0.64Å) in octahedral environment. On initial substitution of 1 and 2 % Cr$^{3+}$ in the lattice feeble shift towards higher two theta was observed, indicating lattice compression (Figure 4-9). On substituting 1% Cr$^{3+}$ in the lattice overall decrease in cell volume was observed from 886.4 of pure LVP to 885.5 Å$^3$. Interestingly the cell compression is observed in spite of slight increase in a (8.5881 to 8.5911 Å) and β (90.5281° to 90.5873°). With increasing Cr$^{3+}$ substitution beyond 2 mol%, along with the characteristic peaks of monoclinic LVP (ICSD #01-078-5405), peaks corresponding to hexagonal Li$_9$V$_3$(P$_8$O$_{29}$) starts appearing as seen in the magnified portion of the plot. The new peaks could be indexed with standard pattern (ICDD #01-081-9390). Furthermore, a third phase of monoclinic LiVP$_2$O$_7$ (ICDD#00-055-0625) begins to nucleate in heavily substituted samples (6 and 8 mol %).
Figure 4-9- XRD patterns of Li$_3$V$_2$(PO$_4$)$_3$: x mol% Cr$^{3+}$ (i) x = 0 (ii) x = 1 (iii) x = 2 (iv) x = 3 (v) x = 4 (vi) x = 6 (vii) x = 8.
The single phase system with a dopant concentration of 2% (mol) was explored to understand the effect of doping in LVP and its efficacy in stabilizing the system at high temperatures.

Figure 4-10 (a to d) shows the SEM image of the as prepared powders of the Cr doped LVP. A comparative estimate of the particle sizes and morphology of the pristine and doped LVP powders was determined. Dopant concentrations from 0, 1, 2 and 4% were examined and the images reveal a degree of particle agglomeration post annealing to form a super-particle between 0.5 and 5µm. While pure LVP powders exhibit diffused particle boundaries (Figure 4-10 (a)), Cr\textsuperscript{3+} doped structures form distinct boundaries, indicating a more controlled crystal nucleation and growth mechanism. Doping of the LVP lattice presents an unaltered morphology up to 2% (Figure 4-10 (b and c)). However, powders with dopant concentration beyond 2% tend to undergo a greater degree of agglomeration presenting increased particle sizes and diffused boundaries. Unlike the pure LVP powders there is a clear grain boundary observed between the agglomerated particles indicating a nucleation growth mechanism forming a large 3D network of particles. The dense network enhances the mechanical rigidity of the electrodes and renders them resistant to severe structural changes during charge and discharge.
Figure 4-10- Scanning electron micrographs of LVP with various doping concentrations. (a) pristine, (b) 1% (c) 2% and (d) 4% doping.

4.3.2.2. Electrochemical characterization of Cr doped LVP

Preliminary characterization of the Cr doped LVP half-cell was performed at room temperature using a 1M solution of LiPF$_6$ in EC/DMC (1:1 v/v) as the electrolyte. The degree of reversibility of the Li intercalation and de-intercalation processes was assessed from cyclic voltammetry (CV) measurements. LVP undergoes a four stage de-lithiation/lithiation process for three Li- ions, with the first being extracted at 3.55
V and 3.65 V, and the remaining two at 4.1 V and 4.5 V, respectively. The half-cells of pristine and 2% Cr3+ doped LVP electrodes were scanned at 0.1 mVs⁻¹ at 25°C with 4.3 V (corresponding to 2 Li- ions) and 4.8 V as cut-off voltages (corresponding to 3 Li- ions). As the structure undergoes lithium insertion and de-insertion, vanadium undergoes compensatory oxidation state changes and Cr³⁺/⁴⁺ with a redox potential over 4.8 V vs Li/Li⁺ remains unaltered under the cycling conditions. Figure 4-11 (a) and (b) show the CV plots for pristine LVP and 2% Cr³⁺ doping with upper cut-off potential of 4.3 V scanned for 5 cycles. As observed from the Figure 4-11 (b), CV plot of 2% doped LVP shows three anodic peaks at 3.65, 3.75, and 4.15 V which are simultaneously shifted up by 50mV from corresponding peaks observed in pristine LVP (Figure 4-11 (a)). A negative shift of similar magnitude was observed for the cathodic peaks. The increased de-lithiation potential for doped samples indicates influence of Cr³⁺ doping on the activation energy of Li removal. Although reversible Li intercalation is evident from Figure 4-11 (a), a gradual decrease in peak current values on subsequent cycling is an indication of diminishing charge transfer in the electrode. Pristine LVP electrodes without any surface modification have been reported to be plagued with severe vanadium dissolution when exposed to the electrolyte resulting in a modified stoichiometry. The altered stoichiometry results in electrochemically inactive phases, reducing the fraction of the active phase in the electrode. However, comparable peak currents for several cycles in Cr³⁺ doped electrodes, as seen from Figure 4-11 (b), implies greater reversibility of the redox process and preservation of the active phase. A significant suppression in vanadium dissolution with the presence of Cr³⁺ in the lattice can be inferred. Further, cathodic
to anodic peak current ratios were observed to be close to 1 in doped samples indicating almost complete reversibility of the lithiation and de-lithiation process.

Figure 4-11- Cyclic Voltammetry plots of half cells of (a) pristine LVP and (b) 2% Cr\(^{3+}\) doped LVP measured at a scan rate of 0.1 mV s\(^{-1}\) between 3- 4.3 V.

During the charging of LVP half-cell up to 3.6 V, half of Li in site 3 is removed, driving transition of half of V\(^{3+}\) in site 1 to V\(^{4+}\) (Figure 4-12). This process forms a mixture of V\(^{3+}\) and V\(^{4+}\) atoms in site 1, but the electrons are still localized on V\(^{3+}\) which is further oxidized on subsequent removal of the remaining half of Li in site 3 at 3.7 V. Due to the size differences from two different oxidation states, the VO\(_6\) octahedra distorts into an ordered structure composed of alternating columns. The Li in site 2 undergoes rearrangement to an environment similar to that Li in site 1 which gets removed completely at a single voltage of 4.1 V on further charging. Localized changes in Li coordination from 5- to 4- induces stress due to distortion in the monoclinic lattice, which has been predicted as one of the reasons for the dissolution of V atoms.
into the electrolyte. During the entire charge process to 4.3 V, vanadium atoms at all sites undergo transition from $V^{3+}$ to $V^{x+}$ ($3<x<5$) with no electron de-localization between the two sites. The instability of partial oxidation states drives a charge compensation reaction in vanadium promoting dissolution as a charge balance mechanism. We hypothesize that the increased redox stability in Cr$^{3+}$ doped system is because of the electron density de-localization between $V^{3+}$ and $V^{4+}$ resulting in unchanged coordination environments of the Li in site 2.
Figure 4-12- Five distinct environments for the three Li sites in Li$_{2.5}$V$_2$(PO$_4$)$_3$: (a) Li(1); (b) Li(2); (c) Li(3). V$^{4+}$ and V$^{3+}$ are shown in cyan and gray, respectively.
XPS measurements were performed on the cycled and uncycled electrodes at different stages of lithium removal in both 2% doped and pristine samples to understand the oxidation state changes of vanadium during the delithiation process. Spectra were collected for uncycled and charged electrodes up to 3.65 and 3.8 V corresponding to the removal of the first Li when the rearrangement in Li atoms are anticipated to occur. Figure 4-13 (a)-(c) correspond to the pristine LVP while Figure 4-13 (d)-(f) correspond to the Cr\(^{3+}\) doped LVP. An uncycled electrode (Figure 4-13 (a) and (d)) has characteristic V\(^{3+}\) peaks corresponding to two vanadium sites at \(~515.0\) and \(~516.5\) eV respectively. Upon charging to 3.65 V, pristine LVP exhibits equal peak fraction of V\(^{3+}\) (BE \(\sim\) 514.70 eV) and V\(^{4+}\) (BE \(\sim\) 517.36 eV) in site 1 (Figure 4-13 (b)) indicating removal of half of Li\(_1\) and no electron delocalization was observed as expected. The peak at \(~515.97\) eV corresponds to the V\(^{3+}\) at site 2. However, charging of Cr\(^{3+}\) doped LVP to 3.65 V (Figure 4-13 (e)) reveals an additional peak corresponding to BE \(\sim\) 515.15 eV which can be matched to the V\(^{3+}\) at site 2. The peaks at \(~516.54\) and \(~513.88\) eV correspond to that of V\(^{4+}\) at site 2 and V\(^{3+}\) at site 1 respectively. Comparable peak ratios of all the oxidation states of vanadium in doped LVP indicates a great degree of delocalization of the electrons in site 1. This delocalization facilitates suppression of Li rearrangement and changes in Li coordination environment. The removal of the other half of Li\(_1\) at 3.8 V is supported by the increased V\(^{4+}\) fraction from complete oxidation of V\(^{5+}\) in site 1 in pristine LVP corresponding to a peak at \(~517.37\) eV as seen in Figure 4-13 (c). Charging of Cr\(^{3+}\) doped samples to 3.8 V reveals an equal ratio of peak intensities for V\(^{4+}\) and V\(^{3+}\) supporting the complete simultaneous oxidation of vanadium in site 1 to V\(^{4+}\) (Figure
Thus, XPS provides significant evidence to confirm the hypothesis of Cr$^{3+}$ atoms promoting electron delocalization in the monoclinic structure. Efficient electron conduction through the lattice explains observed enhancement in the electronic conductivity upon Cr$^{3+}$ doping and suppression of vanadium dissolution owing to decreased atomic rearrangements. Higher Li coordination necessitates higher activation for removal, which is reflected from the increased de-intercalation potentials as observed from CV measurements.

Figure 4-13- XPS spectra resolving the V2p$_{3/2}$ oxidation states at various states of charge in Cr doped and pristine LVP. (a)-(c) Spectra of pristine LVP electrodes for uncycled, cycled to 3.7 V and 3.8 V and (d)-(f) Spectra for 2% Cr doped LVP at same conditions.
The measurement of charge transfer resistances ($R_{ct}$) for the Cr$^{3+}$ doped samples provide further insight for the predicted changes in electronic configuration in the system. Figure 4-14 (a) and (b) shows the $R_{ct}$ values of pristine LVP and Cr$^{3+}$ doped LVP respectively, taken at different potentials of charge and discharge in the first cycle at a C-rate of C/10. The corresponding EIS plots from which the $R_{ct}$ values have been calculated are represented in Figure 4-15. The $R_{ct}$ from doped samples is 50% less than that observed in the pristine LVP, indicating enhanced reaction kinetics upon doping. A high charge transfer resistance in the pristine structure is a result of the low electronic conductivities of the lattice and the absence of conducting surface coatings.

Figure 4-14- Charge transfer resistance measured as a function of voltage in (a) pristine LVP and (b) Cr doped half cells.
Figure 4-15- Electrochemical impedance spectra (EIS) measured for the doped and 2% doped electrodes in a Li half-cell at different charge and discharge voltages.

The galvanostatic intermittent titration technique (GITT) measurements demonstrated in Figure 4-16 support this claim of increased electronic conductivity in the system which is represented as decreased relaxations at specific potential holds. The GITT data was collected by applying intermittent current pulses followed by log relaxation without application of current. The higher the relaxation drop, the greater the overpotential implying lower electronic conductivities. As observed from Figure 4-16 (a), larger iR drops were observed for the pristine LVP samples as
compared to the doped structure (Figure 4-16 (b)) indicating insufficient electron transfer supporting the claim of inhomogeneous electron de-localization. Alternatively, modified electronic configurations in the doped structure promotes efficient charge transfer across the lattice which translates into lower resistances. However, higher resistances were observed in the subsequent discharge process which may be attributed to the smaller unit cell volume trying to undergo strained volume expansion with Li intercalation.

![Galvanostatic Intermittent Titration Technique (GITT) analysis](image)

**Figure 4-16- Galvanostatic Intermittent Titration Technique (GITT) analysis measured for the (a) doped and (b) 2% doped electrodes in a Li half-cell at room temperature.**

Comparative cyclic stability plots for pristine and doped at slow and fast current rates between 3 and 4.3 V are shown in Figure 4-17 (a) and (b) respectively. At C/10 rate, pristine LVP structures exhibit 80.7% capacity retention in 50 cycles while the 2% doped structure reports a retention of 98.2% for 50 cycles. The columbic efficiency for doped samples was observed to be over 99.5% for the Cr doped samples for all
the 50 cycles. Further, the doped samples exhibit higher first cycle discharge capacities (112.4 mAh g⁻¹) as compared to the undoped samples (109.3 mAh g⁻¹). Electrochemical cycling of the doped structure at higher current rates (1C) demonstrates stable cycling for up to 500 cycles with a retention of 84% while the pristine LVP fails under 300 cycles losing 25 % capacity in 100 cycles as shown in Figure 4-17 (b). Doped LVP shows no change in initial discharge capacity when cycled at either C/10 or 1C. However, a significant compromise of about 15 mAh g⁻¹ was observed in pristine LVP. This can be attributed to the lower resistance values observed in Figure 4-14 (b). A columbic efficiency of about 99.2 % at higher C-rates indicates uniform oxidation state changes of vanadium upon substitution of Cr³⁺, which support the hypothesis of improved electron delocalization in the system.

![Figure 4-17 - Comparative cyclic stability plots of pristine and doped LVP half cells at (a) C-rate: C/10 and (b) C-rate: C/1 cycled between 3- 4.3 V at room temperature](image)
The cyclic stability plots for the 4% (mol) and 6% (mol) is shown as Figure 4-18 and Figure 4-19 respectively. The dual phase system with 4% (mol) and the ternary phase system with 6% (mol) doping exhibit reduced capacities of about 55 mAh g\(^{-1}\) and 40 mAh g\(^{-1}\) for charge and discharge respectively and a coulombic efficiency of about 81%. It can be inferred that the secondary phases other than the monoclinic phase are not electrochemically active. Further, the reduced coulombic efficiency can be attributed to the non-ideal stoichiometry of the monoclinic phase which does not exhibit comparable electrochemical properties as the ideal stoichiometric phase.

Figure 4-18- Cyclic stability plot of the 4 mol % Cr doped LVP half- cells using a 1M solution of LiPF\(_6\) in EC/DMC (1:1 v/v) as the electrolyte at 25°C
While Cr$^{3+}$ doping has proven to stabilize the crystal structure efficiently at room temperature, tests were conducted at high temperatures to estimate the efficacy of the dopant stabilization at elevated thermal conditions under high power operation. Doped LVP half cells tested at 60 $^\circ$C at a C-rate of 1C have shown a capacity retention up to 84% at the end of 400 cycles with a columbic efficiency of 99.5 % and a final discharge capacity of 105.3 mAh g$^{-1}$ (Figure 4-20 (a)). The pristine LVP demonstrates 26 % retention at the end of 400 cycles with a final discharge capacity of 25.5 mAh g$^{-1}$. The loss in stability at elevated temperatures can be understood from the voltage profiles of the pristine and the doped samples for cycles 1, 100 and 400 (Figure 4-20 (b) and (c)). While the doped structure (Figure 4-20 (c)) retains its distinct intercalation plateaus up to 400 cycles, the plateaus were observed to merge.
in the pristine sample. The corresponding dQ/dV plots provide a deeper insight of the changing charge transfer at each intercalation potential. The absence of reversible peaks in the dQ/dV plot for the pristine LVP (Figure 4-20 (d)) after 400 cycles is an indication of the complete loss of the active material within the electrode while the evident peak broadening confirms structural transformation that largely affects reaction kinetics. The Cr^{3+} doped structures demonstrate characteristic dQ/dV profile (Figure 4-20 (e)). In comparison, it has been observed that the most common cathode Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2 demonstrates a capacity fade of up to 70% in 100 cycles when cycled at 55 °C albeit conformal conducting C coating when cycled at 1C rate.
Figure 4-20- (a) Comparative cyclic stability plots of pristine and doped LVP half cells at C-rate: C/1 cycled between 3-4.3 V at 60°C. (b) and (c) Voltage profiles
of the pristine and doped electrodes cycled at 60 °C for 1, 100 and 400 cycles. (d) and (e) Corresponding dQ/dV vs V plots of the pristine and doped electrodes at 1, 100 and 400 cycles.

Stability at higher temperature (90°C) of the Cr doped LVP system was estimated using LiTFSI-PP13-TFSI as the electrolyte and quartz microfiber membrane as the separator. CV experiments were conducted to understand the redox reactions and the representative plot is shown in Figure 4-21. The CV plots represent broadening of the peaks and a positive shift in peak potentials during the cathodic scan and a negative shift in the anodic scans. The shift in peak positions can be attributed to the Li ion transference number in the ionic liquids at different temperatures. Decreased ion mobility at lower temperatures leads to charge accumulation on the surface of the electrode necessitating over-potential for the completion of redox reactions. Peak broadening at lower temperatures might be due to the concentration gradient of Li from the surface of the electrode particle to the bulk of the electrode requiring additional energy for diffusion of Li ions. At the beginning of the lithiation process, the incoming Li ions occupy the lattice sites on the surface of the electrode particles and subsequently undergo solid state diffusion into the bulk of the electrode.
Figure 4-21- Cyclic voltammetry of 2 mol % Cr doped LVP half-cells using a LiTFSI-PP13-TFSI as the electrolyte at 90°C

Hence, early lithiation begins at lower voltages and is limited to the surface of the electrode particle. But, an increased flux of Li ions reducing on the surface of the electrode caused by cycling at high scan rates cannot be compensated by the slow diffusion kinetics inside the bulk of the electrode. This increases the activation energy of the subsequent diffusion processes which demand greater energy for the completion of the reaction. Thus, further lithiation occurs at a higher potential which continues until all of the Li ions are intercalated resulting in broadening of the lithiation peaks. Similarly, the de-lithiation process involves reversal of the
mechanism causing broadening towards lower voltages. However, the solid state diffusion coefficient and the Li ion transference number increase with increase in temperature compensating each other for the entire process of lithiation or delithiation. A sharp current peak is an indicative of the efficiency and the reversibility of the redox reactions.

Cyclic stability measurements to estimate the effect of ageing and understanding long term effects of electrochemical cycling at high temperature were performed on similar 2032 coin cells at C/10 and 1C C- rates. Figure 4-22 shows the cyclic stability plot of capacity versus cycle number for 100 cycles at C/10 (corresponding to a current density of 14 mA g⁻¹). Albeit a gradual capacity fade in the first 10 cycles from charge and discharge capacities of 160 mAh g⁻¹ and 126 mAh g⁻¹ respectively to 116 and 110 mAh g⁻¹, the system demonstrates excellent cyclic stability with a capacity of 87 mAh g⁻¹ for both charge and discharge at the end of 100 cycles. This implies a 70% capacity retention at the end of 100 cycles at 90°C as against only 48% in case of un-doped LVP suggesting more than 20% enhancement in capacity retention after doping with Cr. Coulombic efficiencies of 99.8% were obtained for almost all the 100 cycles indicating excellent stability of the crystal structure resisting to atomic rearrangements.
Figure 4-22- Cyclic stability plot of the 2 mol % Cr doped LVP half-cells using LiTFSI-PP13-TFSI as the electrolyte at 90°C at a C rate of C/10.

Charge discharge measurements at higher scan rates demonstrate an expected reduction in stable capacity due to less time available for completion of the lithiation process. A capacity of 100 mAh g⁻¹ was observed when cycled at a C-rate of 1C at 90°C but, shows a higher capacity retention of 83% at the end of 200 cycles. In spite of good cyclic stability at higher C rates, there is a gradual capacity fade at smaller C-rates which can be partially attributed to structural changes in the active material in the electrode, long term ageing of the other components of the electrode and time-dependent degradation reactions of the current collectors.
4.3.3. Summary

The study attempts to understand the behavior of electrochemical performance of phosphate based cathode structures which have been reported to have superior structural stability compared to layered systems. V based phosphate systems were investigated because of their higher lithiation voltages (4.1V vs Li/Li⁺) to achieve stable cathodes with higher energy densities. Albeit, rigid phosphate framework of monoclinic LVP holding great promise under large current rates,

Figure 4-23- Cyclic stability plot of the 2 mol % Cr doped LVP half- cells using LiTFSI- PP13-TFSI as the electrolyte at 90°C at a C rate of 1C.
compromised cycle life due to transition metal dissolution has been a challenge. This may be attributed to the increased V dissolution kinetics resulting from removal of 2 Li atoms per molecule leading to large charge imbalance and inability of V atoms to compensate. The batteries exposed to 120°C were observed to have failed in the first cycle at a C-rate of C/10 indicating the corrosion of the Al current collectors which deposit at the negative electrode leading to short circuit. Unlike PF_6^-, Al is known to form unstable passivation layers under the presence of TFSI^- ions and thus undergoes dynamic corrosion which gets aggravated at high temperatures. Further, attempts were made to stabilize the LVP structure by doping the lattice with Cr atoms at V sites. Cr doped LVP was observed to enhance the structural stability of the system especially at high temperatures. Systematic structural and electrochemical correlated analysis revealed that a 2% doping of Cr^{3+} significantly stabilizes electronic configuration changes in vanadium in LVP during the charge and discharge of a LIB. The retention of the atomic arrangements and the unchanged oxidation state of Cr^{3+} with additional d-electrons facilitates electron cloud delocalization among the Vanadium atoms, thereby minimizing the disproportionation reactions which motivate dissolution. Suppression in loss of active species and increased electron transfer kinetics have been shown as the reason to improve the calendar cycle life of the electrode to over 400 cycles with over 70% capacity retention, facilitating high power operation with minimum degradation over a range of temperatures. The understanding of the influence of doped atoms towards origin of crystal structure stability from the perspective of changes in electronic configuration of transition metal in LVP has been limited. Insights from this study can offer a new dimension to
the design of tailored phosphate based cathode stoichiometries towards realizing a high energy high voltage cathode. Thus, Cr modified LVP was hypothesized as a potential high voltage cathode with high energy densities to realize a 4V battery which can successfully operate at 90°C.

4.4 Conclusion

The development of cathode materials with structural and electrochemical stability is a bottleneck for meeting current and future energy storage requirements. Among several transition metal based cathode materials that can provide high voltages and good capacities, quest for a high temperature sustenance along with consistent performance is a major challenge. The compromise on structural stability, especially during de-lithiation, due to excessive transition metal dissolution is the primary issue which moderates the cycle life of the cell. Some other factors including current collector corrosion, formation of passivation layers on the electrode surface, etc. add to the complexity of understanding the performance of a cathode system. Exposure of such systems to elevated temperatures may be detrimental with faster degradation of the active material. Investigations on commercial layered electrodes, LCO and V$_2$O$_5$, have proven the instability of oxygen anion framework due to kinetically activated degradation reactions and subsequent cell failure with a few hours of shelf life. Poly-phosphate based systems, known for greater structural stability were hypothesized as an optimistic alternative. Commercially employed LFP was investigated to understand the lithiation kinetics at 120°C and was observed to deliver stable cycling behavior for up to 200 cycles with nanometer sized particles.
Doped LVP systems identified for their superior lithiation voltages (>4V) and energy densities demonstrated excellent cyclic stability with over 80% capacity retention at 90°C. An increase in temperature aggravated current collector corrosion reactions limiting the operating temperature for high voltage cathode systems. However, the investigations on current collectors at high temperatures are beyond the scope of this research. Therefore, doped poly anion structures show a new route to explore and develop high energy density cathode materials for advanced lithium-ion batteries.
5.1 Introduction

The discovery of single layer graphene with extraordinary electronic, thermal and chemical properties lead to a paradigm shift in interest in two-dimensional (2D) materials. Inspired by many fascinating features, researchers have focused their attention on their unique optical, electrical, mechanical, and electrochemical properties. The flexibility to tune electrical properties, wide electrochemical window and precise control on the number of deposited layers facilitate application of graphene in diverse areas, one of the recent interests being thin film lithium ion batteries (LIBs) for on-chip energy storage devices as anodes and current collectors [433], [434]. The close packed layered structure forming LiC$_6$ upon lithiation limit bulk graphite structures to low power rate application, while, the present day electronic devices demand higher power densities [435]. Recently, graphene based structures, which provides faster lithium intercalation, have been studied for their synergistic integration into multifunctional devices [436]-[438].
5.2 Graphene as a universal interface for CNT growth as anodes for LIBs

Recent discovery of enhanced catalytic activity of metal and metal oxide nanoparticles decorated graphene has opened the doors for a new perspective of using graphene as a substrate for the catalytic growth of CNTs. The ease of transferability of graphene onto various substrates along with the possibility of graphene-mediated growth of vertically aligned CNTs has been studied for its prospects as interconnects in electronics [439]–[441]. Such applications demand a low contact resistance between CNT and metal electrodes which can be realized by direct growth of CNTs onto conductive substrates. This study [442] establishes graphene as the thinnest conductive substrate for CNT growth owing to its extraordinary electronic properties and its transferability which enables growth of CNTs onto surfaces that would otherwise not support.

5.2.1. Chemical Vapor deposition of graphene/CNT hybrids

5.2.1.1. Graphene growth on Cu and Ni by low-pressure CVD.

Cu and Ni foils (25 mm thick, 99.8%, Alfa Aesar) were used as substrates for monolayer and multi-layer graphene growth, respectively. The foils were loaded into a tubular quartz furnace and purged with Ar/H2 gas mixture (451) at a flow rate of 50 sccm under 90 mTorr pressure for 20 min, followed by ramping up the furnace temperature to 1000°C. Once the temperature was reached, it was held for 30 min to anneal the foils, followed by the introduction of CH4 (8 sccm for Cu and 4 sccm for Ni
substrates) for 10 min along with the Ar/H₂ gases. Following growth, the samples were cooled down to room temperature at a rate of 30°C/min rate under the Ar/H₂ mixture.

### 5.2.1.2. Graphene growth on Cu by atmospheric pressure CVD

Cu foil (25 mm thick, 99.8% purity, Alfa Aesar) was loaded into the center of a tubular quartz furnace and heated to 1000°C under a constant flow of argon (300 sccm) and hydrogen (30–100 sccm). Once the temperature was reached, it was held for 15 minutes to anneal the Cu foils, followed by the introduction of 1–2 sccm of CH₄ for 30 minutes along with the Ar/H₂ gases. Following growth the samples were allowed to cool down to room temperature naturally.

### 5.2.1.3. Carbon nanotube growth by floating catalyst CVD

CNTs were grown at ambient pressure via a floating catalyst CVD method using ferrocene and xylene as the catalyst and carbon source, respectively [443]. Ferrocene (10 wt. %) was dissolved in xylene through mild sonication. The mixture was then loaded into a syringe and delivered into a quartz tube furnace through a capillary connected to a syringe pump. The capillary was placed such that its exit point was just outside the hot zone of the tube furnace. The substrates (graphene-covered Cu, Pt, SiO₂ and diamond) were loaded into the center of the quartz tube furnace, which was heated to the growth temperature of (700 – 800°C) under a constant flow of argon (500 sccm) and hydrogen (60 – 120 sccm). After the furnace reached the growth temperature, the ferrocene/xylene mixture was injected
continuously into the tube furnace at a rate of 1.2 ml hr⁻¹ for the duration of the CNT growth (few seconds to 6 hours). At the end of the growth period the furnace was turned off and allowed to cool down to room temperature under the Ar/H₂ flow. The growth process produced vertically aligned multi-walled carbon nanotubes that grow via root growth on the graphene covered substrates. The heights of the CNT forests could be controlled by the precursor injection time, with typical growth rates at 1 µm min⁻¹. Post-growth characterization of the samples was performed with scanning electron microscopy (Zeiss Ultra 55 Plus) and micro-Raman spectroscopy (Renishaw Raman microscope, 633 nm excitation). To measure the I_D/I_G ratios of the samples, Raman spectra were collected at 50 random spots across the samples, followed by peak fitting to calculate the average I_D/I_G ratio.

5.2.1.4. Graphene transfer to arbitrary substrates.

The graphene was transferred from Cu foils to arbitrary substrates including SiO₂, Pt foils (ESPI Metals) and CVD diamond films (Delaware Diamond Knives) using a wet-chemistry polymer-based process [444]. PMMA (495, Micro Chem) was first spin-coated (4000 RPM for 60 s) on to the graphene-covered Cu foils. Iron chloride (2M solution, Sigma Aldrich) was used to etch the Cu such that the PMMA/graphene film was floated to the surface of the solution in a petri dish. The PMMA/graphene film was then scooped up on to a silicon chip and floated into a second petri dish containing deionized water. After rinsing in the DI water for several minutes to remove the excess iron chloride, the PMMA/ graphene film was placed on to the substrate of interest and left to dry for a few hours. After drying, the substrates were
heated in air to 100°C to enable flattening of the graphene films. Finally, the PMMA was stripped off in an acetone bath, and the samples were dried in air. In addition to flat substrates, graphene was also transferred to patterned quartz substrates. Rectangular patterns (4–6 µm wide, 20–30 µm long and 4 µm deep) were fabricated on quartz substrate via e-beam lithography and graphene was subsequently transferred to make suspended graphene.

5.2.1.5. Electrical Characterization

Two-probe current-voltage (I–V) measurements.

Tungsten needle probes were used for the two-probe electrical measurements, where one probe contacted the top of the CNT forest while the other probe was connected with the Cu foil (see inset in Fig. for a schematic of the setup). The I–V measurement was performed with a Keithley 4200-SCS instrument at room temperature.

Electrochemical Impedance Spectroscopy measurements.

Electrochemical impedance spectroscopy (EIS) measurements on Cu-graphene-CNT electrodes were conducted in a Swagelok-type cell using an AUTO LAB PGSTAT 302 potentiostat/galvanostat (Eco Chemie Utrecht, Netherlands). The test cells were assembled in an argon-filled glove box using the Cu-graphene-CNT as working electrode, lithium metal foil as the counter/reference electrode, 1 M solution of LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte and a glass microfiber filter was used as separator. The cell
was subjected to Galvanostatic charge/discharge cycles and EIS measurements were conducted at OCV and after 6, 12, 18 and 20th cycle by applying a constant dc bias with sinusoidal signal of 10 mV over the frequency range from 70 kHz and 10 mHz.

5.2.2. Results and discussions

5.2.2.1. CNT growth on suspended graphene

CVD growth of CNTs onto suspended graphene was attempted to understand the feasibility and its ability to support direct growth of CNTs. Graphene was first grown using methane as precursor through a CVD process which were then transferred onto a quartz substrate with trenches. The SEM image in Figure 5-1(a) shows the suspended graphene on the quartz trenches and the quality of the graphene films was estimated using Raman spectroscopy (Figure 5-1 (b)). Peaks at 1585 cm\(^{-1}\) and 2650 cm\(^{-1}\) corresponding to the G and G' bands confirm the presence of graphene and with the D band at 1330 cm\(^{-1}\) signifying disorder. The CNT growth using a floating catalyst CVD method using ferrocene and xylene precursors onto the graphene substrates were also characterized using Raman spectroscopy and the peaks from CNTs were found to overlap with those of the underlying graphene. \(^{13}\)C isotope labeled methane was used as precursor for graphene to distinguish between the two C allotropes which demonstrate a red-shift in the Raman spectra of graphene. Figure 5-1 (c) shows the SEM image of the CNT-graphene (\(^{13}\)C) suggesting the growth of the CNTs on the suspended graphene (\(^{13}\)C) which is highlighted by the CNTs along the perimeter of the trench. The inset shows the presence of CNTs on other regions where graphene has pulled off with the CNTs attached. The presence of graphene was
verified directly by Raman spectroscopy using graphene (\(^{13}\text{C}\)) with its shifted G and G’ bands (Figure 5-1 (d)).
5.2.2.2. Graphene as an intermediate layer on alternative substrates

While the suspended graphene layers facilitate the growth of CNTs, the possibility of using graphene as an intermediate to promote forest growth onto other substrates covered with graphene was explored. Copper, which is known as the best choice for graphene growth is inherently unfavorable for CNT growth and thus, was chosen as the obvious substrate to test the effect of a graphene under-layer. Graphene was grown onto Cu by well-established CVD process [346] and CNTs were grown subsequently via a floating catalyst CVD method. Figure 5-2 (a) is an optical microscope image of the graphene covered Cu foil with dense CNT growth as indicated by a sharp contrast between the Cu containing graphene and plain Cu. Corresponding SEM images represented in Figure 5-2 (b) reveal an 80 µm tall CNT forest with an average diameter of 25 nm showing the vertically aligned nature (inset). Since, Pt is not amenable for CNT growth as seen from the SEM image in Figure 5-2 (c), the CVD grown graphene on Cu were transferred onto Pt foils and CVD diamond films (Figure 5-2 (e)) using standard transfer techniques and tested for the role of graphene as an intermediate for growth of CNT on hostile surfaces. Analogous growth conditions for growing CNTs on Cu have resulted excellent forested growth on graphene covered Pt (Figure 5-2 (d)) and diamond (Figure 5-2 (f)) surfaces. This indicates the efficacy of the process to synthesize CNTs on any substrate. To investigate the evolution of the state of the graphene during CNT forest growth we again used $^{13}$C-graphene (containing 80% $^{13}$C isotope) on Cu foil. CNT growths were conducted for 5 and 10 minutes, followed by Raman spectroscopy analysis. Even after 10 minutes of CNT growth, the presence of the $^{13}$C-graphene peaks at 1535 cm$^{-1}$ and
2575 cm\(^{-1}\) (Figure 5-2 (g)) clearly confirm that the graphene layer remains intact. Longer synthesis times resulted in longer and denser tubes, rendering it difficult to identify Raman signals from graphene above the CNT Raman response. As separate confirmation, we performed experiments in which the CNTs were removed from the graphene-Cu substrate and the substrate was reused for CNT growth. Figure 5-2 (h) shows an SEM image of a substrate where the CNTs grown for 30 min. have been partially removed by gently scraping.

There is a significant distinction between the quality of the graphene obtained via exfoliation of the bulk material or grown via CVD methods, the former possessing higher degree of crystallinity. This difference indicates difference in interaction energy between catalyst particles and graphene. The density of the Fe nanoparticles was found to be less in the case of exfoliated graphene also forming a pattern on the grain boundaries in the case of CVD graphene. Thus, it was observed that the degree of crystallinity of the graphene under-layer has a direct influence on the successful growth of CNTs [442].
Figure 5-2- (a) Optical image of plain Cu (left) and graphene-covered Cu (right) after CNT growth. (b) SEM image of a CNT forest grown on graphene-covered Cu foil. The inset shows the vertical alignment of the CNTs. (c) SEM image collected after CNT growth on a bare Pt foil. (d) SEM image showing vertically aligned CNTs on graphene-covered Pt. (e) SEM image collected from bare diamond film after CNT growth. The inset shows a high magnification view of the diamond film with very sparse CNT coverage. (f) SEM image of vertically aligned CNTs on graphene-covered diamond. (g) Raman spectra collected from the CNTs grown on $^{13}$C-graphene for various growth times. The Raman peaks corresponding to both $^{13}$C-graphene and CNTs can be seen even after 10 minutes of growth, indicating that graphene survives the CNT growth process. (h) SEM image collected from a Cu sample from which MWNTs have been partially removed. The inset shows an SEM image of a CNT forest on Cu after re-growth.
5.2.2.3. Electronic contact resistance measurements

The realization of a multifunctional device with the fabricated morphology can be achieved through the effective electric charge conduction between the CNT and graphene layers. Probing I-V characteristics revealed a low ohmic resistance of $\sim 50 \, \Omega \, \mu \text{m}^{-2}$ which is lower than reported values for CNT forests [445]. However, EIS provides detailed evidence on the electrical contact resistance. A cell assembled using the CNT-graphene composites on Cu electrodes as the working electrode and Li metal as the counter and reference electrode was subjected to electrochemical charge and discharge cycles at a constant current density of $20 \, \text{mA g}^{-1}$. The resistance of the electrochemical cell was measured to be unchanged even after 24 cycles which otherwise increases due to increased loss of contact during cycling of conventional cells. Similarity in shape and size of semicircles are clear indications of minimal change in resistance between the current collector (Cu) and active electrode material (nanotubes) due to seamless integration through the graphene interface.
Figure 5-3- a) Two-probe I-V characteristic measured between the CNT forest and Cu foil (schematic in inset) showing linear (Ohmic) behavior. (b) Nyquist plot of EIS spectra collected from an electrochemical cell after 6, 12, 18 and 24 cycles.
5.2.3. Summary

The study demonstrates an effective approach to transform any hostile substrates to CNT growth to support the CVD growth by the introduction of an active intermediate graphene layer. CVD grown graphene can be an excellent mid layer and has been found to support the catalytic CVD growth of CNTs. The degree of crystallinity of the graphene and its influence on the quality of the nanotubes was investigated and understood. The possibility of modifying unfavorable surfaces to CNT growth by creating an ultra-thin universal interfacial substrate can potentially open the doors for new prospects in developing electronic interconnects and reduced ohmic losses for graphitic anodes in LIBs.

5.3 Electrodeposition of MoS$_2$ on 3D graphene current collectors as anodes for high power LIB

CVD grown graphene with few layers puts a constraint on the amount of active material limiting its use as anodes in thin film batteries. The reduced energy densities is a cause of major concern which restricts the performance of a LIB in spite of enhanced properties. However, increase in surface area of the electrode by engineering electrodes in 3D can enhance the energy density of the device without compromise on the power density. Recent efforts demonstrated deposition of few layer graphene onto stainless steel substrates for direct use as electrodes in thin film LIBs. Although 3D nano-structuring enhances the specific surface area, low specific density of graphene results in low gravimetric energy densities motivating the need
for dense packed layered analogues with high theoretical capacities. Previous reports on composites of graphene and electrochemically active ceramic materials like MnO$_2$, MoS$_2$, WS$_2$, etc. demonstrated great increase in capacity (up to 1000 mAh g$^{-1}$ for MoS$_2$) of the electrode compared to pristine graphene electrodes (372 mAh g$^{-1}$). Transition metal di-chalcogenides perform better than oxides having better first cycle efficiencies and smaller volume changes [446], [447]. Attempts to fabricate 3D composites of graphene and MoS$_2$, inspired from recent reports of high theoretical capacity (670 mAh g$^{-1}$), good rate capabilities and cyclic stability of MoS$_2$ [448], [449] with conformal and homogeneous coating on the graphene layers and controlled thickness is still a challenging task. In this report, we attempted electrodeposition of MoS$_2$ onto the 3D stainless steel/graphene substrates. The superior control on the deposit leaves room inside the pore for large volume changes of the ceramic during cycling, thus, reducing the internal stresses developed facilitating cycling at high current rates.

5.3.1. Experimental methods

5.3.1.1. Fabrication of graphene covered 3D stainless steel

The porous 3D graphene on stainless steel structures were fabricated using a method previously reported in literature by Gullapalli et al. with perfluorohexane (aka-C$_6$F$_{14}$ or tetradecafluorohexane, hereby called PFH) (99% purity and sealed under argon, from Sigma Aldrich) as a carbon precursor. Prior to the precursor injection into the evacuated furnace was heated to 950$^\circ$C while flowing Ar/5%H$_2$ and maintaining the pressure in the tube at 10 Torr. The H$_2$ flow was stopped and the
furnace was flushed with pure argon once the desired temperature is reached. Vapors of PFH were then passed for 10 to 12 minutes, while controlling the inlet flow to maintain the pressure at 600 mTorr. The flow of PFH was continued until the temperature reaches 800°C, while purging the tube with pure Ar flow.

### 5.3.1.2. Electro deposition of MOS₂

MoS₂ was deposited from a solution of 0.5g L⁻¹ ammonium tetrathiomolybdate ((NH₄)₂MoS₄), 3g L⁻¹ ammonium chloride (NH₄Cl) and 10.5g L⁻¹ potassium chloride (KCl) in formamide as reported in our previous studies [449]. In the three electrode setup, the graphene covered stainless steel substrate was used as working electrode, Ag/AgCl as reference electrode and platinum wire as counter electrode. Pulsed electrodeposition was carried out at -0.6V using potentiostat/galvanostat (AUTOLAB PGSTAT 302 N ECOCHEMIE) for 5 minutes with ON/OFF time of 10s/10s to ensure uniform deposition on the 3D structure. The electrolyte solution was maintained at 60°C and under constant stirring during the deposition. The substrate after MoS₂ deposition was rinsed using DI water and annealed at 450°C for 4 hours under Ar atmosphere.

### 5.3.1.3. Structural characterization

Morphological analysis of graphene covered 3D stainless steel substrates and thereby MoS₂ electrodeposited 3D structures was carried out using scanning electron microscope (FEI, Environmental SEM). Cross-sectional morphology was analyzed by cooling the sample in liquid nitrogen and thereby sheer cracking it. Vibrational
properties of the graphene and MoS$_2$ were analyzed using Renishaw Raman spectrometer with a 514.5 nm wavelength laser. X-ray photoemission spectroscopy (XPS) studies were carried out with a spectrophotometer (PHI Quantera SXM) using the monochromatic Al Kα radiation (1486.6 eV).

5.3.1.4. Electrochemical Characterization

Electrochemical measurements were performed by assembling the samples in a CR2032 type coin cell packaging. For the half-cell measurements, an electrochemical test cell was assembled in Ar-filled glove box using the fabricated 3D structures as working electrode, lithium metal foil as the counter/reference electrode and 1 M solution of LiPF$_6$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Charge discharge cycling tests were conducted using ARBIN Instruments Battery Analyzer while cyclic voltammetry measurements were carried out using a potentiostat/galvanostat (AUTOLAB PGSTAT 302 N ECOCHEMIE).

5.3.2. Results and Discussions

CVD growth of 3D graphene stainless steel substrates surface using PFH as precursor was adopted from a previous study by Gullapalli et al. Highly ordered surface trenches with conformal coating of few layers of graphene were successfully fabricated and the microstructure is shown in Figure 5-4.
The quality of the stainless steel and the apt choice of precursors controls the growth efficiencies of graphene and dictates the uniformity and conformity of the layers. The number of layers, however, is dependent on the cooling rate and not on the time of exposure. The study demonstrated the performance of deposited graphene layers as anodes for thin film LIBs. Extraordinary rate capabilities with a high capacity of 20 μAh cm\(^{-2}\) at a current density 64 μA cm\(^{-2}\) was obtained as compared to ~ 35 μAh cm\(^{-2}\) at a current density of 2 μA cm\(^{-2}\) for its 2D counterpart. The capability to cycle graphene at high rates with minimum capacity losses can be attributed to the increased electrode/electrolyte interfacial area. However, SEI
formation on graphene electrodes leading to loss in cyclic stability is a persistent challenge.

The preferential etching of the surface layers up to a depth of 10 µm to deposit conformal layers of graphene while still retaining the rest of the substrate enhances its applicability as an efficient current collector for LIBs for high power density. A recent interest in exploring transition metal dichalcogenides (TMDCs) as anodes for LIBs was a motivation to attempt electrodeposition of MoS$_2$ onto the graphene layers.

5.3.2.1. Characterization of electrodeposited layers

Electrodeposition of the MoS$_2$ films on graphene was optimized to obtain uniform conformal coating. Initial attempts for direct continuous deposition resulted in the formation of a bulk thick layer which completely filled the etched pores. This indicates that the continuous deposition favors layer by layer deposition and the rate constant is high for the deposition onto the previously deposited layers instead of that on graphene. Subsequent pulsed deposition resulted in uniform deposition through the entire region of the grain while still retaining significant vacant pore volume to accommodate volume changes during LIB charge and discharge cycles. A high magnification SEM image (Figure 5-5) indicates a controlled and conformal coating and the compact nature of the layer. A closer examination of the layers indicates a defect-free coating devoid of large pores or pin holes or other undesired products which could otherwise clog the pores cutting access of the electrolyte to the interior of the structure.
The quality of the underlying graphene layer has a significant influence on the quality of MoS$_2$ layers. A defective under layer results in the formation of amorphous phases owing to uneven current distribution along the layers. The voltage fluctuations resulting from the uneven currents causes inhomogeneous deposition and may be detrimental for the performance of LIB. Two distinct bands in the Raman spectra (Figure 5-6) of the MoS$_2$ layers at 390 cm$^{-1}$ and 410 cm$^{-1}$ confirms the presence of the MoS$_2$ phase and absence of additional bands reveals the quality of the coating.
5.3.2.2. Electrochemical behavior of MoS$_2$ on 3D graphene

The characteristic features of a layered structure and a low lithiation potential favors the application of MoS$_2$ as an anode for LIBs. Understanding of the enhancement in performance at high current rates with 3D MoS$_2$ by electrodeposition of nanoparticles onto 3D current collectors was attempted. Cyclic voltammetry plots of the MoS$_2$ half-cells was measured between 0.1 and 3V vs Li/Li$^+$. The first discharge shown as the black curve in Figure 5-7 (a), consists of two peaks at 1.1 V and 0.6 V corresponding to Li insertion. The peaks can be attributed to the phase change to form 1T- Li$_x$MoS$_2$ and dissociation into metallic Mo and Li$_2$S on further discharge [450]. Subsequent cycling exhibits reversible anodic peaks at 1.5 V and 2 V and cathodic peaks at 0.8 V and 1.7 V respectively, characteristic of discharge of MoS$_2$. The profile of the CV plot indicates complete reversible nature of the electrode for 10
scans at a slow scan rate of 0.1 mV s\(^{-1}\) indicating no additional redox reactions that may result in loss in efficiency.

In spite of efficient CV measurements, a gauge of the efficacy of the 3D electrodes towards high current rates can be measured by galvanostatic charge-discharge measurements. A voltage charge/discharge profile of a lithium battery versus the normalized areal capacity measured at a high current rate of 190 µA cm\(^{-2}\) is represented in Figure 5-7 (b). The black curve representing the first discharge shows voltage plateaus at ~1.1 V and ~0.8 V respectively which corresponds to the first discharge peaks as seen in the CV curve. The other curves in the plot representing selected cycles demonstrate a sloping lithiation/delithiation profile which can be attributed to the high current rates resulting in increased over-potential. However, a stable normalized areal capacity for up to 50 cycles of charge and discharge at 190 µA cm\(^{-2}\) indicates a very highly stable configuration resilient to high current densities and the structural changes associated with lithium insertion and removal.
Figure 5-7- (a) Cyclic voltammogram at 0.1 mV s\(^{-1}\) (b) Charge discharge voltage profiles at 190 \(\mu\text{A cm}^{-2}\) of the electrodeposited 3D-MoS\(_2\) electrode Lithium half-cell using 1M LiPF\(_6\) in EC/DMC (1:1 v/v)
A comparison with a similar MoS$_2$ layer electrodeposited onto a 2D substrate of graphene on stainless steel as an anode for LIB at the same current rate has been plotted in figure x. While the electrode capacity was normalized with respect to that of the 3D structures as 1 mAh cm$^{-2}$, the 2D electrode exhibits a significantly low capacity of 0.18 mAh cm$^{-2}$, indicating a fivefold increase in the relative capacity of the battery by adopting a 3D electrode instead of a 2D electrode. This emphasizes the hypothesis of increased electrode/electrolyte interfacial area and efficient Li ion diffusion.

Figure 5-8: Cyclic stability plots comparison of the electrodeposited 2D and 3D-MoS$_2$ lithium half-cell using 1M LiPF$_6$ in EC/DMC (1:1 v/v) at 190 µA cm$^{-2}$. 

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5.3.3. Summary

CVD grown 3D graphene architectures were used as a substrate to synthesize bulk 3D electrodes for LIBs. Having a 3D porous architecture combined with a highly conductive and inert surface coating that does not gravimetrically load the structure, makes the etched stainless steel-graphene an ideal candidate for current collectors in high capacity/high rate electrochemical devices. Transition metal di-chalcogenides (TMDCs) which have been known to possess high theoretical capacities have been limited for commercial applications owing to their poor electronic conductivity. The efficacy of the structure to support electrodes under high current rates over prolonged cycling is demonstrated by depositing MoS$_2$ into the pores. The process of electrodeposition was adopted to deposit conformal MoS$_2$ layers onto 3D graphene substrates which provides an increased electrode/electrolyte interfacial surface area and reduced lithium and electron diffusion distances. The 3D architecture had resulted in a 5-fold improvement in discharge capacity as compared to the 2D architecture. The enhanced performance of TMDCs through 3D architecture of the electrodes expands the horizons of the application of TMDCs beyond thin film LIBs.

5.4 Conclusion

The chapter elaborates the application of graphene as a potential current collector for LIBs. The graphitic form of carbon has been widely explored for its application as active electrodes for thin film batteries or flexible electronic interconnects. However, shortage of intercalating layers and low specific density,
restricts the total energy density from the cell. Owing to its excellent electronic conductivity, recent interest is targeted towards use of graphene as an underlying current collector to enhance the efficiency in electron conduction and reduce ohmic losses. A single step CVD approach has been developed to grow MWCNTs onto graphene layers and the interfacial resistances have been analyzed. CVD grown graphene layers can be practically transferred onto any substrate onto which catalytic growth of CNTs was achieved. The reduced interfacial resistance between CNTs and graphene serves to open doors for use of such interconnects into several applications and onto any surfaces. The flexibility of low resistance current collector interfaces can reduce the self-discharge of energy storage devices and enhance the storage life. Application of graphene as a current collector for LiBs has been under the spectrum of research for most of the high performing battery architectures. However, planar nature of graphene sheets cannot extend a high contact surface area with the electrode and the low power density of a battery is limited by the inherent electronic conductivity of the electrode material. However, 3D structuring of graphene onto porous substrates can improve the contact area and a enhanced capacity output was realized from otherwise poor conducting transition metal dichalcogenides. A conformal deposition of electrode materials onto graphene combined with 3D electrode architectures can serve as a useful approach to achieve high power devices and expand the limits of applications of LiBs.
The broad perspective of this thesis is about developing alternatives to critical battery components for realizing a functional LIB at elevated temperatures. In addition, tailored electrode architectures have been investigated for efficient battery performance at high charge rates. Commercial LIBs have been the primary choice for several portable applications since their inception. Using high performing materials, LIBs have been known to deliver highest capacities and energy densities. In spite of wide commercial use, inherent issues of stability and safety continue to plague the battery industry which get more pronounced at high temperatures. Most of the commercially employed active materials become unviable at such conditions and this thesis addresses few of the challenges with critical battery components. The primary focus of this thesis was to identify thermally stable materials which can potentially be combined to fabricate a functional LIB from room temperature to beyond 60°C.

At first, the organic solvent based electrolyte has been identified as the least thermally stable system with low boiling temperatures and high flammability which marks a battery unsafe for use at elevated temperatures.
A stable quasi-solid electrolyte system comprising of naturally occurring clay and a piperidinium based RTIL has been developed and tested for its operation in a LIB at high temperatures. These composites have been found to demonstrate high thermal stability up to 350°C and a wide electrochemical stability window of 3V. While ceramics are known for their extreme thermal stability, piperidinium based RTILs which exhibit negligible vapor pressures and wide temperature stability make the compositions extremely safe to use until a very high operation temperature. The composites have demonstrated a robust operability by surviving temperatures of 120°C for several cycles of charge and discharge at varying C-rates while still facilitating complete reversible lithiation of lithium titanate (LTO) delivering a capacity of 80 mAh g⁻¹. The composites devoid of low melting or boiling organic systems offer several advantages of structural and thermal stability to 350°C and electrochemical stability to 120°C. It can be implied that the electrolyte system can be employed to design a 3V battery which can successfully operate at 120°C. The ability to tune the electrolytes facilitates catering to any design of the battery from thin films to commercial scale batteries.

Beyond the electrolytes, cathodes have been notorious for several uncontrollable and thermally activated degradation kinetics. The next part of the thesis discusses the failure mechanisms of conventional LIB cathode materials, especially the oxide based layered systems. Although layered materials have been proven for their 2D lithiation mechanisms and good electrochemical stability with high intercalation potentials, the simultaneous transition metal dissolution and oxygen evolution are major contributors for reduced lifetime. It has been observed in
this study that these degradation reactions are kinetically dominated and the rate of
degradation enhances at high temperatures although there is no evidence for
structural transformations. The thesis also highlights the design of an alternate
cathode framework based on poly phosphates known for their high structural
stability and durability. Doped vanadium based phosphates have been identified to
be resistant to both thermal and electrochemical stimuli and have been structurally
resilient for an extended time period. Trace amounts of doping the structure with Cr
at V sites binds the structure effectively resulting a 20% enhancement in capacity
retention at 90°C. The measurements were limited to 90°C owing to the increased
corrosion kinetics of the current collectors investigations of which are beyond the
scope of the present study.

Attempts were made to improve the rate capabilities of the bulk LIBs by
engineering the electrode architectures. While a 2D planar electrode offers a limited
electrode/electrolyte interfacial area, 3D design of the electrodes increase the
interfacial area resulting in effective charge transfer. However, conformal deposition
of the electrodes onto 3D patterned current collectors is a major challenge. CVD and
electrodeposition techniques were optimized to yield conformal layers of LIB
electrodes and their electrochemical performance was evaluated. However, the
contact resistance between the current collector and the active material is generally
poor and leads to significant ohmic loses. CVD grown graphene was demonstrated as
a universal interface for efficient charge transfer between CNTs and metallic
substrates. MWCNTs were grown onto the graphene pre-grown on Cu substrates and
assembled in a lithium battery. No change in contact resistance was found after
several cycles of charge and discharge indicating a strong adhesion between the CNTs and graphene. Further, graphene grown on in-situ surface etched porous stainless steel substrates were used to deposit MoS$_2$ layers using electrodeposition process. The 3D electrode demonstrated a fivefold increase in the capacity as compared to the 2D analogue when assembled in a lithium battery and was found to survive high charge rates. The CVD graphene has been demonstrated to provide efficient charge transfer from the bulk electrode owing to its extraordinary electronic properties. The study projects graphene from the perspective of a charge transfer interface between the active material and the current collector and the efficient binding properties of graphene to both the surfaces facilitate significant reduction in ohmic losses and improve cycle life of a battery.
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