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Multivalent Rechargeable Batteries

by

Sudhaprasanna Kumar Padigi

A dissertation submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
in
Electrical and Computer Engineering

Dissertation Committee:

Raj Solanki, Chair
Robert Bass
Branimir Pejcinovic
David Evans
Gary Goncher
Tammy Lasseter Clare

Portland State University
2015

Abstract

Li^+ ion batteries have been the mainstay of high energy storage devices that have revolutionized the operating life time of consumer electronic devices for the past two decades. However, there is a steady increase in demand for energy storage devices with the ability to store more energy and deliver them at high power at low cost, without comprising safety and lifetime.

Li-ion batteries have had significant challenges in increasing the amount of stored energy without affecting the overall lifetime and the ability to deliver stored energy. In order to store and deliver more energy, more lithium ions need to be inserted and extracted from a given electrode (cathode or anode). Upon inserting a large number of Li ions, the crystal lattice of the materials undergo severe mechanical distortions, leading to un-desirable structural changes. This results in underutilization of theoretical energy storage capacities of the electrodes and early failure of the batteries owing to instabilities in the electrode materials.

Unlike monovalent Li^+ ions, multivalent rechargeable batteries offer a potential solution to the above problems. Multivalent cations, such as Ca^{2+} , are doubly-ionized as opposed to Li^+ which is a monovalent cation. The advantages of using Ca^{2+} ions instead of Li^+ ions are multifold. Due to the doubly-ionized nature, only half the number of Ca^{2+} ions need to be inserted and extracted from a given electrode to store and deliver energy from

a high capacity cathode as compared to Li^+ ions. This reduces the probability of lattice distortion and un-desirable structural changes, further leading to increased utilization of high theoretical energy storage capacities of the electrodes (cathode and anode). The use of Ca^{2+} ions also helps in delivering twice the amount of current density as compared to Li^+ ions due to its doubly ionized nature.

In this work, a set of eight metal hexacyanoferrate compounds were synthesized using the following metal ions: Ba^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+} , Fe^{3+} , Al^{3+} , Sn^{4+} , Mo^{5+} . The resulting metal hexacyanoferrate compounds were subjected to physical characterization using scanning electron microscope (SEM) and powder x-ray diffraction (XRD), to determine physical properties such as size, morphology, unit cell symmetry and unit cell parameters. This was followed by electrochemical characterization utilizing cyclic voltammetry and galvanic cycling, to determine the specific capacity and kinetics involved in the transport of Ca^{2+} ions to store charge. Optical characterization of the metal hexacyanoferrates using Fourier transform infrared (FTIR) spectroscopy, allowed for the identification of metal-nitrogen stretching frequency, which was used as a measure of the strength of the metal-nitrogen bond to understand the role of the above mentioned metal ions in electron density distribution across the unit cell of the metal hexacyanoferrates.

The specific capacity utilization of the metal hexacyanoferrates, when compared to the electronegativity values (χ_i) of the above mentioned metal ions, the σ -parameter, and the metal-nitrogen stretching frequency (ν), revealed an empirical trend suggesting that the materials (FeHCF, CaCoHCF and CaZnHCF) that possessed intermediates values for the

above mentioned parameters demonstrated high capacity utilization ($\geq 50\%$). Based on these empirical trends, it is hypothesized that a uniform distribution of electron density around a unit cell, as reflected by intermediate values of the electronegativity (χ_i) of the above mentioned metal ions, the σ -parameter and the metal-nitrogen stretching frequency (ν), results in minimal electrostatic interactions between the intercalating cation and the host unit cell lattice. This results in relatively easy diffusion of the cations, leading to high specific capacity utilization for metal hexacyanoferrate cathodes. These parameters may be used to select high efficiency cathode materials for multivalent batteries.

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1.0 Energy Storage: Purpose

The twentieth century has been marked by a scale and rate of industrialization and automation that has never been witnessed since the founding of human civilization. A major driver for this industrialization and automation has been energy. The ability to produce and use energy on demand has revolutionized our abilities as human beings to automate and improve the standard of living. Rapid growth in demand for mobile computing devices in the later-half of twentieth century has generated a need to develop energy storage devices with the ability to store enough energy to power mobile devices for longer durations of usage per charging cycle. There are different types of energy storage mechanisms, as illustrated in Figure 1.1 below:

Figure 1.1. Efficiency versus lifetime for different energy storage mechanisms [1]

This figure illustrates the difference in efficiency and lifetime for various energy storage technologies. Though pumped hydroelectric storage, fly wheels, and compressed air energy storage (CAES) offer efficiencies on the order of 70-95% with a life time of greater than 10,000 cycles, it is clear that Li-ion batteries and electrochemical capacitors offer a more practical choice with excellent efficiencies and competitive lifetimes. The large physical size, coupled with large financial investments, prohibit the usage of non-electrochemical technologies for powering mobile electronic and computing devices. Hence, it is of importance to develop electrochemical systems that consolidate the inherent advantages such as cost, size, and efficiency and overcome disadvantages such as lifetime and power density, to satiate the ever increasing demand for portable power sources with very high energy and power densities. The electrochemical systems can be classified as either batteries or capacitors.

1.1 Batteries versus Capacitors

1.2 Capacitors

Capacitors are passive electrical components that have a pair of electrodes separated by a dielectric medium. In the case of a parallel plate capacitor, two identical electrodes in the form of parallel plates are separated by a dielectric medium. The capacitor stores energy by storing charge on the electrode plates. There are several types of capacitors that can be used to store charge. Below is a brief description of the different types of capacitors:

I. Ceramic Capacitors

Ceramic capacitors are made of alternating layers of metal and ceramic film, where by the ceramic film behaves as a dielectric. The voltage generated by the ceramic capacitors can be controlled by controlling the thickness of the ceramic film. The schematic of a ceramic capacitor is illustrated in Figure 1.2(a).

II. Electrolytic Capacitors

Electrolytic capacitors are made of a metallic anode with an insulator or dielectric coating on its surface and a wet or solid electrolyte, which acts like a cathode as illustrated in Figure 1.2(b).

Figure 1.2. Schematic of (a) ceramic capacitor and (b) electrolytic capacitor.

III. Super Capacitors

Supercapacitors are a class of capacitors capable of storing large amounts of charge as compared to electrolytic and ceramic capacitors. Supercapacitors can be further classified as follows:

III.a. Double Layer Capacitors: In a double layer capacitor, the charge storage is achieved by a separation of charge in the Helmholtz double layer at the interface of the

electrode and the electrolyte solution. The charges stored are electrostatic in nature. The double layer capacitor is illustrated in Figure 1.3(a).

III.b. Pseudo Capacitors: In pseudo capacitors, the charge is stored by electrostatic as well as Faradaic means, which involves the storage of ions and an equivalent number of electrons on the surface of both electrodes, as represented by Figure 1.3(b).

III.c. Hybrid Capacitors: Hybrid capacitors are characterized by asymmetric electrodes that allow the storage of charge through both electrostatic as well as Faradaic means as shown in Figure 1.3(c).

Figure 1.3. Schematics of (a) Double layer capacitor. (b) Pseudo capacitors (c) Hybrid capacitor.

Energy storage in all types of capacitors is mainly a surface dominated phenomenon and most of the volume of the electrodes does not participate in the energy storage process. This, results in capacitors having significantly lower energy density than batteries.

1.3 Batteries

Batteries are electrochemical devices that store energy through a Faradaic means of charge transfer between the positive and negative electrodes that constitute the electrochemical cell. The process of storing charge in a battery is a bulk or volume based phenomenon, whereby there is a propagation of a reaction front through the bulk of the electrodes [2], ideally resulting in complete utilization of electrodes for the purpose of storing charge. This ability to utilize the bulk of the electrode results in large energy density. Figure 1.4 illustrates the concept of reaction front propagation in a battery. Batteries can be broadly classified into two groups: a) Primary batteries and b) Secondary batteries.

Figure 1.4. Schematic representation of reaction front propagation.

1.4 Primary or non-rechargeable battery

Primary batteries are NOT rechargeable. The operation of such batteries is characterized by the formation of discharge product not capable of reversible dissociation into the initial reactants that would allow “recharging” of the battery electrochemically. Some of the major advantages associated with the primary batteries are:

- 1) Ability to maximize energy density as design considerations for enabling recharging can be ignored.
- 2) Excellent choice for low cost and low drain applications such as watches.
- 3) Preferred power source for single use applications.
- 4) Lower initial cost.
- 5) Convenience of replacing a completely discharged battery with a fully charged battery.

Some of the disadvantages associated with the primary batteries are:

- 1) Incapable of handling high drain applications such as power tools due to the cost of constant replacement.
- 2) Disposal of primary batteries after single use generates large amounts of waste.
- 3) From an overall efficiency standpoint, primary batteries are highly inefficient as 98% of the energy used to produce them is non-recoverable.

Hence there is a need to develop batteries that can support high drain applications, with the ability to recharge over 1000 cycles and maintain a gravimetric or volumetric capacity of around 80% as compared to its initial capacity.

1.5 Secondary or rechargeable battery

Secondary batteries or rechargeable batteries enable the reversal of the discharging process, allowing the battery to be recharged many times. There are several types of rechargeable batteries as illustrated in Figure 1.5.

Figure 1.5. Classification of rechargeable batteries.

1.5.a. Liquid Flow Battery

Liquid flow based batteries involve the use of catholytes and anolytes which act as cathodes and anodes, respectively, and are separated by a membrane that allows the diffusion of the H^+ ions and prevents the diffusion the catholyte and anolyte species during the process of charging and discharging. The catholytes and anolytes are soluble ionic species that undergo oxidation and reduction during the process of charging and discharging. The catholyte and anolyte solution is stored in separate tanks and are pumped through an electrochemical cell comprising of two chambers separated by a membrane. Each chamber includes a carbon based current collector. The catholyte undergoes oxidation during the process of charging and reduction during the process of discharging. The anolyte undergoes oxidation during the process of discharging and reduction during the process of charging. They are used in

grid scale energy storage, with specific energies typically in the range of 10-20 Wh/kg.

1.5.b. Concentration Cell

The second major type of liquid battery is the concentration cell. Concentration cells rely on the process of diffusion of charged ions from one chamber to another driven by the difference in concentration of the charged ions between the two chambers in order to store energy. The reactant species or the charged species can be the same or different in nature in both the chambers. The diffusion of charged species from one chamber to another is thermodynamically driven to reach equilibrium, resulting in the generation of voltage. The voltage generated by concentration cells is very small compared to the liquid flow type battery.

1.5.c. Solid State Batteries

The solid state battery can be defined as a battery in which the electrodes, both the cathode (positive electrode during recharging) and anode (negative electrode), are in the form of solids and the electrolyte can either be in a solid state or liquid state. The advantage of a solid state battery is that it can possess a large energy density in a very compact form factor, like pouch cells or button cells. The disadvantage associated with a solid state battery is that it suffers from poor power density, as power density is diffusion limited. The rate of diffusion of ions determines the rate at which current is delivered and hence affects the power density. The solid state battery can be further

classified as a reaction type battery such as a lead-acid battery, or an intercalation type battery such as a Li-ion battery.

1.5.d Reaction type battery

Reaction type batteries operate on the principle of reversibly converting the chemical and structural nature of the electrodes (cathode and anode) to store and discharge energy. The process of discharging is represented by the reaction between the electrodes and the electrolyte (which together are referred to as reactants) to form a reaction product and the process of recharging the battery is represented by the dissociation or reconversion of the previously described reaction product to the reactants. It is important to note that the chemical and structural nature of the reactants and the reaction product are different from each other. Let us consider the example of a lead acid battery:

The positive electrode (cathode) and negative electrode (anode) are made of lead oxide (PbO_2) and lead (Pb), respectively, and the electrolyte is a solution of sulfuric acid. During the process of discharging, the lead anode and lead oxide cathode react with the sulfuric acid, resulting in the formation of lead sulfate on the anode side as well as the cathode side. During the process of recharging, the lead sulfate anode reduces back to metallic lead and the lead sulfate cathode converts to lead oxide, respectively. The above described reaction is illustrated in the equation below:

At the anode:

At the cathode:

1.5.e Intercalation type battery

The second major type of solid-state rechargeable battery is known as the intercalation type battery. Intercalation type batteries are also known as rocking chair or zebra batteries. This type of battery relies on insertion and extraction of charged ions into/out of the interstitial spaces present in the lattice of the electrodes, accompanied by the transfer of an equivalent number of electrons, which are stored by reducing the oxidation state of the lattice during the process of discharging and are given up by oxidizing the lattice to a higher oxidation state during the process of recharging. The above described process is illustrated in the equation below:

1.6. Concept of Intercalation and De-intercalation

The Intercalation type batteries rely on the principle of reversibly inserting and extracting charged species such as metal ions from the interstitial sites or interstitial diffusion pathways present in the electrode materials. The process of inserting charged species is called intercalation and the process of extracting the charged species is called de-intercalation.

1.6.a Intercalation: Intercalation is governed by a two-step process. The first step involves the adsorption of solvated ions on the surface of the electrode and the second step involves the process of the adsorbed ions overcoming an energy barrier present at the interface of the electrode and the electrolyte to get inserted or intercalated into the electrode host lattice. If the size of the solvated ion is larger than the diameter of the interstitial opening of the host lattice, then the solvated ion undergoes the process of de-solvation and overcomes this energy barrier to get inserted or intercalated into the interstitial space of the lattice.

The intercalation of ions is accompanied by the simultaneous transfer of an equivalent number of electrons to redox capable metal ions that are part of the lattice. The process of adding electrons results in maintaining charge neutrality of the host lattice with the guest ions in its interstitial space. The concept of intercalation is illustrated in Figure 1.6(a). Once the guest ion is intercalated into the host lattice, it diffuses through the lattice and resides in guest sites present in the interstitial spaces. If the guest ion has to de-solvate before getting intercalated, then the guest ion present in the lattice is bare without any solvation sheath around it. The bare ions encounter electrostatic forces from the host lattice, as illustrated in Figure 1.6(b).

The intensity and nature of the electrostatic forces depends on the amount of charge and nature of the charge presented by the host lattice. If the guest ion does not have to undergo de-solvation or has to undergo only partial de-solvation to get inserted into the host lattice, then the amount of electrostatic force encountered by the diffusing

ions is reduced, due to the shielding provided the solvation sheath, as shown in Figure 1.6(c), resulting in faster and farther diffusion of the solvated or partially solvated guest ions into the host lattice. At the cathode, the process of discharging involves intercalation of ions into the unit cell interstitial sites of the cathode. The process of intercalating a cation in a cathode is a thermodynamically driven process, wherein the cation resides in a lower energy state when present within the interstitial sites of the lattice of the cathode as opposed to solvated cation in the electrolyte. The difference between the free energy state (higher energy) of solvated ions and the free energy state (lower energy state) of intercalated ions, drives the process of discharging (intercalation) in a cathode.

Figure 1.6(a). Concept of intercalation of ions into a Prussian Blue crystal lattice.

Figure 1.6(b). Schematic of a sub-unit cell of Prussian Blue with the intercalated Ca^{2+} ion experiencing electrostatic interactions with the host lattice.

Figure 1.6(c). Schematic of a sub-unit cell of Prussian Blue with the partially solvated Ca^{2+} ion experiencing electrostatic interactions with the host lattice.

Figure 1.6(d). Schematic representation of the concept of de-intercalation of ions from the Prussian Blue lattice.

1.6.b. De-intercalation: The process of de-intercalation is exactly the opposite of intercalation. The guest ions present inside the interstitial sites in the host lattice diffuse outwards and desorb from the surface of the electrode host lattice with the concurrent removal of equivalent number of electrons to maintain charge neutrality, as shown in Figure 1.6(d). The ions undergoing de-intercalation are affected by the electrostatic forces in the same manner as they would be during the process of intercalation. From a cathode's point view, the process of charging involves de-intercalation of ions from the unit cell interstitial sites of the cathode.

1.7 Metal Hexacyanometallates

The processes of intercalation and de-intercalation involve reversibly insertion and extraction of ions. Hence, it is important to identify cathode materials that will allow these processes to occur multiple times without degrading. This work is focused on investigating metal hexacyanometallates as the cathode materials for rechargeable batteries.

Metal hexacyanometallates are a class of inorganic coordination polymers which are capable of storing and giving up electrons through the process of reduction and oxidation. These materials can be represented by a general formula: $A_xSP(CN)_6$, wherein the S metal ion is coordinated to nitrogen end of the cyanide ligand (CN) and the P metal ion is coordinated to the carbon end of the cyanide ligand (CN), and A represents the large interstitial tunnel sites that are populated by the hydrated cations in order to maintain charge neutrality of the host lattice [3, 4]. The most well-known metal hexacyanometallate is Prussian Blue (PB). Prussian Blue is a dark blue colored dye, which has been known for over three centuries. It is also known as Iron hexacyanoferrate. Figure 7 shows the unit cell of Prussian Blue.

Figure 1.7. Schematic illustration of a Prussian Blue unit cell.

Prussian Blue is represented by the chemical formula, $\text{KFe}^{3+}\text{Fe}^{2+}(\text{CN})_6$. Its basic unit comprises of a cyanide (CN^-) ligand that bridges the Fe^{3+} ion on the carbon end and Fe^{2+} ion on the nitrogen end. The position of Fe^{3+} and Fe^{2+} can be interchanged based on the precursor used for its synthesis. The basic unit repeats itself, resulting in the formation of a face centered cubic (FCC) lattice belonging to the $Fm3m$ family of crystals.

The lattice of Prussian Blue crystals resembles that of ABX_3 perovskites, with unit cell parameter $a=10.26 \text{ \AA}$ [3-6], and an interstitial tunnel opening of about $1.6 \text{ \AA}$, based on the hard sphere model [2, 3]. Prussian Blue can be synthesized in two forms, where the first form is called the “soluble version”, which is represented by the formula, $\text{KFe}^{3+}\text{Fe}^{2+}(\text{CN})_6$. “Soluble Prussian Blue” possesses the structure that is described above [4-6]. Prussian Blue is in fact a highly insoluble compound. The

presence of K^+ ions in the interstitial sites allows it to be easily peptized, resulting the in the suspension of the extremely small colloids of Prussian Blue.

The other version of Prussian Blue is called the “insoluble version” [4-6]. The “insoluble” Prussian Blue has the exact same crystal symmetry as possessed by the “soluble version”. However the difference between the soluble and in-soluble versions of Prussian Blue is that, about one-fourth of the ferrocyanide ligands ($Fe^{2+}(CN)_6^{4-}$) are missing from the lattice of the insoluble version of Prussian Blue. The missing ligands are replaced by water molecules that coordinate with the Fe^{3+} ions in the lattice. The insoluble version of Prussian Blue is represented by $Fe^{3+}_4(Fe^{2+}(CN)_6)^{4-}_3$.

The lattice structure of “soluble” Prussian Blue and “in-soluble” Prussian Blue is presented in Figure 1.8(a) and Figure 1.8(b), respectively. The “soluble” Prussian Blue is synthesized by mixing the ferrocyanide precursor and ferric nitrate in 1:1 molar ratio. The “insoluble” Prussian Blue is synthesized by mixing the ferrocyanide precursor and ferric nitrate in 1:2 molar ratio.

Figure 1.8(a). Illustration of “Soluble” Prussian Blue unit cell.

Figure 1.8(b) Illustration of “Insoluble” Prussian Blue unit cell.

The cathode material undergoes charging through the process of oxidation. This involves donation or removal of electrons from the lattice and de-intercalation of cations from the A sites in the interstitial space. In the case of Prussian Blue, during the process of charging, as illustrated in Figure 1.9, the lattice undergoes oxidation by removal of K^+ ions from the A sites in the interstitial spaces, and the Fe^{2+} ions present in the lattice undergo oxidation by donating the electron, resulting in Prussian Blue turning into Prussian Green (PG) which is a fully oxidized state of Prussian Blue. During the process of discharging, Prussian Blue accepts an additional K^+ ion and an electron, and reduces the oxidation of the Fe^{3+} ions in the lattice to Fe^{2+} by adding the electron to the lattice. A schematic representation of charging and discharging processes is presented in Figure 1.9.

1.8 Valency of the guest ions

In all intercalation type batteries, guest ions are reversibly inserted and extracted from the unit cell interstitial sites of both the cathode and the anode materials during the process of charging and discharging the battery. The guest ions are charged species such as Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} . As discussed in the section 1.6, the charge present on the guest ions influences their ability to diffuse and rate of diffusion in the interstitial spaces of the cathode and anode materials, owing to the electrostatic interactions between the guest ions and the host lattice. For an intercalation type battery to utilize a higher fraction of the theoretical capacity, the guest ions would have to reversibly diffuse as far as possible, or more preferably all the way to the last unit cell present in every grain of the cathode and anode material. For this to happen, the ions need to avoid electrostatic interactions with

the host lattice, which might impede their motion. The possibility of this happening in reality is complicated by the fact that, if a bare ion intercalates into the host lattice, the presence of a nominal amount of charge on the ion introduces some level of electrostatic interactions between the bare ion and the host lattice. This complication is further intensified when the charge of the guest ion increases as in the case of Ca^{2+} and Mg^{2+} ion as compared to Li^+ and K^+ ions. Hence, based on the just concluded discussion, it would be fair to assume that having a highly charged species would make it harder for a battery to be charged and discharged to full theoretical capacity. But, there are certain inherent advantages associated with using divalent cations, especially Ca^{2+} over using monovalent cations such as Li^+ . Let us draw a comparison between the popular monovalent cation (Li^+) and a divalent cation (Ca^{2+}).

Figure 1.10. Schematic representation of difference in lattice distortion in a high capacity cathode with lithium and calcium as guest ions.

1.8.a Lithium (Li^+):

The advantages of lithium ions are summarized below:

- Lithium (Li) is a light metal, resulting in a high theoretical gravimetric capacity of about 3,840 mAh/g, when used as an anode.
- Li^+ ions are monovalent and small in size, which allows the Li^+ ions to diffuse relatively quickly in solid media.

- Li metal oxidizes at a potential of -3.05 V vs Standard hydrogen electrode (SHE).

This is important because, the battery voltage is defined as $V_{\text{cathode}} - V_{\text{anode}}$.

Hence, the more negative the anode potential, the higher the total battery output voltage.

- Li ion battery technology has been extensively investigated for over three decades now. This has resulted in development of a large body of knowledge regarding various aspects of Li^+ ion batteries.

Dis-advantages:

- Li salts are scarce and hence, are expensive to use.
- With recent focus on increasing the energy storage capacity of the batteries, there is a need to use cathode materials with fundamentally high theoretical capacities. The potential problem of using Li^+ ions to store energy in such materials is that, it would require a large number of Li^+ ions and an equivalent number of electrons to be inserted into the host interstitial sites to utilize the gravimetric capacities offered by the materials. The large number of Li^+ ions inserted into the interstitial spaces, increase the amount of mechanical deformation in host lattice [16], as shown in Figure 1.10, leading to disruption of ion diffusing pathways, further resulting in reduced reversibility and reduced gravimetric capacity utilization, ultimately impacting the overall lifetime of the battery.

1.8.b Calcium (Ca^{2+}):

Advantages:

- Calcium is an abundant metal compared to lithium and is inexpensive.
- Calcium (Ca^{2+}) ions are divalent. This results in the transfer of two electrons per transfer of one Ca^{2+} ion, translating to twice the amount of current for a given capacity.
- Calcium metal oxidizes at a potential of -2.87 V Vs SHE, resulting a small voltage penalty compared to lithium.
- As mentioned above, with the focus on high energy density capacity batteries, replacing Li^+ ion with Ca^{2+} ions, would result in half the number of Ca^{2+} ions for the same number of electrons to utilize the high gravimetric capacity offered by the cathode materials. This would result in decreased mechanical deformations in the host lattice [16], resulting in increased probability of utilization of a larger fraction of theoretical capacity offered by the electrode materials. This concept is illustrated in Figure 1.10.

Disadvantages:

- Calcium metal is heavier (molar mass of 40.07 g/mole) compared to lithium (6.94 g/mole). In spite of having twice the number of electrons transferred per mole of calcium, the larger weight of calcium results in theoretical gravimetric capacity of 1,338 mAh/g, when used as an anode, which is a large loss compared to lithium.

- Calcium (Ca^{2+}) ion being divalent in nature, also complicates the process of the intercalation and de-intercalation as it encounter enhanced electrostatic interactions with the host lattice and results in slower diffusion through the interstitial space [17] and in some cases, ceases to diffuse due to the electrostatic bonds between the Ca^{2+} ion and the host lattice.

To recap, even though there is a loss in the possible theoretical capacity offered by calcium as compared to lithium, there are several advantages Ca^{2+} ions offer over Li^+ ions, such as lower cost and widespread availability of the electrolyte salts and the ability to deliver twice the amount of current for a given capacity as compared to lithium and the ability to induce less damage to high capacity cathodes.

Among the divalent guest cations, Mg^{2+} ions have been a subject of intense study [17-21]. Magnesium, when used as an anode electrode, results in a theoretical capacity of 2,206 mAh/g. But, magnesium, when used as an anode, reversibly oxidizes at a higher potential of -2.36 V vs SHE. This would result in reducing the over voltage generated by the battery. The biggest challenge associated with Mg^{2+} ion rechargeable batteries is that the popular electrolytes such as $\text{Mg}(\text{ClO}_4)_2$, do not reduce Mg^{2+} ions back to Mg metal on the anode. This is due to properties of the MgO layer that forms on the surface of Mg anode, which is both ionically and electronically insulating. To solve this problem, various research groups [17-21] have developed glyme-based electrolytes that strip the magnesium anode allowing for electro-deposition of magnesium during the charging process. However, glyme-based electrolytes are expensive and toxic. From an electrolyte

stand point, Ca^{2+} ion batteries with a calcium metal anode is rechargeable with commonly available, low cost and non-toxic electrolytes such as calcium perchlorate $\text{Ca}(\text{ClO}_4)_2$ [16, 22, 23]. In addition to the low cost and non-toxic electrolyte, Ca metal has lower oxidation potential of -2.87 V vs SHE, resulting in higher total voltage of the battery. As an overall summary, Ca^{2+} ion batteries with a calcium metal anode provide higher voltage compared to Mg^{2+} ions and calcium ions can be electroplated to calcium metal using low cost, non-toxic electrolytes during recharging process. The only disadvantage of calcium metal over magnesium metal is that of a lower theoretical capacity of a calcium metal anode.

The field of calcium ion rechargeable batteries is in its infancy. Overall, only a handful of papers have been published in this field. The most notable contributions include a V_2O_5 -based cathode for Ca^{2+} ion batteries [16, 22]. This work demonstrates only a few cycles of charging and discharging. The other major contribution describes the use of nickel hexacyanoferrate as a cathode for divalent cations [24]. This paper demonstrates about 2,000 cycles of charging and discharging in aqueous medium. The use of an aqueous medium allows for high power operation due to the small size of water molecules, allowing the ions to diffuse quickly between the electrodes. But, the use of water, limits the voltage range of the battery to 1.2 V due to hydrolysis of water. Water also prohibits the use of metal anodes such as calcium, as it leads to hydrogen gas generation. Hence, there is a need to study and identify cathode materials capable of calcium ion intercalation and de-intercalation in a non-aqueous medium. This would allow the usage

of a metal anode such as calcium allowing an increase in the voltage generated by the battery.

The rest of this dissertation is organized as follows: Chapter 2 discusses the synthesis and material characterization of metal hexacyanoferrate materials, followed by a description of electrochemical characterization techniques. Results are presented in Chapter 3. Chapter 4 is a discussion and summary of the results. Chapter 5 contains conclusions, as well as suggestions for future work.

Chapter 2. Materials and Methods

2.1 Metal Hexacyanoferrates as Cathode Material

The goal of identifying suitable cathode materials for rechargeable non-aqueous Ca^{2+} ion batteries was approached by synthesizing and testing a series of metal hexacyanoferrate compounds. Below (Fig. 2.1) is the schematic representation of the lattice of metal hexacyanoferrate compound. Our approach was to replace M'^{+} by different metal ions of increasing valency to produce a set of metal hexacyanoferrate analogues.

Figure 2.1. Cross-section of metal hexacyanoferrate complex.

The following is the list of metal ions that were inserted in place of M'^{+} , to synthesize various metal hexacyanoferrate compounds: Ba^{2+} , Zn^{2+} , Co^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Sn^{4+} , Mo^{5+} . The different M'^{+} metals ions were classified as: divalent cations (Ba^{2+} , Zn^{2+} ,

Co²⁺, Mn²⁺), trivalent cations (Al³⁺, Fe³⁺), tetravalent cation (Sn⁴⁺), and pentavalent cation (Mo⁵⁺). In addition to classifying them according to valency, these metal ions were also classified according to the different blocks of elements present in the periodic table, as follows: Ba²⁺ ions represented the s-block, Zn²⁺, Mn²⁺, Fe³⁺, Co²⁺, and Mo⁵⁺ ions represented the d-block. Al³⁺, Sn⁴⁺ ions represented the p-block. The s, p, and d blocks represented the orbitals occupied by the valence electrons of each of the metal species. Metal hexacyanoferrate compounds synthesized by using the above discussed metal ions allowed a study of the effect of the metal valency on the lattice arrangement and lattice constants of the resulting compounds. This exercise also allowed a study of the nature, and most importantly the strength of the bonds existing between Fe²⁺-C, CN, and Mⁿ⁺-N and its impact on the electrochemical performance of the materials during Ca²⁺ ion intercalation. To summarize, a list of metal hexacyanoferrate compounds that were synthesized using the above mentioned metal ions has been provided in Table 2.1.

2.2 Synthesis of Metal Hexacyanoferrate compounds

All of the above mentioned metal hexacyanoferrate compounds were synthesized using direct chemical precipitation technique, wherein an aqueous metal ion solution was added to an equimolar aqueous ferrocyanide salt solution, in a drop-wise manner under magnetic stirring, leading to the precipitation of a metal hexacyanoferrate complex. The precipitated metal hexacyanoferrate compounds were cleaned using centrifugation in deionized (DI) water and allowed to dry in air overnight, resulting in a dry metal hexacyanoferrate powders as shown below in Figure 2.2.

Metal Hexacyanoferrate	Chemical Formula	Metal ion (M')- (Periodic Table Block)	Valency of M'	Possible Redox States for M'	Redox activity status of M'	Expected Redox Potential (Volts) VS Ag/AgCl (1M KCl)
Potassium barium hexacyanoferrate	$K_2BaFe(CN)_6$	Ba-(s)	2+	only 2+	Inactive	0.24 V (Fe^{2+})
Calcium Zinc hexacyanoferrate	$Ca_{0.5}Zn_{1.5}Fe(CN)_6$	Zn-(d)	2+	only 2+	Inactive	0.24 V (Fe^{2+})
Calcium Cobalt hexacyanoferrate	$CaCoFe(CN)_6$	Co-(d)	2+	2+, 3+	active	0.24 V (Fe^{2+}); 1.585 V (Co^{2+})
Manganese hexacyanoferrate	$Mn_2Fe(CN)_6$	Mn-(d)	2+	2+, 3+	active	0.24 V (Fe^{2+}); 1.285 V (Mn^{2+})
Iron hexacyanoferrate	$Fe_4(Fe(CN)_6)_3$	Fe-(d)	3+	2+, 3+	active	0.24 V (Fe^{2+}); 0.9 V (Fe^{3+})
Calcium Aluminum hexacyanoferrate	$Ca_{0.5}AlFe(CN)_6$	Al-(p)	3+	only 3+	Inactive	0.24V (Fe^{2+})
Tin hexacyanoferrate	$SnFe(CN)_6$	Sn-(p)	4+	2+, 4+	active	0.24 V (Fe^{2+}); -0.085 (Sn^{4+})
Molybdenum Oxide hexacyanoferrate	$MoOFe(CN)_6$	Mo-(d)	5+	3+, 4+, 5+	un-known	0.24V (Fe^{2+}); un-known (Mo^{5+})

Table 2.1. List of metal hexacyanoferrate compounds synthesized using metal ions of increasing valency.

Figure 2.2. Process outlining synthesis, cleaning and drying of metal hexacyanoferrate powders.

2.2.1 Potassium Barium Hexacyanoferrate ($K_2BaFe(CN)_6$)

2.2.1.a. Synthesis Protocol (Room Temperature)

5 mmoles of potassium ferrocyanide ($K_4Fe(CN)_6$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmoles of barium nitrate ($Ba(NO_3)_2 \cdot 3H_2O$) was dissolved in 25 ml DI water under magnetic stirring at 60°C. Both the solutions were cooled to room temperature and the solution of barium nitrate was slowly added to potassium ferrocyanide solution in a drop-wise fashion under magnetic stirring, resulting in the precipitation of large crystallites of highly crystalline potassium barium hexacyanoferrate, $K_2BaFe(CN)_6$. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in yellow colored potassium barium hexacyanoferrate powders as shown in Figure 2.3(a).

2.2.1.b. Synthesis Protocol (Elevated Temperature)

5 mmoles of potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmoles of barium nitrate ($\text{Ba}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was dissolved in 25 ml of DI water under magnetic stirring at 60°C . The heated solution of barium nitrate was slowly added to potassium ferrocyanide in a drop-wise fashion under magnetic stirring, resulting in the precipitation of smaller crystallites, highly crystalline yellow colored potassium barium hexacyanoferrate, $\text{K}_2\text{BaFe}(\text{CN})_6$. The solution with the precipitate was maintained at 60°C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in small grained yellow colored potassium barium hexacyanoferrate powders, as shown in Figure 2.3(b).

Figure 2.3 Optical image of (a) Potassium barium hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$) synthesized at room temperature (RT). (b) Potassium barium hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$) synthesized at elevated temperature (60°C).

2.2.2 Calcium Zinc Hexacyanoferrate ($\text{Ca}_{0.5}\text{Zn}_{1.5}\text{Fe}(\text{CN})_6$)

2.2.2.a. Synthesis Protocol (Elevated Temperature)

5 mmoles of calcium ferrocyanide ($\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmoles of zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 25 ml DI water under magnetic stirring. Zinc nitrate solution was added in a drop-wise manner to solution of calcium ferrocyanide solution under magnetic stirring at 60°C , resulting in the precipitation of calcium zinc hexacyanoferrate, $\text{Ca}_{0.5}\text{Zn}_{1.5}\text{Fe}(\text{CN})_6$. The solution with the precipitate was maintained at 60°C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in white calcium zinc hexacyanoferrate powders as shown Figure 2.4(b).

Figure 2.4. Optical image of (a) Calcium zinc hexacyanoferrate ($\text{Ca}_{0.5}\text{Zn}_{1.5}\text{Fe}(\text{CN})_6$) synthesized at room temperature (RT). (b) Calcium zinc hexacyanoferrate ($\text{Ca}_{0.5}\text{Zn}_{1.5}\text{Fe}(\text{CN})_6$) synthesized at elevated temperature (60°C).

2.2.2.b. Synthesis Protocol (Room Temperature)

Calcium zinc hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure. The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60° C, resulting in white calcium zinc hexacyanoferrate powders as shown Figure 2.4(a).

2.2.3 Calcium Cobalt hexacyanoferrate ($\text{CaCoFe}(\text{CN})_6$)

2.2.3.a. Synthesis Protocol (Elevated Temperature)

5 mmoles of calcium ferrocyanide ($\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$) were dissolved in 25 ml DI water and heated to 60° C on a hot plate under magnetic stirring. 2.5 mmoles of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 25 ml DI water under magnetic stirring. Cobalt chloride solution was added in a drop-wise manner to solution of calcium ferrocyanide solution under magnetic stirring at 60° C, resulting in the precipitation of calcium cobalt hexacyanoferrate, $\text{CaCoFe}(\text{CN})_6$. The solution with the precipitate was maintained at 60° C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in bright green colored calcium cobalt hexacyanoferrate powders. The ferrocyanide to cobalt ion ratio was chosen to be 2:1, as it was previously reported in the literature [25], that such a ratio would lead to accessing the redox activity associated with cobalt. The resulting precipitate is shown in Figure 2.5(b)

Figure 2.5. Optical of (a) Calcium cobalt hexacyanoferrate (CaCoFe(CN)_6) synthesized at room temperature (RT). (b) Calcium cobalt hexacyanoferrate (CaCoFe(CN)_6) synthesized at elevated temperature (60°C).

2.2.3.b. Synthesis Protocol (Room Temperature)

Calcium cobalt hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure. The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60°C . The resulting in green colored calcium cobalt hexacyanoferrate is shown in Figure 2.5(a)

2.2.4. Manganese Hexacyanoferrate ($\text{Mn}_2\text{Fe(CN)}_6$)

2.2.4.a. Synthesis Protocol (Elevated Temperature)

5 mmoles of calcium ferrocyanide ($\text{Ca}_2\text{Fe(CN)}_6 \cdot 12\text{H}_2\text{O}$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmoles of manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 25 ml DI water under magnetic stirring. Manganese chloride solution was added in a drop-wise manner to solution of calcium

ferrocyanide solution under magnetic stirring at 60° C, resulting in the precipitation of manganese hexacyanoferrate, $\text{Mn}_2\text{Fe}(\text{CN})_6$. The solution with the precipitate was maintained at 60° C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in off-white colored manganese hexacyanoferrate powders. Figure 2.6(b) shows the optical image of manganese hexacyanoferrate.

Figure 2.6. Optical micrograph of (a) Manganese hexacyanoferrate ($\text{Mn}_2\text{Fe}(\text{CN})_6$) synthesized at room temperature (RT). (b) Manganese hexacyanoferrate ($\text{Mn}_2\text{Fe}(\text{CN})_6$) synthesized at elevated temperature (60° C).

2.2.4.b Synthesis Protocol (Room Temperature)

Manganese hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure. The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60° C. Figure 2.6(a) shows the optical micrograph of the resulting in half-white colored manganese hexacyanoferrate.

2.2.5. Iron Hexacyanoferrate ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$)

2.2.5.a. Synthesis Protocol (Elevated Temperature)

5 mmoles of Potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 10 mmoles of iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 25 ml DI water under magnetic stirring. Iron nitrate solution was added in a drop-wise manner to solution of potassium ferrocyanide solution under magnetic stirring at 60°C , resulting in the precipitation of dark blue iron hexacyanoferrate, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$. The solution with the precipitate was maintained at 60°C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in iron hexacyanoferrate powders. Figure 2.7(b) shows the optical image of iron hexacyanoferrate.

Figure 2.7. Optical image of (a) Iron hexacyanoferrate ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) synthesized at room temperature (RT). (b) Iron hexacyanoferrate ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) synthesized at elevated temperature (60°C).

2.2.5.b. Synthesis Protocol (Room Temperature)

Iron hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure, resulting in dark blue iron hexacyanoferrate, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ as shown in Figure 2.7(a). The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60°C .

2.2.6. Calcium Aluminum Hexacyanoferrate ($\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$)

2.2.6.a. Synthesis Protocol (Elevated Temperature)

5 mmols of calcium ferrocyanide ($\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmols of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 25 ml DI water under magnetic stirring. Aluminum nitrate solution was added in a drop-wise manner to solution of calcium ferrocyanide solution under magnetic stirring at 60°C , resulting in the precipitation of calcium aluminum hexacyanoferrate, $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$. The solution with the precipitate was maintained at 60°C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in bluish green calcium aluminum hexacyanoferrate powders as shown in Figure 2.8(b).

Figure 2.8. Optical image of (a) Calcium aluminum hexacyanoferrate ($\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$) synthesized at room temperature (RT). (b) Calcium aluminum hexacyanoferrate ($\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$) synthesized at elevated temperature (60°C).

2.2.6.b. Synthesis Protocol (Room Temperature)

Calcium aluminum hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure. The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60°C , resulting in bluish green calcium aluminum hexacyanoferrate powders as shown in Figure 2.8(a).

2.2.7. Tin (IV) Hexacyanoferrate ($\text{Sn}(\text{IV})\text{Fe}(\text{CN})_6$)

2.2.7.a. Synthesis Protocol (Elevated Temperature)

5 mmol of calcium ferrocyanide ($\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmol of tin (IV) chloride ($\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in 25 ml DI water under magnetic stirring. Tin (IV) chloride solution was added in a drop-wise manner to solution of calcium ferrocyanide solution

under magnetic stirring at 60° C, resulting in the precipitation of tin (IV) hexacyanoferrate, $\text{SnFe}(\text{CN})_6$. The solution with the precipitate was maintained at 60° C for 2 hours under constant magnetic stirring. The precipitates were cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in tin hexacyanoferrate powders. Tin (IV) hexacyanoferrate powders were dark blue colored and are shown in Figure 2.9 (b).

Figure 2.9. Optical image of (a) Tin(IV) hexacyanoferrate ($\text{SnFe}(\text{CN})_6$) synthesized at room temperature (RT). (b) Tin (IV) hexacyanoferrate ($\text{SnFe}(\text{CN})_6$) synthesized at elevated temperature (60° C).

2.2.7.b. Synthesis Protocol (Room Temperature)

Tin hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure. The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60° C. The dark blue colored tin (IV) hexacyanoferrate powders are shown in Figure 2.9(a).

2.2.8. Molybdenum Oxide Hexacyanoferrate ($\text{MoOFe}(\text{CN})_6$)

2.2.8.a. Synthesis Protocol (Elevated Temperature)

5 mmoles of calcium ferrocyanide ($\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$) were dissolved in 25 ml DI water and heated to 60°C on a hot plate under magnetic stirring. 5 mmoles of molybdenum (V) chloride (MoCl_5) was dissolved in 25 ml DI water under magnetic stirring, resulting in a vigorous reaction and the formation of MoO^{3+} ions and HCl vapors [41, 42]. MoO^{3+} solution was added in a drop-wise manner to solution of calcium ferrocyanide solution under magnetic stirring at 60°C , resulting in the precipitation of molybdenum oxide hexacyanoferrate, $\text{MoOFe}(\text{CN})_6$. The solution with the precipitate was maintained at 60°C for 2 hours under constant magnetic stirring. The precipitates are cleaned with DI water using centrifugation at 7,000 rpm and dried in air, resulting in dark greenish brown colored molybdenum oxide hexacyanoferrate powders, as shown in Figure 2.10(b).

Figure 2.10. Optical image of (a) Molybdenum oxide hexacyanoferrate ($\text{MoOFe}(\text{CN})_6$) synthesized at room temperature (RT). (b) Molybdenum oxide hexacyanoferrate ($\text{MoOFe}(\text{CN})_6$) synthesized at elevated temperature (60°C).

2.2.8.b. Synthesis Protocol (Room Temperature)

Molybdenum oxide hexacyanoferrate was also synthesized and cleaned at room temperature using the exact same ratio of the precursors as mentioned in the elevated temperature procedure. The main difference being that the precursor solutions were prepared and mixed at room temperature as opposed to 60° C, resulting in dark greenish brown colored molybdenum oxide hexacyanoferrate powders, as shown in Figure 2.10(a).

2.3. Characterization of Metal Hexacyanoferrates

Structural and electrochemical properties of a material determine its ability to store and discharge energy as an electrode in a battery. The structural properties include the grain size or the particle size and the particle morphology. The importance of these parameters stem from the fact that a smaller particle size would require a shorter diffusion length for an intercalating ion, thereby increasing the probability of completely utilizing the energy storage capacity of such a particle. The morphology of the particles affects the accessibility of the intercalating ions to the interstitial sites. In order to determine the size and morphology, as prepared metal hexacyanoferrate compounds were imaged using a scanning electron microscope (SEM). This technique allowed us to examine and determine the average size as well as identify the morphology of the synthesized particles.

The second structural parameter that influences the intercalation and diffusion of ions is the unit cell structure and unit cell parameters. The unit cell structure, or lattice

arrangement of materials, determine the physical size of the interstitial openings, interstitial sites, and the diffusion pathways available for the intercalation and diffusion of ions. These parameters were determined using powder X-ray diffraction (P-XRD). This technique involved exposing the metal hexacyanoferrate powders to a moving x-ray source and detecting the diffracted x-rays from the powder through a moving detector, resulting in determining the diffraction peaks, representative of the directionality of the crystal planes that define the unit cell lattice arrangement of the constituent metal atoms.

There is strong inter-dependence between the unit cell structure, or lattice arrangement, and the nature as well as the strength of the bonds of the materials. The nature and the strength of the bonds determine a structural arrangement of atoms that is thermodynamically stable. One of the most important parameters that governs the nature and strength of the bonds is the electron cloud density associated with a bond between two atoms. In a material with a lattice structure constituting multiple atoms, the electron cloud density distribution across the different bonds vary based on the level of interactions between the different atoms.

A qualitative measure of the electron cloud density distribution around a unit cell is helpful in determining the charge polarity associated with a unit cell structure. This was ascertained through Fourier transform infrared spectroscopy (FTIR). The FTIR technique involved exposing the material to a band of infrared frequencies, some of which would be absorbed due to the nature and strength of the existing bonds. An increase in the bond strength was usually indicated by an increase in the frequency of the peak as well as the

intensity or the extinction ratio depending on whether transmission or reflectance is being measured.

2.4. Cathode Paste Preparation

The process of turning as-prepared metal hexacyanoferrate powders into a cathode paste is shown in Figure 2.11. The metal hexacyanoferrate powder, which is the active material, was combined with polyvinylidene fluoride (PVDF), multi-walled carbon nanotubes, and activated carbon (AC) in a ratio of 80:9:9:2 by weight. The combined mixture was ground to a fine powder as shown in Figure 2.12 using a mortar and pestle. The fine powder was turned into a paint-like cathode paste using N-methyl-2-pyrrolidone (NMP) as a solvent.

Once the paste was prepared, a piece of carbon paper, which was used as a current collector, was cut to a dimension of 2 cm x 1cm (L x W). The carbon current collector was washed with DI water and ethanol and dried in an oven at 60° C for 2 hours to remove all solvents. Once dry, the carbon current collector was rubbed with a clean paper to remove any loosely bound particles. The carbon current collector was weighed to measure the dry weight. The cathode paste was then applied to the front side and allowed to dry at room temperature, following which the paste was applied to the other side and allowed to dry at room temperature. Once both the sides were dry, the electrode was loaded into a vacuum oven and heated at 100° C for 1.5 hours under vacuum to remove

all solvents. Upon cooling, the electrode was removed from the furnace and re-weighed to determine the weight of the cathode material on the carbon current collector.

Figure 2.11. Process of cathode paste preparation.

2.5. Electrochemical Measurement Techniques and Testing Apparatus

The cathode electrodes were electrochemically evaluated using cyclic voltammetry and galvanic cycling. In order to understand the above mentioned techniques, it is important to first understand the experimental set-up, which is shown in Figure 2.12.

Figure 2.12. Electrochemical testing apparatus.

The cathode electrode was tested using a three-electrode glass cell, which is comprised of a graphite counter electrode or anode, the working electrode or cathode, and the Ag/AgCl reference electrode in an electrolyte solution. The electrodes were connected to a PAR 273A potentiostat/galvanostat. It is important to determine the ability of a metal hexacyanoferrate compound to undergo redox and also ascertain the reversibility of the process. This was determined using a technique known as cyclic voltammetry.

Figure 2.13. Voltage waveform representative of the voltage sweep for 10 cycles in cyclic voltammetry.

Cyclic voltammetry involves subjecting the working electrode or the cathode to a voltage sweep with respect to the reference electrode, and measuring the current during the voltage sweep. It is useful to use a reference electrode with known reference potential, such as Ag/AgCl (Sat.KCl), as it provides a common point to compare the voltage generated by different materials. The voltage sweep range is defined by two extreme end points, at which the voltage sweep is reversed in direction. Figure 2.13 shows a sample of the voltage waveform used during the cyclic voltammetry. Figure 2.14 shows a typical cyclic voltammetry curve for a PB electrode in 1M aqueous KNO_3 electrolyte.

Cyclic voltammetry allows for studying the kinetics involved in the intercalation of ions as well as electron transfer associated with the intercalation of ions within the lattice of the active material.

Figure 2.14. Cyclic voltammetry curve for PB electrode in 1M KNO₃ aqueous electrolyte at a scan rate of 0.5 mV/s.

The above shown cyclic voltammetry curve is characterized by the presence of oxidation peaks and corresponding reduction peaks in the reverse sweep. The process of oxidation is associated with the removal of K⁺ ions from the interstitial sites and concurrent removal of electrons from the lattice. This is characterized by peak oxidation voltages V₁, V₂ and corresponding peak oxidation currents I₁, I₂. The process of reduction is associated with the insertion of K⁺ ions into the interstitial sites and additions of electrons to the lattice in order to maintain charge neutrality. This is characterized by peak reduction voltages V₃, V₄ and corresponding peak reduction currents I₃, I₄. The reversibility of the insertion and extraction of K⁺ ions is reflected by the difference between the peak oxidation and reduction voltages V₁, V₄ and V₂, V₃, respectively. The smaller the difference between the oxidation and reduction potentials, the higher the

reversibility associated with the redox process, in other words, insertion and removal of K^+ ions [26].

Another parameter that reflects the reversibility associated with redox process is the ratio of the peak oxidation and peak reduction currents, I_1 , I_4 and I_2 , I_3 , respectively. A ratio of 1 reflects maximum reversibility [26]. The shape and the separation of the peaks are usually dependent on the scan rate or the rate at which the voltage is scanned as indicated in Figure 2.15. This is due to the fact that the ions often lag behind a fast changing electric field associated with the fast scan rate. Hence, a cyclic voltammetry curve obtained at a slow scan rate such as 0.1 to 0.5 mV/S, reflects the real kinetics associated with the ion and electron transfer in a certain electrode material. The shape of the peak currents is related to the kinetics of electron and ion transfer process, in other words, the resistance associated with the insertion, partial diffusion and extraction of ions, as well as the ability of the cathode material lattice to conduct the equivalent number electrons added to the cathode.

The mobility of the ions in the interstitial sites is a diffusion limited process. The process of diffusion is dependent on the amount of electrostatic interactions between the intercalating ions and the host lattice.

Figure 2.15. Cyclic voltammetry curve for PB electrode in 1M KNO₃ aqueous electrolyte at a scan rate of a) 25 mV/S and (b) 0.5 mV/S.

A sharp peak indicates low resistance associated with the insertion, diffusion and extraction of ions and electrons from the lattice, due to reduced electrostatic interactions between the intercalating and diffusing ions. Similarly, a broad peak indicates increased resistance to insertion, diffusion and extraction of ions and electrons from the lattice, due to enhanced electrostatic interactions between the intercalating and diffusing ions. Hence, the cyclic voltammetry technique not only provides a means to observe and quantify the presence and reversibility of the redox processes associated with an electrode material,

but also reflects the intensity of electrostatic interactions between the interacting ions and the host lattice of the electrode material.

Figure 2.16. Galvanic cycling of a PB electrode at a current density of 111 mA/g, using an aqueous solution of 1M KNO_3 as electrolyte.

Upon initial characterization of the cathode using cyclic voltammetry, the cathode is subjected to constant current to determine the amount of charge the cathode can store per unit weight of the cathode. Figure 2.16 shows a typical galvanic cycling curve representing the process of charging and discharging the cathode. Figure 2.17 shows a detailed description of a galvanic cycle.

Figure 2.17. Detailed description of a charge-discharge profile for PB electrode with K^+ ions as the intercalating ions.

In galvanic cycling, an upper cut-off voltage and lower cut-off voltage are defined and the working electrode or cathode is subjected to a constant current. The voltage of the cathode is monitored with respect to Ag/AgCl reference electrode.

During the charging cycle, as the voltage of the cathode reaches the upper cut-off voltage, the polarity of the current reverses and the cathode is subjected to the process of discharging. As the voltage reaches the lower cut-off voltage, the process of discharging ends by again reversing current polarity, marking the beginning of the charging cycle again.

As Figure 2.17 indicates, the charging process involves the extraction of ions from the interstitial sites and the oxidation or extraction of equivalent number electrons from the cathode lattice. The discharging process involves the insertion of ions into the interstitial

sites and the reduction or addition of equivalent number of electrons to the cathode lattice.

Figure 2.18. Charge-discharge profile of PB electrode with Ca^{2+} as the intercalating ions.

The magnitude of electrostatic interactions between the intercalating ions and the host lattice determines the resistance encountered by the diffusing ions. This is reflected by the shape of the charge and discharge profile.

A flat charge-discharge profile is indicative of reduced electrostatic interactions between the intercalating ion and the host lattice, leading to a decrease in resistance to the diffusion of the ions through the lattice interstitial sites, as indicated in Figure 2.17.

Enhanced electrostatic interactions between the intercalating ions and the host lattice is indicated by a sloped charge discharge profile, due to increased resistance encountered by the intercalating ions, as shown in Figure 2.18.

Once the process of charging and discharging an electrode has been completed, the specific capacity associated with charging cycle and the specific capacity associated with

the discharging cycle is calculated by the following equation: specific capacity= $I \cdot t / g$, where I is the current applied to the electrode during charging and discharging, t is the time it took for the electrode to reach the upper cut-off voltage during charging and lower cut-off voltage during discharging and g is the mass of the cathode material on the carbon electrode. The experimentally measured specific capacities for all the previously mentioned metal hexacyanoferrate compounds will be compared against the theoretical limits. A general example for calculating theoretical capacity is presented below.

Let us consider lithium iron phosphate (LiFePO_4 or LPF) as the cathode material. In order to determine the theoretical capacity of LiFePO_4 , we need to determine the number of moles of Li^+ ions that will intercalate into LPF.

From the above equation, 1 mole of FePO_4 can intercalate 1 mole of lithium and LPF also takes up one mole of electrons in order to maintain charge neutrality or charge balance.

1 mole of electrons = $9.64 \cdot 10^4$ Coulombs of charge.

of coulombs in 1 mAh = 3.6.

Therefore, mAh per mole = $9.64 \cdot 10^4 / 3.6 = 2.677 \cdot 10^4$.

Now, mAh/g of 1 mole of LPF = $2.677 \cdot 10^4 / 158 \text{g}$ (molar mass of LPF) = 170 mAh/g.

Table 2.2 Indicates the expected theoretical specific capacities for all metal hexacyanoferrate compounds under investigation.

Metal hexacyanoferrate	Molecular weight (g/mole)	Theoretical specific capacity (mAh/g)
$\text{Ca}_{0.5}\text{KBaFe}(\text{CN})_6$	407.94	65.94
$\text{Ca}_{0.5}\text{Zn}_{1.5}\text{Fe}(\text{CN})_6$	330	81.5
$\text{CaCoFe}(\text{CN})_6$	310.86	86.53
$\text{Ca}_{0.5}\text{Mn}_{1.5}\text{Fe}(\text{CN})_6$	314.26	85.59
$\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$	258.83	103.92
$\text{Ca}_2\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$	939	114.58
$\text{Ca}_{0.5}\text{SnFe}(\text{CN})_6$	353.56	76.08
$\text{Ca}_{0.5}\text{MoOFe}(\text{CN})_6$	343.8	78.24

Table 2.2. List of metal hexacyanoferrate compounds under study as cathode materials and their theoretical specific capacities

All of the above molecular weights have been calculated for the anhydrous version of the metal hexacyanoferrate compounds, as it was very challenging to determine the precise number of water molecules present in the compounds, as the number of water molecules in a compound is a function of temperature, humidity and the hygroscopic nature of the compound itself.

Eight metal hexacyanoferrates were synthesized to identify and study suitable cathode materials for Ca^{2+} ion based non-aqueous rechargeable batteries. The metal hexacyanoferrates were synthesized using different metal ions with varying oxidation states to study the influence of oxidation state on the electrochemical performance of the metal hexacyanoferrates, when used as cathode electrode. Characterization and testing of the above listed metal hexacyanoferrates with the help of the methods and techniques outlined above will be discussed in chapter 3.

Chapter 3. Results

Chapter 3 discusses the results related to physical characterization: scanning electron microscopy (SEM) and X-ray diffraction (XRD), and electrochemical characterization: cyclic voltammetry (CV) and galvanic cycling (GC) of all the metal hexacyanoferrate cathode materials. This is followed by bond vibrational measurement and analysis of metal hexacyanoferrates using Fourier transform infrared spectroscopy (FTIR).

3.0 Experimental Conditions

XRD: X-ray diffraction measurement data was collected in a focused beam (Bragg–Brentano) geometry on a Rigaku Model Ultima IV X-ray diffraction system using graphite-monochromatized Cu K α radiation.

Electrochemical Measurements: All the electrochemical measurements (CV and GC) were performed with a three electrode arrangement in a glass beaker type cell. The electrodes (working or cathode, counter or anode, and the reference electrode) were connected to a PAR 273A potentiostat/galvanostat, which was computer controlled using GPIB, allowing for data collection using CORRWARE/CORRVIEW software. A metal hexacyanoferrate cathode was used as the working electrode and a graphite rod was used as the counter electrode in all measurements, and the electrolyte was made up of calcium perchlorate in acetonitrile (for Ca²⁺ ion measurements) and lithium perchlorate in acetonitrile (for Li⁺ ion measurements). Ag/AgCl (1M Na(ClO₄)) was used as a reference electrode.

FTIR: The FTIR measurements were performed using a Nicolet 6700 FT-IR spectrometer. The detector used for the Far-IR region was a DTGS detector with polyethylene (PE) window. The beamsplitter was made from a solid substrate. The sample chamber was purged with purified air (Parker Balston FT-IR purge gas generator, Model 75-52, equipped with additional hydrocarbon filters) to minimize the level of moisture. The spectra were obtained with 4 cm^{-1} resolution, and a total of 64 scans were collected and averaged for each sample. The sample was sandwiched between two PE sheets. All the spectra were processed using a spectrum of two pieces of pure PE sheets as the background.

3.1 Potassium Barium Hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$)

3.1.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized potassium barium hexacyanoferrate (K_2BaHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 1(a) and 1(b) represent the SEM images of $\text{K}_2\text{BaFe}(\text{CN})_6$ synthesized at room temperature. The materials when imaged using a 20 kV acceleration voltage resulted in charging of the materials due to their insulating nature. In order to avoid the charging effect, the materials were imaged with an acceleration of 5 kV. The room temperature synthesized $\text{K}_2\text{BaFe}(\text{CN})_6$ resulted in an average particle size of about 2-3 microns.

Figure 3.1(a). Scanning electron micrograph of $\text{K}_2\text{BaFe}(\text{CN})_6$ (a) with a scale bar of $2\mu\text{m}$, (b) expanded inset box with a scale bar of $1\mu\text{m}$.

Figure 3.1(c) and 3.1(d) represent the SEM images of $\text{K}_2\text{BaFe}(\text{CN})_6$ synthesized at 60°C . The resulting particles were about 500 nm in size as compared to $2\text{--}3\mu\text{m}$ particles resulting from room temperature synthesis. The $\text{K}_2\text{BaFe}(\text{CN})_6$ particles in Figure 3.1(d) closely resemble a tetragonal shape. Based on the average size of the crystals, the crystals synthesized at 60°C were chosen for further characterization, due to their smaller size.

3.1.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the $\text{K}_2\text{BaFe}(\text{CN})_6$ sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of $10^\circ\text{--}80^\circ\ 2\theta$ at room temperature. The PXRD spectrum is shown in Figure 3.2. The dominant peaks occur at 16.10° , 32.50° and 49.50° . It is evident from the width of the peaks that the as-formed $\text{K}_2\text{BaFe}(\text{CN})_6$ possessed good crystallinity. $\text{K}_2\text{BaFe}(\text{CN})_6$ has been synthesized previously [27], where the unit cell lattice symmetry was determined to

be tetragonal and the unit cell parameters were determined to be $a_0 = b_0 = 15.22 \text{ \AA}$ and $c_0 = 21.96 \text{ \AA}$.

Figure 3.1(c). Scanning electron micrograph of $\text{K}_2\text{BaFe}(\text{CN})_6$ (a) with a scale bar of $2\mu\text{m}$, (d) expanded inset box with a scale bar of 500 nm .

Figure 3.2. Raw powder XRD pattern of the as-synthesized $\text{K}_2\text{BaFe}(\text{CN})_6$ (60°C).

A very good match was obtained between our spectrum and reference [27], hence further refinement of peaks using the Rietveld technique was not attempted.

3.13 Electrochemical Characterization: Cyclic Voltammetry (CV) and Galvanic Cycling

The as-synthesized barium hexacyanoferrate powder was used as an active material to prepare the cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The potassium barium hexacyanoferrate cathode was subjected to electrochemical characterization to confirm redox activity and identify redox potentials. The electrochemical experimental set-up discussed in Section 3.0 at the beginning of the chapter was used to perform cyclic voltammetry with Ca^{2+} ions. The voltage on the cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.3. Cyclic voltammogram (CV) of potassium barium hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.3 shows a cyclic voltammetry curve for potassium barium hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement did not indicate a redox behavior and the shape of the curve could be approximated to a rectangle, indicative of a capacitive behavior of the electrode. Subsequently, the K_2BaHCF cathode was subjected to galvanic cycling, which involved charging and discharging the cathode by subjecting it to constant current and the cathode voltage was measured against Ag/AgCl (1M NaClO_4) reference electrode with respect to time. An upper cut-off voltage of 1 V and a lower cut-off voltage of 0 V were limits of charging and discharging process.

Figure 3.4, shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g. Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, the mass of the active cathode material, and the applied current, the K_2BaHCF cathode demonstrated a reversible specific capacity of 29.5 mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging. This resulted in 44.73% capacity utilization as compared to the calculated theoretical specific capacity of 65.94 mAh/g, based on equation (3.2).

To study the effect of increasing current density on the specific capacity, the K_2BaHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g over 30 cycles and 100 mA/g over 100 cycles, resulting in a reversible specific capacity of 27.80 mAh/g and 22.61 mAh/g, respectively. A minimal effect of increasing current density on reversible specific capacity, combined with CV and GC profiles shown in Figures 3.3-3.5, are indicative of a lack of a Faradaic storage mechanism or redox process, and confirm a capacitive charge storage mechanism in the K_2BaHCF cathode.

Figure 3.4. Galvanic cycling (GC) of potassium barium hexacyanoferrate in 1M $Ca(ClO_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.6 shows the specific capacity as well as the coulombic efficiency of the K_2BaHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.7 shows the specific capacity as well as the coulombic efficiency of the K_2BaHCF cathode at a current density of 100 mA/g. Based on Figures 3.6 and 3.7, it is evident that the specific capacity was fairly consistent over a number of cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.5. Charge-discharge profile of potassium barium hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.6. Reversible specific capacity and coulombic efficiency versus number of cycles for K_2BaHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at current density of 25 mA/g and 50 mA/g.

Figure 3.7. Reversible specific capacity and coulombic efficiency versus number of cycles for K_2BaHCF electrode in 1M $Ca(ClO_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.1.4. FTIR Measurement and Analysis

In order to understand the reason behind the lack of intercalation of Ca^{2+} ions in the interstitial spaces of K_2BaHCF , the as-synthesized K_2BaHCF was subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with the Ba^{2+} -N bond.

Figure 3.8 shows the FTIR spectrum of K_2BaHCF powders in the far-IR frequency region. Based on previously reported literature [31-35], the NC- Fe^{2+} bending mode occurs at 588 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 424 cm^{-1} . Ba^{2+} -N vibrational frequencies were identified as follows: 112 cm^{-1} (Ba^{2+} -N stretch), 314 cm^{-1} (Ba^{2+} -N bend) [34-36].

Figure 3.8 Far-IR spectrum of potassium barium hexacyanoferrate.

Figure 3.9. Far-IR spectrum of potassium ferrocyanide (K₄Fe^{II}(CN)₆).

K₂BaHCF was determined to be an ionic compound based on the similarity of the far-IR spectrum of the ionic compound potassium ferrocyanide as shown in Figure 3.9. In addition to similarities between the IR spectra, the difference in the electronegativities [28] of Ba (1.126) and N (2.939) was determined to be 1.813, which would characterize the nature of the bond between nitrogen and barium as ionic. As the strength of the bonding between barium and nitrogen is weak, the Ba²⁺-N stretching mode was assigned the lowest frequency of 112 cm⁻¹ as it involves the displacement of Ba²⁺-N bond along a single axial direction and as Ba²⁺ is octahedrally coordinated to nitrogen. Moreover, due

to the presence of a strong Fe^{2+} -C-N bond, the higher vibrational frequency of 314 cm^{-1} was assigned to the Ba^{2+} -N bending mode as the bending of Ba^{2+} -N bond would involve a larger force compared to the stretching mode due to the displacement of five other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Ba^{2+} -N and higher frequencies to Fe^{2+} -C bonds can be justified by the larger difference in the electronegativity values (2.14) between Ba and N as compared to that of 0.99 between Fe (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe^{2+} and C would result in a sigma (coordinate covalent) bond [43] between Fe^{2+} and C, which is a far stronger bond, resulting in higher vibration frequencies, as compared to the weak ionic bonding between Ba^{2+} and N.

Hence, based on the large difference in the electronegativity of Ba^{2+} and Fe^{2+} and the bond vibrational frequencies identified from the FTIR spectrum, it is hypothesized that due to the weak nature of the Ba^{2+} -N bonding and strong nature of Fe^{2+} -C bonding, there is a large polarity in the bond strengths across the unit cell, leading to a larger electron cloud density in the vicinity of the Fe^{2+} -CN bond. This would lead to enhanced electrostatic interactions between a doubly electron-deficient Ca^{2+} ions and the electron-rich Fe^{2+} -CN region of the lattice, resulting in the lack of intercalation of Ca^{2+} ions into the interstitial spaces of K_2BaHCF . This is reflected by lack of redox response in the CV plot in Figure 4 and a capacitive charge-discharge profile in the GC plot shown in Figure 3.5, leading to the reduced capacity utilization of 44.73%.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^+ ions and CV and GC measurement were performed on a new K_2BaHCF cathode. Figure 3.10 and Figure 3.11 show the CV and GC measurement curves of K_2BaHCF cathode with Li^+ ions.

Figure 3.10. Cyclic voltammogram (CV) of potassium barium hexacyanoferrate in 1M $\text{Li}(\text{ClO}_4)$ in acetonitrile with a scan rate of 0.5 mV/sec.

The cyclic voltammogram of K_2BaHCF cathode with Li^+ ions demonstrated a redox behavior at -0.14 V (reduction peak) and at 0.007 V (oxidation peak), with a peak separation of ΔV of 0.133 V, as shown in Figure 3.10. The $I_{\text{ox}}/I_{\text{red}}$ ratio was found to be 0.47. The peak separation of 0.133 V was rather large and the $I_{\text{ox}}/I_{\text{red}}$ ratio was rather small, but, nevertheless is indicative of a quasi-reversible electrochemical system. This indicates diffusion of Li^+ ions in the interstitial sites of the K_2BaHCF lattice, resulting from reduced electrostatic interactions between a monovalent Li^+ ion and the polarized electron cloud density of the lattice as compared to that of the divalent Ca^{2+} ions. The CV

measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.11.

Figure 3.11. Charge-discharge profile of potassium barium hexacyanoferrate in 1M Li(ClO₄) in acetonitrile at a current density of 25 mA/g.

The reversible specific capacities were about 29 mAh/g, similar to the specific capacity with Ca²⁺ ions. The lack of increase in specific capacity was due to the lower cut-off voltage of 0 V set during the GC cycling. In order to take advantage of the redox process, the cut-off voltage should have been set to -0.2 V. This was avoided because of the low breakdown voltage of acetonitrile solvent which is around -0.21V. Based on the electrochemical measurements and the FTIR data analysis, it was observed that with a monovalent cation such as Li⁺ ion, the magnitudes of electrostatic interactions were reduced, resulting in enhanced diffusion of the monovalent cation compared to that of the divalent cation, thereby, hinting at the existence of electron density polarization in the unit cell lattice of K₂BaHCF.

3.2 Manganese Hexacyanoferrate ($\text{Mn}_2\text{Fe}(\text{CN})_6$)

3.2.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized manganese hexacyanoferrate (MnHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 3.12(a) and 3.12(b) show SEM images of $\text{Mn}_2\text{Fe}(\text{CN})_6$ synthesized at room temperature. The materials were imaged with an acceleration of 5 kV due to the insulating nature of the materials. The room temperature synthesized $\text{Mn}_2\text{Fe}(\text{CN})_6$ resulted in an average particle size of about 2-3 microns.

Figure 3.12 Scanning electron micrograph of $\text{Mn}_2\text{Fe}(\text{CN})_6$ synthesized at room temperature with (a) a scale bar of 1 μm , (b) Expanded inset showing $\text{Mn}_2\text{Fe}(\text{CN})_6$ with a scale bar of 200 nm.

Figure 3.12(c) and 3.12(d) show SEM images of MnHCF synthesized at 60° C. The size of the resulting particles were also 2-3 μm . However, the MnHCF particles synthesized at 60° C had a large number of cracks or openings, leading to enhanced surface area as compared to MnHCF particles synthesized at room temperature. Based on the surface

area of the MnHCF crystals, the material synthesized at 60° C was chosen for further characterization.

Figure 3.12. Scanning electron micrograph of Mn₂Fe(CN)₆ synthesized at 60° C (c) with a scale bar of 1 μm, (d) expanded inset box with a scale bar of 200 nm.

3.2.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the 60° C Mn₂Fe(CN)₆ sample was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10°–80° 2θ at room temperature. The PXRD spectrum is shown in Figure 3.13 (a).

Figure 3.13(a). Raw powder XRD pattern of the as-synthesized $\text{Mn}_2\text{Fe}(\text{CN})_6$ (60°C).

The dominant peaks occur at 14.10° , 16.40° , 17.30° , 18.70° , 20.20° , 21.9° , 23.7° , 25° , 25.9° , 28.1° , 29.4° and 30.70° , 31.0° , 33.1° , 33.8° and 35.7° . It is evident from the width of the peaks that the as-formed $\text{Mn}_2\text{Fe}(\text{CN})_6$ possessed good crystallinity.

Figure 3.13(b). Rietveld refined powder XRD pattern of the as-synthesized $\text{Mn}_2\text{Fe}(\text{CN})_6$ (60°C).

The XRD spectrum was analyzed by Rietveld analysis using the XRD peak indexing software DicVol under the FULLPROF suite, as shown in Figure 3.13 (b). The unit cell lattice symmetry was identified as triclinic and belonging to the P-1 space group, with the

unit cell parameters determined to be as follows: $a_0 = 7.64095 \text{ \AA}$, $b_0 = 6.33765 \text{ \AA}$, $c_0 = 13.43897 \text{ \AA}$, $\alpha = 97.2976^\circ$, $\beta = 98.8095^\circ$, and $\gamma = 96.8572^\circ$.

3.2.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized manganese hexacyanoferrate powder was used as an active material to prepare a cathode paste and make cathodes as described in Section 2.4 of Chapter 2.

The manganese hexacyanoferrate cathode was subjected to electrochemical characterization to confirm redox activity and identify redox potentials. The electrochemical experimental set up described in Section 3.0 was used to perform cyclic voltammetry with Ca^{2+} ions. The voltage on the cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.15. Cyclic voltammogram (CV) of manganese hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.15 shows a cyclic voltammetry curve for manganese hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement showed an oxidation peak and a reduction peak, with an oxidation potential of 0.184V and a reduction potential of 0.138V, with a peak separation ΔV of 0.046 V indicative of Faradaic behavior of the electrode. The $I_{\text{ox}}/I_{\text{red}}$ ratio was found to be 0.72, indicative of a reversible electrochemical system. The peaks were well-defined but broad, which is indicative of resistance in the cathode system. Since the cathode paste recipe and the method of preparation was identical for all the materials, the resistance was assumed to be indicative of the diffusion process of Ca^{2+} ions in the MnHCF lattice. Subsequently, the MnHCF cathode was subjected to galvanic cycling, which involved charging and discharging it by applying a constant current and measuring its voltage against an Ag/AgCl (1M NaClO_4) reference electrode as a function of time. An upper cut-off voltage of 1 V and a lower cut-off voltage of 0 V were defined to mark the limits of the charging and discharging processes.

Figure 3.16 shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g. Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, the mass of the active cathode material and the applied current, the MnHCF cathode demonstrated a reversible specific capacity of 35.54 mAh/g at a current density of 25 mA/g over 30 cycles which resulted in 41.52% capacity utilization as compared to the calculated theoretical specific capacity of 85.59mAh/g, based on equation (3.4). The

charge discharge profile in Figure 3.17 was observed to be sloped, which is again an indication of the resistance encountered by the diffusing Ca^{2+} ions.

To study the effect of increasing current density on the specific capacity, the MnHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g over 30 cycles and 100 mA/g over 100 cycles, resulting a reversible specific capacity of 33.18 mAh/g and 29.11 mAh/g, respectively. A minimal loss of specific capacity at higher current densities suggests excellent rate capability for cycling Ca^{2+} ions using a MnHCF cathode.

Figure 3.16. Galvanic cycling (GC) of manganese hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.18 show the specific capacity as well as the coulombic efficiency of MnHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.20 shows the specific capacity as well as the coulombic efficiency of MnHCF cathode at current

density of 100 mA/g. Based on Figures 3.18 and 3.19, it is evident that the specific capacity was fairly consistent over multiple cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.17. Charge-discharge profile of manganese hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.18. Reversible specific capacity and coulombic efficiency versus number of cycles for MnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at current density of 25 mA/g and 50 mA/g.

Figure 3.19. Reversible specific capacity and coulombic efficiency versus number of cycles for a MnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.2.4. FTIR Measurement and Analysis

In order to understand the factors governing reduced specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of MnHCF, the as-synthesized MnHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with the Mn^{2+} -N bond. Figure 3.20 shows the FTIR spectrum of MnHCF powders in the far-IR frequency region. Based on previously reported literature [31-35, 37], NC- Mn^{2+} bending mode occurs at 588 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 453 cm^{-1} . Mn^{2+} -N vibrational frequencies were identified as follows: 175 cm^{-1} (Mn^{2+} -N stretch); 336 cm^{-1} (Mn^{2+} -N bend) [34-36].

Figure 3.20. Far-IR spectrum of manganese hexacyanoferrate.

MnHCF was determined to be a covalent compound based on the difference in the electronegativities [28] of Mn^{2+} (1.263) and N (2.939) of 1.676, which would characterize the nature of the bond between nitrogen and manganese as coordinate covalent. The Mn^{2+} -N stretching mode was assigned the lower frequency of 175 cm^{-1} as it involves the displacement of Mn^{2+} -N bond along a single axial direction and as Mn^{2+} is octahedrally coordinated to nitrogen. Due to the presence of a strong Fe^{2+} -C-N bond, the higher vibrational frequency of 336 cm^{-1} was assigned to the Mn^{2+} -N bending modes as the bending of Mn^{2+} -N bond would involve a larger force compared to the stretching mode due to the displacement of five other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Mn^{2+} -N and higher frequencies to Fe^{2+} -C bonds can be justified by the larger difference in the electronegativity values (1.676) between Mn^{2+} and N as compared to that of 0.99 between Fe (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe^{2+} and C would result in a sigma (coordinate covalent) bond [43] between Fe^{2+} and C,

which is a stronger bond, resulting in higher vibration frequencies, as compared to the coordinate covalent bond between Mn^{2+} and N.

Hence, based on the difference in electronegativity of Mn^{2+} and Fe^{2+} and the bond vibrational frequencies identified from the FTIR spectrum, it is hypothesized that due to the relatively weaker nature of the Mn^{2+} -N bonding and relatively stronger of Fe^{2+} -CN bonding, there is a large polarity in the bond strengths across the unit cell, leading to a larger electron density in the vicinity of the Fe^{2+} -CN bond. It is proposed that this leads to enhanced electrostatic interactions between a doubly electron deficient Ca^{2+} ions and the electron-rich (Fe^{2+} -CN) segment of the lattice, resulting in increase of resistance towards intercalation of Ca^{2+} ions into the interstitial spaces of MnHCF. This is similar to K_2BaHCF , leading to reduced capacity utilization of 43.96%.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^+ ions and CV and GC measurement were performed on a new MnHCF cathode. Figure 3.21 and Figure 3.22 show the CV and GC measurement curves of MnHCF cathode with Li^+ ions.

Figure 3.21. Cyclic voltammogram (CV) of manganese hexacyanoferrate in 1M Li(ClO₄) in acetonitrile with a scan rate of 0.5 mV/sec.

The cyclic voltammogram of MnHCF cathode with Li⁺ ions demonstrated a redox behavior at -0.118 V (reduction peak) and at 0.138 V (oxidation peak) as shown in Figure 3.21, with a peak separation ΔV of 0.020V, which was less than 0.046V separation observed for Ca²⁺ ions, which is indicative of highly reversible electrochemical system. The I_{ox}/I_{red} ratio was found to be 0.70. This is indicative of improved diffusion of Li⁺ ions in the interstitial sites of the unit cells of MnHCF lattice, due to reduced electrostatic interactions between a monovalent Li⁺ ion and the electron-rich Fe²⁺-CN segment of the lattice as compared to that of the divalent Ca²⁺ ions. The CV measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.22. The charge discharge profile in Figure 3.22 was observed to be less sloped for Li⁺ ions as compared to Ca²⁺ ions, which is again an indication of decreased resistance encountered by the diffusing Li⁺ ions.

Figure 3.22. Charge-discharge profile of manganese hexacyanoferrate in 1M Li(ClO₄) in acetonitrile at a current density of 25 mA/g.

The reversible specific capacity was 65.93mAh/g, resulting in a capacity utilization of 82.5% for Li⁺, as compared to a capacity utilization of 43.94% for Ca²⁺ ions. This increase in reversible capacity with a monovalent cation such as Li⁺ ion indicates the effect of reduced electrostatic interactions between Li⁺ ions and the MnHCF host lattice, resulting in improved diffusion of Li⁺ ions and thereby, increasing the capacity utilization of MnHCF, as compared to that of the divalent cation, hinting at the existence of electron density polarization in the unit cell lattice of MnHCF.

3.3 Zinc Hexacyanoferrate (Zn₂Fe(CN)₆)

3.3.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized zinc hexacyanoferrate (ZnHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 3.23(a) and 3.23(b) represent the SEM images of Zn₂Fe(CN)₆ synthesized at room temperature. The materials were imaged with an acceleration of 5KV due to the insulating nature of the materials. The room temperature synthesized

$\text{Zn}_2\text{Fe}(\text{CN})_6$ resulted in a mixed phase composition, wherein, phase I was identified as cubic from the SEM images with an average particle size of about 5-6 microns in length and width. The phase II was distinct from phase I, in its irregular shape with an average particle size of around 200-300 nm. From SEM images, phase II was observed to be a dominant phase as compared to phase I.

Figure 3.23. Scanning electron micrograph of $\text{Zn}_2\text{Fe}(\text{CN})_6$ synthesized at room temperature (a) with a scale bar of 5 μm , showing two different phases. (b) Expanded inset showing the second phase of $\text{Zn}_2\text{Fe}(\text{CN})_6$ with a scale bar of 500 nm.

Figure 3.23(c) and 3.23(d) represent the SEM images of ZnHCF-HT synthesized at 60°C. The resulting particles were also observed to have two distinct phases: phase I and phase II, as in the case of ZnHCF synthesized at room temperature. However, the phase II (dominant) ZnHCF crystals synthesized at 60°C had an average size of about 100-150 nm, leading to improved surface area as compared to ZnHCF particles synthesized at

room temperature. Based on the increased surface area of the ZnHCF-HT crystals, the crystals synthesized at 60°C were chosen for further characterization.

Figure 3.23(c). Scanning electron micrograph of $\text{Zn}_2\text{Fe}(\text{CN})_6$ synthesized at 60°C (a) with a scale bar of 5 μm . (d) expanded inset box with a scale bar of 200 nm.

3.3.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the $\text{Zn}_2\text{Fe}(\text{CN})_6$ sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10°–80° 2 θ at room temperature. The PXRD spectrum is shown in Figure 3.24.

Figure 3.24. Powder XRD pattern of the as synthesized $\text{Zn}_2\text{Fe}(\text{CN})_6$ (60°C).

The dominant peaks occur at 11.9° , 15.90° , 16.70° , 17.70° , 18.60° , 20.10° , 22.8° , 23.0° , 24.7° , 24.9° , 32.1° , 33.8° and 35.10° . It is evident from the width of the peaks that the as formed $\text{Zn}_2\text{Fe}(\text{CN})_6$ possessed good crystallinity. The SEM images indicated a mixed phase for $\text{Zn}_2\text{Fe}(\text{CN})_6$, wherein the first phase was cubic and this was indicated by the peaks at 17.70° , 24.7° , which are the major peaks for a cubic symmetry represented by Fm3m space group. Due to the large number of peaks and the presence of a different phase, it was not possible to index and refine the second and the more dominant phase $\text{Zn}_2\text{Fe}(\text{CN})_6$. However, a very good fit for the peaks of the second phase was identified by manually indexing the peaks to the x-ray diffraction spectrum of $\text{Mn}_2\text{Fe}(\text{CN})_6$ that was found in literature [37]. Hence, it is speculated that the second and dominant phase of $\text{Zn}_2\text{Fe}(\text{CN})_6$ could possess a monoclinic symmetry belonging to $\text{P}2_1/\text{n}$ space group with the unit cell parameters were determined to be $a_0 = 9.36$, $b_0 = 12.27 \text{ \AA}$ and $c_0 = 7.48 \text{ \AA}$ and $\alpha=\gamma=90^\circ$, $\beta=98.91652$.

3.3.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized zinc hexacyanoferrate powder was used as an active material to prepare cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The zinc hexacyanoferrate cathode was subjected to electrochemical characterization to confirm redox process and identify redox potentials. The experimental set up to perform cyclic voltammetry with Ca^{2+} ions has been detailed in Section 3.0. The voltage on the

cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.25. Cyclic voltammogram (CV) of zinc hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.25 shows a cyclic voltammetry curve for zinc hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement showed two peak oxidation peaks and two reduction peaks, with the peak oxidation potentials of 0.404V and 0.58V, respectively and a reduction potential ranging from 0.28 V to 0.56 V, indicative of faradaic behavior of the electrode. The peaks were observed to be broad, suggesting a fair degree of resistance in the cathode electrode. Since, the cathode paste recipe and the method of preparation were identical for all the materials, the resistance was assumed to be associated with the diffusion process of Ca^{2+} ions in the ZnHCF lattice.

This behavior of two oxidation potentials and two reduction potentials for ZnHCF has been reported previously in literature [39] and can be explained as the insertion of Ca^{2+} ions into the interstitial sites with different energies at the two reduction potentials, resulting in the removal of the Ca^{2+} at two different oxidation potentials. Subsequently, the ZnHCF cathode was subjected to galvanic cycling, which involved charging and discharging it, by applying a constant current and the measuring the cathode voltage against Ag/AgCl (1M NaClO_4) reference electrode with respect to time. An upper cut-off voltage of 1V and a lower cut-off voltage of 0V were defined to mark the limits of charging and discharging process. Figure 3.26 shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g and Figure 3.27 shows a single charge and discharge curve for the ZnHCF cathode.

Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, mass of the active cathode material and the applied current, the ZnHCF cathode demonstrated a reversible specific capacity of 39.47 mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging which resulted in 54.16% capacity utilization as compared to the calculated theoretical specific capacity of 72.44 mAh/g based on equation (3.6). The charge discharge profile in Figure 3.27 was observed to be sloped, which is again an indication of the resistance encountered by the diffusing Ca^{2+} ions.

To study the effect of increasing current density on the specific capacity, the ZnHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g over 30 cycles and 100 mA/g over 100 cycles resulting in a reversible specific capacity of 35.5mAh/g and 30.38mAh/g, respectively. A minimal loss of specific capacity loss at higher current densities suggests excellent rate capability for cycling Ca^{2+} ions using ZnHCF cathode.

Figure 3.26. Galvanic cycling (GC) of zinc hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.28 shows the specific capacity as well as the coulombic efficiency of ZnHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.29 shows the specific capacity as well as the coulombic efficiency of ZnHCF cathode at current density of 100 mA/g. Based on Figures 3.28 and 3.29, it is evident that the specific capacity was fairly consistent over a number of cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.27. Charge-discharge profile of zinc hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.28. Reversible specific capacity and coulombic efficiency versus number of cycles for ZnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at current density of 25 mA/g and 50 mA/g.

Figure 3.29. Reversible specific capacity and coulombic efficiency versus number of cycles for ZnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.3.4. FTIR Measurement and Analysis

In order to understand the factors governing the specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of ZnHCF, the as-synthesized ZnHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with the Zn^{2+} -N bond. Figure 3.30 shows the FTIR spectrum of ZnHCF powders in the far-IR frequency region. Based on previously reported literature [31-35, 37], NC- Fe^{2+} bending mode occurs at 592 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 488 cm^{-1} . Zn^{2+} -N vibrational frequencies were identified as follows: 187 cm^{-1} (Zn^{2+} -N stretch); 476 cm^{-1} (Zn^{2+} -N bend) [34-36, 38].

Figure 3.30. Far-IR spectrum of zinc hexacyanoferrate.

ZnHCF was determined to be a covalent compound based on the difference in the electronegativities of Zn^{2+} [28] (1.336) and N (2.939) was determined to be 1.603, which would characterize the nature of the bond between nitrogen and zinc as coordinate covalent. The Zn^{2+} -N stretching mode was assigned the lower frequency of 187 cm^{-1} as it involves the displacement of Zn^{2+} -N bond along a single axial direction and as Zn^{2+} is tetrahedrally coordinated to nitrogen and due to the presence of a strong Fe^{2+} -CN bond, the higher vibrational frequency of 476 cm^{-1} was assigned to the Zn^{2+} -N bending modes as the bending of Zn^{2+} -N bond would involve a larger force as compared to the stretching mode due to the displacement of three other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Zn^{2+} -N and higher frequencies to Fe^{2+} -C bonds can be justified by the larger difference in the electronegativity values (1.603) between Zn^{2+} ions and N as compared to that of 0.99 between Fe (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe^{2+} and C would result in a sigma (coordinate covalent) bond [43] between Fe^{2+} and C,

which is a stronger bond, resulting in higher vibration frequencies, as compared to the coordinate covalent bond between Zn^{2+} and N.

Hence, based on the difference in electronegativity of Zn^{2+} and Fe^{2+} and the bond vibrational frequencies identified from the FTIR spectrum, it is hypothesized that the amount of polarity in the bond strengths across the unit cell is reduced as compared to MnHCF and K_2BaHCF . This leads to a relatively uniform distribution of electron density between Zn^{2+} -N, CN, Fe^{2+} -C bonds, further resulting in relatively lower amounts of electrostatic interactions between a doubly electron deficient Ca^{2+} ions and the electron density across the lattice, translating into a slight reduction of resistance towards intercalation of Ca^{2+} ions into the interstitial spaces of ZnHCF as compared to MnHCF and K_2BaHCF , leading to a capacity utilization of 49%.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^+ ions and CV and GC measurement were performed on a new ZnHCF cathode. Figure 3.31 and Figure 3.32 show the CV and GC measurement curves of ZnHCF cathode with Li^+ ions.

The cyclic voltammogram of ZnHCF cathode with Li^+ ions demonstrated a pair of redox peaks at 0.201 V and 0.5V (reduction peaks) and 0.301 V, 0.503 V (oxidation peak) as shown in Figure 3.31, resulting a peak voltage difference ΔV of 0.1V and 0.103V, respectively. The $I_{\text{ox}}/I_{\text{red}}$ ratios were found to 0.9 and 1.28 for the two sets of redox peaks. The redox peaks were well-resolved as compared to the peaks with Ca^{2+} .

Figure 3.31. Cyclic voltammogram (CV) of zinc hexacyanoferrate in 1M Li(ClO₄) in acetonitrile with a scan rate of 0.5 mV/sec.

This is indicative of improved diffusion of Li⁺ ions in the interstitial sites of the unit cells of ZnHCF lattice, due to reduced electrostatic interactions between monovalent Li⁺ ions and the lattice, as compared to that of the divalent Ca²⁺ ions, due to relatively uniform electron density distribution across the lattice. The CV measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.36. The charge discharge profile in Figure 3.32 was observed to be less sloped for Li⁺ ions as compared to Ca²⁺ ions, which is again an indication of decreased resistance encountered by the diffusing Li⁺ ions.

The reversible specific capacity was 51.47 mAh/g, resulting in a capacity utilization of 68.2% for Li⁺, as compared to a capacity utilization of 49% for Ca²⁺ ions.

Figure 3.32. Charge-discharge profile of zinc hexacyanoferrate in 1M Li(ClO₄) in acetonitrile at a current density of 25 mA/g.

This increase in reversible capacity with a monovalent cation such as Li⁺ ion indicates the effect of reduced electrostatic interactions between Li⁺ ions and the ZnHCF host lattice, resulting in improved diffusion of Li⁺ ions and thereby, increasing the capacity utilization of ZnHCF, as compared to that of the divalent cation, hinting at the existence of relatively lower electron density polarization in the unit cell lattice of ZnHCF as compared to MnHCF.

3.4 Calcium Cobalt Hexacyanoferrate (CaCoFe(CN)₆)

3.4.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized calcium cobalt hexacyanoferrate (CaCoHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 3.33(a) and 3.33(b) represent the SEM images of CaCoFe(CN)₆ synthesized at 60°C with the Co²⁺:Fe(CN)₆⁴⁻ ratio of 1:2. The images indicate a porous platelet-like morphology with a thickness in the range of 30-50 nm.

Each of the platelets was further composed of nanoparticles with the sizes in the range of 15-25 nm. The $\text{CaCoFe}(\text{CN})_6$ powders were imaged using a 20 KV beam.

Figure 3.33. Scanning electron micrograph of $\text{CaCoFe}(\text{CN})_6$ synthesized at 60°C (a) with a scale bar of 500 nm. (b) Expanded inset showing $\text{CaCoFe}(\text{CN})_6$ with a scale bar of 200 nm.

3.4.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the $\text{CaCoFe}(\text{CN})_6$ sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10° – 70° 2θ at room temperature. The PXRD spectrum is shown in Figure 3.34.

Figure 3.34 (a). Raw powder XRD pattern of the as synthesized CaCoFe(CN)_6 (60°C).

The dominant peaks occur at 16.7° , 18.70° , 21.40° , 23.10° , 24.20° , 25.0° , 28.90° , 30.5° , 32.2° , 33.7° and 37.9° . It is evident from the width of the peaks that the as formed CaCoFe(CN)_6 possessed good crystallinity, indicative of a well-defined symmetry.

Figure 3.34 (b). Rietveld refined powder XRD pattern of the as synthesized CaCoFe(CN)_6 (60°C).

The XRD spectrum was analyzed by Rietveld analysis using a XRD peak indexing software, DicVol under the FULLPROF suite, as shown in Figure 3.36 (b), to identify the unit cell lattice symmetry as monoclinic belonging to the $P 2_1/m$ space group, with the unit

cell parameters determined to be as follows: $a_0 = 10.76778 \text{ \AA}$, $b_0 = 3.92032 \text{ \AA}$ and $c_0 = 9.59701 \text{ \AA}$ and $\alpha = \gamma = 90^\circ$, $\beta = 98.91652^\circ$. A unit cell for these parameters is shown in Figure 3.35.

Figure 3.35. Schematic of unit cell of CaCoFe(CN)_6 .

3.4.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized calcium cobalt hexacyanoferrate powder was used as an active material to prepare cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The CaCoHCF cathode was subjected to electrochemical characterization to confirm redox process and identify redox potentials. The experimental set up used to perform cyclic voltammetry with Ca^{2+} ions, is detailed in Section 3.0. The voltage on the CaCoHCF cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.36 shows a cyclic voltammetry curve for CaCoHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement showed a peak oxidation peak and a reduction peak, with the peak oxidation potentials of 0.439V and a reduction potential of 0.347 V with a peak separation ΔV of 0.092V, indicative of faradaic behavior of the electrode. The $I_{\text{ox}}/I_{\text{red}}$ ratio was found to be 0.72, indicative of a reversible electrochemical system. The peaks were relatively sharp, suggesting low resistance in the cathode electrode as well as fast kinetics associated with the intercalation and de-intercalation of Ca^{2+} ions. Since, the cathode paste recipe and the method of preparation was identical for all the materials, the resistance was assumed to be associated with the diffusion process of Ca^{2+} ions in the CaCoHCF lattice.

Figure 3.36. Cyclic voltammogram (CV) of calcium cobalt hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Subsequently, the CaCoHCF cathode was subjected to galvanic cycling, which involved charging and discharging the cathode, by applying a constant current and measuring the cathode voltage against Ag/AgCl (1M NaClO₄) reference electrode with respect to time. An upper cut-off voltage of 0.8V and a lower cut-off voltage of 0V were defined to mark the limits of charging and discharging process.

Figure 3.37 shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g and Figure 3.38 shows a single charge and discharge curve for the CaCoHCF cathode. Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, mass of the active cathode material and the applied current, the CaCoHCF cathode demonstrated a reversible specific capacity of 55.04 mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging which resulted in 63.60% capacity utilization as compared to the calculated theoretical specific capacity of 86.53 mAh/g, based on equation (3.7). The charge discharge profile in Figure 3.38 was observed to be quite flat which is indicative of relatively low resistance associated with the diffusion of Ca²⁺ ions in the CaCoHCF lattice.

To study the effect of increasing current density on the specific capacity, the CaCoHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g over 30 cycles and 100 mA/g over 100 cycles resulting a reversible specific capacity of

55mAh/g and 44.22 mAh/g, respectively. CaCoHCF electrodes appeared to demonstrate excellent rate capability as indicated by marginal loss in reversible specific capacity.

Figure 3.39 shows the specific capacity as well as the coulombic efficiency of CaCoHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.40 shows the specific capacity as well as the coulombic efficiency of CaCoHCF cathode at current density of 100 mA/g. Based on Figures 3.39 and 3.40, it is evident that the specific capacity was fairly consistent over a number of cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.37. Galvanic cycling (GC) of calcium cobalt hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.38. Charge-discharge profile of calcium cobalt hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.39. Reversible specific capacity and coulombic efficiency versus number of cycles for CaCoHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g and 50 mA/g.

Figure 3.40. Reversible specific capacity and coulombic efficiency versus number of cycles for CaCoHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.4.4. FTIR Measurement and Analysis

In order to understand the factors governing the specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of CaCoHCF, the as-synthesized CaCoHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with the Co^{2+} -N bond. Figure 3.41 shows the FTIR spectrum of CaCoHCF powders in the far-IR frequency region. Based on previously reported literature [31-35, 37, 40], NC- Fe^{2+} bending mode occurs at 598 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 523 cm^{-1} . Co^{2+} -N vibrational frequencies were identified as follows: 222 cm^{-1} (Co^{2+} -N stretch); 498 cm^{-1} (Co^{2+} -N bend) [34-36, 40].

Figure 3.41. Far-IR spectrum of calcium cobalt hexacyanoferrate.

CaCoHCF was determined to be a covalent compound based on the difference in the electronegativities [28] of Co²⁺ ions (1.321) and N (2.939) was determined to be 1.618, which would characterize the nature of the bond between nitrogen and cobalt ions as coordinate covalent. The Co²⁺-N stretching mode was assigned the lower frequency of 222 cm⁻¹ as it involves the displacement of Co²⁺-N bond along a single axial direction and as Co²⁺ is octahedrally coordinated to nitrogen and due to the presence of a strong Fe²⁺-CN bond, the higher vibrational frequency of 498 cm⁻¹ was assigned to the Co²⁺-N bending modes as the bending of Co²⁺-N bond would involve a larger force as compared to the stretching mode due to the displacement of five other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Co²⁺-N and higher frequencies to Fe²⁺-C bonds can be justified by the larger difference in the electronegativity values (1.618) between Co²⁺ and N as compared to that of 0.99 between Fe²⁺ (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe²⁺ and C would result in a sigma (coordinate covalent) bond [43] between Fe²⁺ ions and

C, which is a stronger bond, resulting in higher vibration frequencies, as compared to the coordinate covalent bond between Co^{2+} and N.

Hence, based on the difference in electronegativity of Co^{2+} and Fe^{2+} and the bond vibrational frequencies identified from the FTIR spectrum, it is hypothesized that the bond strengths are more balanced across the unit cell as compared to MnHCF and K_2BaHCF . This could lead to a more uniform distribution of electron density between Co^{2+} -N, CN, Fe^{2+} -C bonds, further resulting in reduced electrostatic interactions between a doubly electron deficient Ca^{2+} ions and the CoHCF lattice. This could translate into slight reduction of resistance towards intercalation of Ca^{2+} ions into the interstitial spaces of CaCoHCF as compared to MnHCF and K_2BaHCF , leading to a capacity utilization of 63.60%.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^+ ions and CV and GC measurement were performed on a new CaCoHCF cathode. Figure 3.42 and Figure 3.43 show the CV and GC measurement curves of CaCoHCF cathode with Li^+ ions.

The cyclic voltammogram of CaCoHCF cathode with Li^+ ions demonstrated redox peaks at 0.326V (reduction peak) and 0.414 V (oxidation peak), with a peak separation, ΔV of 0.88V and a $I_{\text{ox}}/I_{\text{red}}$ ratio of 0.82, as shown in Figure 3.42. The redox peaks were well-defined. This is indicative of relatively easy diffusion of Li^+ ions in the interstitial sites of CoHCF lattice, due to reduced electrostatic interactions between a monovalent Li^+ ion and a well-balanced electron density across the lattice.

Figure 3.42. Cyclic voltammogram (CV) of calcium cobalt hexacyanoferrate in 1M Li(ClO₄) in acetonitrile with a scan rate of 0.5 mV/sec.

The CV measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.43. The charge discharge profile in Figure 3.43 was observed to a similar slope for Li⁺ ions as compared to Ca²⁺ ions, which is again an indication of similar, low resistance encountered by the diffusing Li⁺ ions.

Figure 3.43. Charge-discharge profile of calcium cobalt hexacyanoferrate in 1M Li(ClO₄) in acetonitrile at a current density of 25 mA/g.

The reversible specific capacity was 42.37mAh/g, resulting in a capacity utilization of 47.13% for Li^+ , as compared to a capacity utilization of 63.60% for Ca^{2+} ions. This result was a departure from the trend, when compared to MnHCF and ZnHCF, where, GC measurements with Li^+ ions provided higher capacity utilization. The slopes of the charge discharge profiles in Figure 3.43 indicated a similar level of resistance encountered by the Li^+ ions as that by Ca^{2+} ions.

This decrease in capacity utilization with Li^+ ions for CaCoHCF as compared to Ca^{2+} ions is speculated to be a result of fewer number of Li^+ ions accessing the interstitial sites present in CaCoHCF lattice due to the change in symmetry of the unit cell, when cycling Li^+ ions [44]. In general, the electron density distribution appeared to be more uniform in the case of CaCoHCF lattice, resulting in enhanced capacity utilization with Ca^{2+} ions.

3.5 Iron Hexacyanoferrate ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$)

3.5.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized iron hexacyanoferrate (FeHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figures 3.46 (a) and 3.46 (b) represent the SEM images of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ synthesized at 60°C with the $\text{Fe}^{3+}:\text{Fe}(\text{CN})_6^{4-}$ ratio of 2:1. The images indicate a 5-10 μm agglomeration made up 15-20 nm sized particles, resulting in a porous surface morphology for the larger agglomeration. The $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ powders were imaged using a 20 KV beam.

Figure 3.44. Scanning electron micrograph of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ synthesized at 60°C (a) with a scale bar of $5\mu\text{m}$. (b) Expanded inset showing $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ with a scale bar of 200 nm .

3.5.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10° – 70° 2θ at room temperature. The PXRD spectrum is shown in Figure 3.45 (a).

Figure 3.45 (a). Raw powder XRD pattern of the as synthesized $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(60^\circ\text{C})$.

The dominant peaks occur at 17.40° , 24.50° , 35.20° , 39.30° , 43.10° , 50.2° , 53.8° , and 56.9° . It is evident from the width of the peaks that the as formed $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ possessed good crystallinity, indicative good symmetry in unit cells.

Figure 3.45 (b). Rietveld refined powder XRD pattern of the as synthesized $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(60^\circ \text{C})$.

The XRD spectrum was analyzed by Rietveld analysis using a XRD peak indexing software, DicVol under the FULLPROF suite as shown in Figure 3.45(b), wherein the unit cell lattice symmetry was identified as cubic belonging to the $\text{Pm}\bar{3}\text{m}$ space group [5], with the unit cell parameters determined to be $a_0 = 10.13\text{\AA}$, $b_0 = 10.13\text{\AA}$ and $c_0 = 10.13\text{\AA}$ and all the three angles ($\alpha=\beta=\gamma=90^\circ$) were found to be equal. A unit cell for these parameters is shown in Figure 3.46.

Figure 3.46. Schematic of unit cell of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$.

3.5.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized iron hexacyanoferrate powder was used as an active material to prepare cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The FeHCF cathode was subjected to electrochemical characterization to identify redox potentials. The experimental set up used to perform cyclic voltammetry with Ca^{2+} ions has been detailed in Section 3.0. The voltage on the FeHCF cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.47. Cyclic voltammogram (CV) of iron hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.47 shows a cyclic voltammetry curve for FeHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement showed two oxidation peaks and two reduction peaks, with the peak oxidation potentials of 0.605V and 0.875 V and two peak reduction potentials of 0.319 V and 0.586, with a peak separation ΔV of 0.286 V and 0.289 V, indicative of Faradaic behavior of the electrode. The $I_{\text{ox}}/I_{\text{red}}$ ratios were found to be 0.97 and 1.63, indicative of a reversible electrochemical system. The peaks were relatively broad, suggesting the presence of some resistance in the cathode electrode. Since, the cathode paste recipe and the method of preparation was identical for all the materials, the resistance was assumed to be associated with the diffusion process of Ca^{2+} ions in the FeHCF lattice.

Subsequently, the FeHCF cathode was subjected to galvanic cycling, which involved charging and discharging the FeHCF cathode by applying a constant current and measuring the cathode voltage against Ag/AgCl (1M NaClO₄) reference electrode with respect to time. An upper cut-off voltage of 1V and a lower cut-off voltage of 0V were defined to mark the limit of charging and discharging process. Figure 3.48, shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g and Figure 3.49 shows a single charge and discharge curve for the FeHCF cathode. Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, mass of the active cathode material and the applied current, the FeHCF cathode demonstrated a reversible specific capacity of 86.56 mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging which resulted in 75.54% capacity utilization as compared to the calculated theoretical specific capacity of 114.58 mAh/g based on equation (3.8).

The charge discharge profile in Figure 3.49 was observed to be slightly more sloped as compared to CaCoHCF, indicative of the relatively more resistance associated with the diffusion of Ca²⁺ ions in the FeHCF lattice.

To study the effect of increasing current density on the specific capacity, the FeHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g for 30 cycles and 100 mA/g for 100 cycles resulting a reversible specific capacity of

75.12mAh/g and 62.25 mAh/g, respectively. FeHCF electrodes appeared to demonstrate excellent rate capability as indicated by marginal loss in reversible specific capacity.

Figure 3.48. Galvanic cycling (GC) of iron hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.50 shows the specific capacity and coulombic efficiency of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.51 shows the specific capacity and coulombic efficiency of FeHCF cathode at current density of 100 mA/g. Based on Figures 3.50 and 3.51, it is evident that the specific capacity was fairly consistent over a number of cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.49. Charge-discharge profile of iron hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.50. Reversible specific capacity and coulombic efficiency versus number of cycles for FeHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g and 50 mA/g.

Figure 3.51. Reversible specific capacity and coulombic efficiency versus number of cycles for FeHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.5.4. FTIR Measurement and Analysis

In order to understand the factors governing the specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of FeHCF, the as-synthesized FeHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with the Fe^{3+} -N bond. Figure 3.52 shows the FTIR spectrum of FeHCF powders in the far-IR frequency region. Based on previously reported literature [31-35, 37], NC- Fe^{2+} bending mode occurs at 598 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 523 cm^{-1} . Fe^{3+} -N vibrational frequencies were identified as follows: 239 cm^{-1} (Fe^{3+} -N stretch); 500 cm^{-1} (Fe^{3+} -N bend) [34-38].

Figure 3.52. Far-IR spectrum of iron hexacyanoferrate.

FeHCF was determined to be a covalent compound based on the difference in the electronegativities [28] of Fe³⁺ ions (1.556) and N (2.939) was determined to be 1.383, which would characterize the nature of the bond between nitrogen and cobalt as coordinate covalent. The Fe³⁺-N stretching mode was assigned the lower frequency of 239 cm⁻¹ as it involves the displacement of Fe³⁺-N bond along a single axial direction and as Fe³⁺ is octahedrally coordinated to nitrogen and due to the presence of a strong Fe²⁺-CN bond, the higher vibrational frequency of 500 cm⁻¹ was assigned to the Fe³⁺-N bending modes as the bending of Fe³⁺-N bond would involve a larger force as compared to the stretching mode due to the displacement of five other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Fe³⁺-N and higher frequencies to Fe²⁺-C bonds can be justified by the larger difference in the electronegativity values (1.383) between Fe³⁺ ions and N as compared to that of 0.99 between Fe²⁺ ions (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe²⁺ and C would result in a sigma (coordinate covalent) bond [43] between Fe²⁺ and C, which is a relatively stronger bond, resulting in higher vibration frequencies, as

compared to the coordinate covalent bond between Fe^{3+} and N. With the presence of Fe^{2+} ion at the carbon end and Fe^{3+} ion at the nitrogen end, there is a possibility for the electron density to be slightly higher around the CN-Fe^{3+} end due to the higher positive charge and electronegativity value of 1.556 on Fe^{3+} as compared to Fe^{2+} [34-36], resulting in slight electron density polarization across FeHCF lattice. This is reflected by the higher stretching frequency of $\text{Fe}^{3+}\text{-N}$ as compared to the $\text{Co}^{2+}\text{-N}$ stretching frequencies as well as a slight decrease in $\text{Fe}^{2+}\text{-CN}$ stretching frequencies in FeHCF as compared to CaCoHCF which is mentioned in previous section. This should result in slight increase in electrostatic interactions between Ca^{2+} ions and the FeHCF lattice when compared to CaCoHCF, as is observed by the slightly sloped charge discharge profile shown in Figure 3.49.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^{+} ions and CV and GC measurement were performed on a new FeHCF cathode. Figure 3.53 and Figure 3.54 show the CV and GC measurement curves of FeHCF cathode with Li^{+} ions.

The cyclic voltammogram of FeHCF cathode with Li^{+} ions demonstrated a pair of redox peaks at 0.43V, 0.828 V (reduction peaks) and 0.428 V, 0.779 V (oxidation peaks), with a peak separation, ΔV of 0.002V and 0.049V and a $I_{\text{ox}}/I_{\text{red}}$ ratio of 1.69 and 0.29, as shown in Figure 3.53. The redox peaks were well-defined. This is indicative of relatively easy diffusion of Li^{+} ions in the interstitial sites of the unit cells of FeHCF lattice, due to

reduced electrostatic interactions between a monovalent Li^+ ion and a well-balanced electron cloud density of the lattice.

Figure 3.53. Cyclic voltammogram (CV) of iron hexacyanoferrate in 1M $\text{Li}(\text{ClO}_4)$ in acetonitrile with a scan rate of 0.5 mV/sec.

The CV measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.54. The charge-discharge profile in Figure 3.54 was observed to have a similar slope for Li^+ ions as compared to Ca^{2+} ions, which is again an indication of similar, low resistance encountered by the diffusing Li^+ ions.

The reversible specific capacity was 104.93 mAh/g, resulting in a capacity utilization of 87.12% for Li^+ , as compared to a capacity utilization of 75.12% for Ca^{2+} ions. This increase in reversible capacity with a monovalent cation such as Li^+ ion indicates the effect of reduced electrostatic interactions between Li^+ ions and the FeHCF host lattice, resulting in improved diffusion of Li^+ ions further increasing the capacity utilization of FeHCF, as compared to a divalent cation.

Figure 3.54. Charge-discharge profile of iron hexacyanoferrate in 1M Li(ClO₄) in acetonitrile at a current density of 25 mA/g.

This is indicative of the existence of a relatively low polarization of electron density across the lattice of FeHCF as compared to MnHCF and ZnHCF, but a slightly higher degree of polarization in electron density distribution as compared to CaCoHCF.

3.6 Calcium Aluminum Hexacyanoferrate (Ca_{0.5}AlFe(CN)₆)

3.6.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized calcium aluminum hexacyanoferrate (CaAlHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 3.55 (a) and 3.55 (b) represent the SEM images of Ca_{0.5}AlFe(CN)₆ synthesized at room temperature with the Al³⁺:Fe(CN)₆⁴⁻ ratio of 1:1. The images indicate a 5-10 μm agglomeration made up 75-120 nm sized particles, resulting in a porous surface morphology on the edges for the larger agglomeration. The Ca_{0.5}AlFe(CN)₆ powders were imaged using a 5 KV beam.

Figure 3.55 Scanning electron micrograph of $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$ synthesized at room temperature (a) with a scale bar of 1 μm . (b) Expanded inset showing $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$ a scale bar of 500 nm.

3.6.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$ sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10° – 70° 2θ at room temperature. The PXRD spectrum is shown in Figure 3.56 (a).

Figure 3.56 (a). Raw powder XRD pattern of the as synthesized $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$ (60°C).

The dominant peaks occur at 17.70°, 25.0°, 30.80°, 35.80°, 39.90°, 51.2°, 54.9°, and 58.3°. It is evident from the width of the peaks that the as formed $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$ possessed good crystallinity.

The XRD spectrum was indexed using DicVol and the spectrum was refined by Rietveld analysis using the FULLPROF suite, as shown in Figure 3.56 (b), wherein the unit cell lattice symmetry as identified as tetragonal belonging to the $\text{Fm}\bar{3}\text{m}$ space group, with the unit cell parameters determined to be $a_0 = 10.153\text{\AA}$, $b_0 = 10.153\text{\AA}$ and $c_0 = 10.153\text{\AA}$ and all the three angles ($\alpha=\beta=\gamma=90^\circ$) were found to be equal. A unit cell for these parameters is shown in Figure 3.57.

3.6.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized calcium aluminum hexacyanoferrate powder was used as an active material to prepare cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The CaAlHCF cathode was subjected to electrochemical characterization to identify redox potentials. The experimental set up to perform cyclic voltammetry with Ca^{2+} has been described in Section 3.0. The voltage on the CaAlHCF cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.56 (b). Rietveld refined powder XRD pattern of the as synthesized $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$ (60°C).

Figure 3.57. Schematic of unit cell of $\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$.

Figure 3.58. Cyclic voltammogram (CV) of calcium aluminum hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.58 shows a cyclic voltammetry curve for CaAlHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement did not indicate a pronounced redox behavior and the shape of the curve could be approximated to a rectangle, with the presence of very broad oxidation and reduction features, indicative of a pseudocapacitive behavior of the electrode.

Subsequently, the CaAlHCF cathode was charged and discharged by subjecting it to galvanic cycling by applying a constant current and measuring the cathode voltage against Ag/AgCl (1M NaClO_4) reference electrode with respect to time. An upper cut-off voltage of 1V and a lower cut-off voltage of 0V were defined to mark the limit of charging and discharging process. Figure 3.59, shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g and Figure 3.60 shows a single charge and discharge curve for the CaAlHCF cathode.

Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, mass of the active cathode material and the applied current, the CaAlHCF cathode demonstrated a reversible specific capacity of 27.26mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging which resulted in a capacity utilization of 26.20% as compared to the calculated theoretical specific capacity of 103.92 mAh/g, based on equation (3.9). The charge-discharge profile in Figure 3.62 was observed to resemble the charge discharge profile of a pseudocapacitor, indicative of surface adsorption of Ca^{2+} ions supported by surface redox process and lack of diffusion of Ca^{2+} ions in the CaAlHCF lattice.

To study the effect of increasing current density on the specific capacity, the CaAlHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g for 30 cycles and 100 mA/g for 100 cycles, resulting in a reversible specific capacity of 22.95 mAh/g and 19.25 mAh/g, respectively. CaAlHCF electrodes appeared to demonstrate excellent rate capability as indicated by marginal loss in reversible specific capacity.

Figure 3.61 shows the specific capacity and coulombic efficiency of CaAlHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.62 shows the specific capacity and coulombic efficiency of CaAlHCF cathode at current density of 100 mA/g. Based on Figures 3.61 and 3.62, it is evident that the specific capacity was fairly

consistent over a number of cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.59. Galvanic cycling (GC) of calcium aluminum hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.60. Charge-discharge profile of calcium aluminum hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.61. Reversible specific capacity and coulombic efficiency versus number of cycles for CaAlHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g and 50 mA/g.

Figure 3.62. Reversible specific capacity and coulombic efficiency versus number of cycles for CaAlHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.6.4. FTIR Measurement and Analysis

In order to understand the factors governing the specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of CaAlHCF, the as-synthesized CaAlHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with

the Al^{3+} -N bond. Figure 3.63 shows the FTIR spectrum of FeHCF powders in the far-IR frequency region. Based on previously reported literature [31-34, 36, 37], NC-Fe^{2+} bending mode occurs at 596 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 513 cm^{-1} . In addition to the bending and stretching modes associated with Fe^{2+} -C bond, there was an additional strong vibrational frequency at 552 cm^{-1} that was identified. Al^{3+} -N vibrational frequencies were identified as follows: 345 cm^{-1} (Al^{3+} -N stretch); 492 cm^{-1} (Al^{3+} -N bend) [34-38].

Figure 3.63. Far-IR spectrum of calcium aluminum hexacyanoferrate.

CaAlHCF was determined to be a covalent compound based on the difference in the electronegativities [28] of Al^{3+} ions (1.513) and N (2.939) was determined to be 1.426, which would characterize the nature of the bond between nitrogen and aluminum ions as coordinate covalent. The Al^{3+} -N stretching mode was assigned the lower frequency of 345 cm^{-1} as it involves the displacement of Al^{3+} -N bond along a single axial direction and as Al^{3+} is octahedrally coordinated to nitrogen and due to the presence of a strong Fe^{2+} -CN bond, the higher vibrational frequency of 492 cm^{-1} was assigned to the Al^{3+} -N

bending modes as the bending of Al^{3+} -N bond would involve a larger force as compared to the stretching mode due to the displacement of five other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Al^{3+} -N bonds and higher frequencies to Fe^{2+} -C bonds can be justified by the larger difference in the electronegativity values (1.426) between Al^{3+} ions and N as compared to that of 0.99 between Fe^{2+} ions (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe^{2+} and C would result in a sigma (coordinate covalent) bond [43] between Fe^{2+} and C, which is a relatively stronger bond, resulting in higher vibration frequencies, as compared to the coordinate covalent bond between Al^{3+} and N.

However, due to a charge of +3 and the high charge to size (ionic radius) ratio of Al^{3+} ion, the bond between Al^{3+} ion and nitrogen is very strong as indicated by the increase in Al^{3+} -N [34-38] stretching frequency of 345 cm^{-1} as compared to Fe^{3+} -N stretching frequency of 239 cm^{-1} . Also, in view of the broad and less defined Fe^{2+} -C stretching mode (513 cm^{-1}) and bending mode (596 cm^{-1}) and the presence of an additional Fe^{2+} -C vibrational mode (552 cm^{-1}), it is hypothesized that the Fe^{2+} -C bond is weaker in CaAlHCF as compared to FeHCF, resulting in the generation of an additional vibrational mode (552 cm^{-1}). This would result in the electron density to be higher around CN- Al^{3+} region of the lattice, resulting in polarization of electron density distribution across the AlHCF lattice. This should result in strong electrostatic interactions between Ca^{2+} ions and the AlHCF lattice, when compared to CaCoHCF and FeHCF, as is observed by the pseudo capacitive charge discharge profile shown in Figure 3.60.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^+ ions and CV and GC measurement were performed on a new CaAlHCF cathode. Figure 3.64 and Figure 3.65 show the CV and GC measurement curves of CaAlHCF cathode with Li^+ ions.

Figure 3.64. Cyclic voltammogram (CV) of calcium aluminum hexacyanoferrate in 1M $\text{Li}(\text{ClO}_4)$ in acetonitrile with a scan rate of 0.5 mV/sec.

The cyclic voltammogram of CaAlHCF cathode with Li^+ ions demonstrated redox peaks at 0.423V (reduction peak) and 0.541 V (oxidation peak), with a peak separation, ΔV of 0.118V and a $I_{\text{ox}}/I_{\text{red}}$ ratio of 1.04, as shown in Figure 3.64. The redox peaks were observable as compared to the CV curve with Ca^{2+} ions, but, the peaks were relatively broad. This is indicative of relatively easy diffusion of Li^+ ions in the interstitial sites of the unit cells of CaAlHCF lattice, due to reduced electrostatic interactions between a monovalent Li^+ ion and electron density across the lattice. The CV measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.65. The charge discharge profile in Figure 3.67 was observed to indicate

intercalation of Li^+ ions into CaAlHCF lattice which was not observed with Ca^{2+} ions, which is again an indication of relatively low resistance encountered by the diffusing Li^+ ions.

Figure 3.65. Charge-discharge profile of calcium aluminum hexacyanoferrate in 1M $\text{Li}(\text{ClO}_4)$ in acetonitrile at a current density of 25 mA/g.

The reversible specific capacity was 35.76mAh/g, resulting in a capacity utilization of 34.41% for Li^+ , as compared to a capacity utilization of 26.20% for Ca^{2+} ions. This increase in reversible capacity with a monovalent cation such as Li^+ ion indicates the effect of reduced electrostatic interactions between Li^+ ions and the AlHCF host lattice, resulting in improved diffusion of Li^+ ions as compared to that of the divalent cation. This is indicative of the presence of a larger polarization of electron density distribution across lattice of AlHCF as compared to previously discussed metal hexacyanoferrates.

3.7 Tin Hexacyanoferrate ($\text{SnFe}(\text{CN})_6$)

3.7.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized tin hexacyanoferrate (SnHCF) powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 3.66 (a) and 3.66 (b) represent the SEM images of $\text{SnFe}(\text{CN})_6$ synthesized at room temperature with the $\text{Sn}^{4+}:\text{Fe}(\text{CN})_6^{4-}$ ratio of 1:1. The images indicated large particles with a size of $20\mu\text{m}$, and a smooth surface morphology. The particles had step like features. The $\text{SnFe}(\text{CN})_6$ powders were imaged using a 5 KV beam.

Figure 3.66(a). Scanning electron micrograph of $\text{SnFe}(\text{CN})_6$ synthesized at room temperature (a) with a scale bar of $1\mu\text{m}$. (b) Expanded inset showing $\text{SnFe}(\text{CN})_6$ with a scale bar of 200nm .

Figure 3.66(c) and 3.66(d) represent the SEM images of SnHCF synthesized at 60°C . The resulting particles were about $5\mu\text{m}$ in size. However, the SnHCF particles synthesized at 60°C had a large number of cracks or openings in each of the particles, leading to enhanced surface area as compared to SnHCF particles synthesized at room temperature.

Based on the surface area of the SnHCF crystals, the crystals synthesized at 60°C were chosen for further characterization.

Figure 3.66(c). Scanning electron micrograph of SnFe(CN)₆ synthesized at 60°C (a) with a scale bar of 1 μm. (d) Expanded inset showing SnFe(CN)₆ with a scale bar of 200 nm.

3.7.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the SnFe(CN)₆ sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10°–70° 2θ at room temperature. The PXRD spectrum is shown in Figure 3.67.

Figure 3.67. Powder XRD pattern of the as synthesized SnFe(CN)₆ (60°C).

The peaks were observed to be very broad, suggesting that the as formed $\text{SnFe}(\text{CN})_6$ possessed poor crystallinity and the unit cells of SnHCF lacked symmetry. Hence, the unit cell symmetry with a certain space group could not be identified for SnHCF.

3.7.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized tin hexacyanoferrate powder was used as an active material to prepare cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The SnHCF cathode was subjected to electrochemical characterization to confirm and identify redox potentials. The experimental set up discussed in Section 3.0 was used to perform cyclic voltammetry. The voltage on the cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.68. Cyclic voltammogram (CV) of tin hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.68 shows a cyclic voltammetry curve for SnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement did not indicate a pronounced redox

behavior and the shape of the curve could be approximated to a rectangle, with the presence of very broad oxidation and reduction features, indicative of a pseudocapacitive behavior of the electrode, similar to CaAlHCF.

Subsequently, the SnHCF cathode was subjected to galvanic cycling, which involved charging and discharging the cathode electrode, by applying a constant current and measuring the voltage against Ag/AgCl (1M NaClO₄) reference electrode with respect to time. An upper cut-off voltage of 1V and a lower cut-off voltage of 0V were defined as limits for charging and discharging process. Figure 3.69, shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g and Figure 3.70 shows a single charge and discharge curve for the SnHCF cathode. Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, mass of the active cathode material and the applied current, the SnHCF cathode demonstrated a reversible specific capacity of 13.8 mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging which resulted in a capacity utilization of 18.29% when compared to the calculated theoretical specific capacity of 75.43 mAh/g, based on equation (3.11).

The charge discharge profile in Figure 3.70 was observed to resemble the charge discharge profile of a pseudocapacitor, indicative of surface adsorption of Ca²⁺ ions supported by surface redox process and lack of diffusion of Ca²⁺ ions in the SnHCF lattice.

To study the effect of increasing current density on the specific capacity, the SnHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g over 30 cycles and 100 mA/g over 100 cycles resulting a reversible specific capacity of 11.40 mAh/g and 9.47 mAh/g, respectively. SnHCF electrodes appeared to demonstrate excellent rate capability as indicated by marginal loss in reversible specific capacity at higher current densities.

Figure 3.69. Galvanic cycling (GC) of tin hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.71 shows the specific capacity and the coulombic efficiency of SnHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.72 shows the specific capacity and the coulombic efficiency of SnHCF cathode at current density of 100 mA/g. Based on Figures 3.71 and 3.72, it is evident that the specific capacity is fairly consistent

over a number of cycles and the process of charging and discharging is highly reversible as indicated by very high coulombic efficiency.

Figure 3.70. Charge-discharge profile of tin hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.71. Reversible specific capacity and coulombic efficiency versus number of cycles for SnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g and 50 mA/g.

Figure 3.72. Reversible specific capacity and coulombic efficiency versus number of cycles for SnHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g.

3.7.4. FTIR Measurement and Analysis

In order to understand the factors governing the specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of SnHCF, the as-synthesized SnHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with the $\text{Sn}^{4+}\text{-N}$ bond. Figure 3.73 shows the FTIR spectrum of SnHCF powders in the far-IR frequency region. Based on previously reported literature [31-34, 37, 38], NC-Fe^{2+} bending mode occurs at 598 cm^{-1} and the $\text{Fe}^{2+}\text{-C}$ stretching mode occurs at 532 cm^{-1} . In addition to the bending and stretching modes associated with $\text{Fe}^{2+}\text{-C}$ bond. $\text{Sn}^{4+}\text{-N}$ vibrational frequencies were identified as follows: 208 cm^{-1} ($\text{Sn}^{4+}\text{-N}$ stretch); 499 cm^{-1} ($\text{Sn}^{4+}\text{-N}$ bend) [34-38].

Figure 3.73. Far-IR spectrum of tin hexacyanoferrate.

SnHCF was determined to be a covalent compound based on the difference in the electronegativities [28] of Sn⁴⁺ ions (1.706) and N (2.939) was determined to be 1.233, which would characterize the nature of the bond between nitrogen and tin ions as coordinate covalent. The Sn⁴⁺-N stretching mode was assigned the lower frequency of 208 cm⁻¹ as it involves the displacement of Sn⁴⁺-N bond along a single axial direction and as Sn⁴⁺ is octahedrally coordinated to nitrogen and due to the presence of a strong Fe²⁺-CN bond, the higher vibrational frequency of 499 cm⁻¹ was assigned to the Sn⁴⁺-N bending modes as the bending of Sn⁴⁺-N bond would involve a larger force as compared to the stretching mode due to the displacement of five other nitrogen ends in varying degrees of freedom to induce a bending mode. The assignment of lower frequencies to Sn⁴⁺-N and higher frequencies to Fe²⁺-C bonds can be justified by the larger difference in the electronegativity values (1.233) between Sn⁴⁺ ions and N as compared to that of 0.99 between Fe²⁺ (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe²⁺ and C would result in a sigma (coordinate covalent) bond [43] between Fe²⁺ and C,

which is a stronger bond, resulting in higher vibration frequencies, as compared to the coordinate covalent bond between Sn^{4+} and N.

However, it is speculated that, in spite of a charge of +4 and high electronegativity value of 1.706, due to its large size, the charge to size (ionic radius) ratio of Sn^{4+} ion is less than that of Al^{3+} ion. This would result in a weaker bond between Sn^{4+} ion and nitrogen when compared to Al^{3+} -nitrogen as indicated by the decrease in Sn^{4+} -N stretching frequency of 208 cm^{-1} , when compared to Al^{3+} -N stretching frequency of 345 cm^{-1} . Additionally, the broad x-ray diffraction peaks, indicate a lack of or poor symmetry for the unit cells of SnHCF. This is also reflective of the weak bonding between Sn^{4+} ions and nitrogen. In view of a weaker Sn^{4+} -N bond and poor unit cell symmetry, the electron density distribution is speculated to be higher around Fe^{2+} -CN part of the lattice, resulting in polarization of electron density distribution across the SnHCF lattice. This should result in large increase in electrostatic interactions between Ca^{2+} ions and the SnHCF lattice, when compared to CaCoHCF and FeHCF, as is observed by the pseudo capacitive charge discharge profile shown in Figure 3.70.

In order to confirm the effect of charge on the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^{+} ions and CV and GC measurement were performed on a new SnHCF cathode. Figure 3.74 and Figure 3.75 show the CV and GC measurement curves of SnHCF cathode with Li^{+} ions.

Figure 3.74. Cyclic voltammogram (CV) of tin hexacyanoferrate in 1M Li(ClO₄) in acetonitrile with a scan rate of 0.5 mV/sec.

The cyclic voltammogram of SnHCF cathode with Li⁺ ions demonstrated a pseudocapacitive behavior with very broad redox peaks, as shown in Figure 3.74, similar to Ca²⁺ ions. This indicated a similar level of resistance encountered by Li⁺ ions in the interstitial sites of SnHCF lattice (if present) as in the case of Ca²⁺. It is speculated that this could be a result of lack of symmetry or poor symmetry (from x-ray diffraction patterns) in the unit cell of SnHCF, further resulting in poorly defined ion diffusion pathways. This would lead to a significant increase in diffusion resistance for both monovalent Li⁺ ions and divalent Ca²⁺ ions. The CV measurements were followed by the galvanic cycling at 25 mA/g current density for 10 cycles, as shown in Figure 3.75. The charge discharge profile for SnHCF in Figure 3.75 was observed to indicate a pseudo capacitive behavior with Li⁺ ions, as in the case of Ca²⁺ ions.

Figure 3.75. Charge-discharge profile of tin hexacyanoferrate in 1M Li(ClO₄) in acetonitrile at a current density of 25 mA/g.

The reversible specific capacity was 13.43 mAh/g, resulted in a capacity utilization of 17.3% for Li⁺, as compared to a capacity utilization of 18.14% for Ca²⁺ ions. As previously mentioned, the reduced capacity utilization for both Ca²⁺ ions and Li⁺ ions indicates a synergetic effect of lack of well-defined unit cell symmetry and polarization of electron density distribution across the SnHCF lattice on the intercalation process.

3.8 Molybdenum Oxide Hexacyanoferrate (MoOFe(CN)₆)

3.8.1 Physical Characterization: Scanning Electron Microscopy (SEM)

The as-synthesized molybdenum oxide hexacyanoferrate (MoOHCF) [41, 42] powders were analyzed using scanning electron microscopy (SEM) to determine the morphology and size distribution of the particles. Figure 3.76 (a) and 3.76 (b) represent the SEM images of MoOFe(CN)₆ synthesized at room temperature with the MoO³⁺:Fe(CN)₆⁴⁻ ratio of 1:1. The images indicated large agglomerations with a size of 10 μm that were made

up of smaller particles with sizes ranging from 150 nm to 200 nm. The $\text{MoOFe}(\text{CN})_6$ powders were imaged using a 5 KV beam.

Figure 3.76 (a).Scanning electron micrograph of $\text{MoOFe}(\text{CN})_6$ synthesized at room temperature (a) with a scale bar of 5 μm . (b) Expanded inset showing $\text{MoOFe}(\text{CN})_6$ a scale bar of 200 nm.

Figures 3.76 (c) and 3.76 (d) represent the SEM images of MoOHCF synthesized at 60°C . The resulting agglomerations were in a size range of 5-10 μm that were made up of smaller particles with sizes ranging from 75 nm to 120 nm. However, the MoOHCF particles synthesized at 60°C had smaller sizes, leading to enhanced surface area as compared to MoOHCF particles synthesized at room temperature. Based on the surface area of the MoOHCF crystals, the crystals synthesized at 60°C were chosen for further characterization.

Figure 3.76 (c).Scanning electron micrograph of MoOFe(CN)_6 synthesized at 60°C with a scale bar Scanning (a) with a scale bar of $5\ \mu\text{m}$. (d) Expanded inset showing MoOFe(CN)_6 a scale bar of $200\ \text{nm}$.

3.8.2 Physical Characterization: Powder X-ray Diffraction (PXRD)

The phase composition of the MoOFe(CN)_6 sample (60°C) was characterized using powder X-ray diffractometry (PXRD). Scans were performed over an angular range of 10° – $70^\circ\ 2\theta$ at room temperature. The PXRD spectrum is shown in Figure 3.77.

Figure 3.77. Raw powder XRD pattern of the as synthesized MoOFe(CN)_6 (60°C).

The peaks were observed to be very broad, suggesting that the as formed MoOFe(CN)_6 possessed poor crystallinity and the unit cells of MoOHCF lacked symmetry. Hence, the unit cell symmetry with a certain space group could not be identified for MoOHCF.

3.8.3 Electrochemical Characterization: Cyclic Voltammetry (CV) and

Galvanic Cycling (GC)

The as-synthesized molybdenum oxide hexacyanoferrate (60°C) powder was used as an active material to prepare cathode paste and make cathodes as described in Section 2.4 of Chapter 2. The MoOHCF cathode was subjected to electrochemical characterization to identify redox potentials. The experimental set up discussed in Section 3.0 was used to perform cyclic voltammetry with Ca^{2+} ions. The voltage on the MoOHCF cathode was scanned with respect to the Ag/AgCl reference electrode and the resulting current was measured.

Figure 3.78. Cyclic voltammogram (CV) of molybdenum oxide hexacyanoferrate in 1M $\text{Ca(ClO}_4)_2$ in acetonitrile with a scan rate of 0.5 mV/sec.

Figure 3.78 shows a cyclic voltammetry curve for MoOHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile. The cyclic voltammetry measurement indicates redox behavior akin to a pseudocapacitive system and the shape of the curve could be approximated to a rectangle, with the presence of very broad oxidation and reduction features, similar to SnHCF. Subsequently, the MoOHCF cathode was subjected to galvanic cycling, which involved charging and discharging the cathode by applying a constant current and measuring the cathode voltage against Ag/AgCl (1M NaClO_4) reference electrode with respect to time. An upper cut-off voltage of 1V and a lower cut-off voltage of 0V were defined as limits to charging and discharging processes.

Figure 3.79 shows a galvanic cycling curve involving charging and discharging the cathode with a constant current density of 25 mA/g and Figure 3.80 shows a single charge and discharge curve for the MoOHCF cathode. Based on the amount of time required to reach the upper cut-off voltage for charging and lower cut-off voltage for discharging, mass of the active cathode material and the applied current, the MoOHCF cathode demonstrated a reversible specific capacity of 33.38 mAh/g at a current density of 25 mA/g over 30 cycles of charging and discharging which resulted in a capacity utilization of 42.60% when compared to the calculated theoretical specific capacity of 78.24 mAh/g based on equation (3.12). The charge-discharge profile in Figure 3.80 was observed to resemble the charge discharge profile of a pseudocapacitor with a larger faradaic component as compared to SnHCF and CaAlHCF, indicative of surface adsorption of Ca^{2+} ions supported by surface redox process and some degree of diffusion of Ca^{2+} ions in the MoOHCF lattice.

To study the effect of increasing current density on the specific capacity, the MoOHCF cathode was subjected to galvanic cycling at two additional current densities of 50 mA/g over 30 cycles and 100 mA/g over 100 cycles resulting a reversible specific capacity of 31.05 mAh/g and 27.44 mAh/g, respectively. MoOHCF electrodes appeared to demonstrate excellent rate capability as indicated by marginal loss in reversible specific capacity.

Figure 3.79. Galvanic cycling (GC) of molybdenum oxide hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.81 shows the specific capacity and the coulombic efficiency of MoOHCF cathode at current densities of 25 mA/g and 50 mA/g, respectively. Figure 3.82 shows the specific capacity and the coulombic efficiency of MoOHCF cathode at current density of 100 mA/g. Based on Figures 3.81 and 3.82, it is evident that the specific capacity was fairly consistent over a number of cycles and the process of charging and discharging was highly reversible as indicated by very high coulombic efficiency.

Figure 3.80. Charge-discharge profile of molybdenum oxide hexacyanoferrate in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g.

Figure 3.81. Reversible specific capacity and coulombic efficiency versus number of cycles for MoOHCF electrode in 1M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 25 mA/g and 50 mA/g.

3.8.4. FTIR Measurement and Analysis

In order to understand the factors governing the specific capacity utilization of intercalation of Ca^{2+} ions in the interstitial spaces of MoOHCF, the as-synthesized MoOHCF were subjected to Fourier transform infrared spectroscopy (FTIR) in the far-IR frequency end of the infrared spectrum, to determine the bond strength associated with

the MoO^{3+} -N bond. Figure 3.83 shows the FTIR spectrum of MoOHCF powders in the far-IR frequency region. Based on previously reported literature [31-34, 37, 38, 41, 42], NC-Fe^{2+} bending mode occurs at 594 cm^{-1} and the Fe^{2+} -C stretching mode occurs at 525 cm^{-1} . In addition to the bending and stretching modes associated with Fe^{2+} -C bond. MoO^{3+} -N vibrational frequencies were identified as follows: 231 cm^{-1} (MoO^{3+} -N stretch); 499 cm^{-1} (MoO^{3+} -N bend) [34-38, 41, 42].

Figure 3.82. Reversible specific capacity and coulombic efficiency versus number of cycles for MoOHCF electrode in $1\text{M Ca}(\text{ClO}_4)_2$ in acetonitrile at a current density of 100 mA/g .

Figure 3.83. Far-IR spectrum of molybdenum oxide hexacyanoferrate.

MoOHCF was determined to be a covalent compound based on the difference in the electronegativities [28] of Mo^{5+} ions (2.006) and N (2.939), which was determined to be 0.933, which would characterize the nature of the bond between nitrogen and molybdenum ions as coordinate covalent. However, Mo ions exist in the form of a polycation in the form of MoO^{3+} ions [41, 42], that form the bonds with the $\text{Fe}(\text{CN})_6^{4-}$ ligands. Unfortunately, the electronegativity data for MoO^{3+} ion was not available. However, based on the fact that MoO^{3+} has a lower amount of charge as compared to Mo^{5+} , the electronegativity of MoO^{3+} would be less than that of Mo^{5+} . The MoO^{3+} -N stretching mode was assigned the lower frequency of 231cm^{-1} as it involves the displacement of MoO^{3+} -N bond along a single axial direction and as MoO^{3+} is pentahedrally coordinated to nitrogen (the sixth coordination is between Mo and O) and due to the presence of a strong Fe^{2+} -CN bond, the higher vibrational frequency of 499cm^{-1} was assigned to the MoO^{3+} -N bending modes as the bending of MoO^{3+} -N bond would involve a larger force as compared to the stretching mode due to the displacement of four other nitrogen ends in varying degrees of freedom to induce a bending mode.

The assignment of lower frequencies to MoO^{3+} -N bond and higher frequencies to Fe^{2+} -C bond can be justified by the larger difference in the electronegativity values between MoO^{3+} and N as compared to that of 0.99 between Fe^{2+} (1.390) and C (2.380). A difference of 0.99 in the electronegativity between Fe^{2+} and C would result in a sigma (coordinate covalent) bond [43] between Fe^{2+} and C, which is a stronger bond, resulting in higher vibration frequencies, as compared to the coordinate covalent bond between MoO^{3+} and N. However, it is speculated that, in spite of a charge of +3, due to its large

size, the charge to size (ionic radius) ratio of MoO^{3+} ion is less than that of Al^{3+} ion. This would result in a weaker bond between MoO^{3+} ion and nitrogen, when compared to Al^{3+} -nitrogen as indicated by the decrease in MoO^{3+} -N stretching frequency of 231 cm^{-1} as compared to Al^{3+} -N stretching frequency of 345 cm^{-1} , but a stronger bond as compared to Sn^{4+} -N bond.

Additionally, the broad x-ray diffraction peaks indicated a relatively poor symmetry for the unit cells of MoOHCF (more defined symmetry over SnHCF). This is also indicative of a weak bonding between MoO^{3+} ions and nitrogen, as indicated by the lowering and broadening in MoO^{3+} -N stretching frequency. In view of a weaker MoO^{3+} -N bond and poor unit cell symmetry, the electron density is speculated to be higher around Fe^{2+} -CN part of the lattice, resulting in polarization of electron density distribution across the MoOHCF lattice. This would result in an increase in electrostatic interactions between Ca^{2+} ions and the MoOHCF lattice when compared to CaCoHCF and FeHCF, as is observed by the pseudo capacitive charge discharge profile shown in Figure 3.82.

In order to confirm the effect of charge of the intercalating cation, Ca^{2+} ions were replaced by the monovalent Li^{+} ions and CV and GC measurement were performed on a new MoOHCF cathode. Figure 3.84 and Figure 3.85 show the CV and GC measurement curves of MoOHCF cathode with Li^{+} ions. The cyclic voltammogram of MoOHCF cathode with Li^{+} ions demonstrated a markedly improved redox behavior over Ca^{2+} ions, with an oxidation potential of 0.519 V and a reduction potential of 0.354 V and $I_{\text{ox}}/I_{\text{red}}$ ratio of 1.14, shown in Figure 3.84. This raises a possibility of lower level of resistance

encountered by Li^+ ions in the interstitial sites of the MoOHCF lattice as opposed to Ca^{2+} ions.

Figure 3.84. Cyclic voltammogram (CV) of molybdenum oxide hexacyanoferrate in 1M $\text{Li}(\text{ClO}_4)$ in acetonitrile with a scan rate of 0.5 mV/sec.

It is also speculated that a generally higher specific capacity for MoOHCF over SnHCF could be a result of a better defined symmetry (from x-ray diffraction patterns) in the unit cell of MoOHCF over SnHCF lattice. It is speculated that ion diffusion pathways are relatively poorly defined (but more defined compared to SnHCF), leading to a significant increase in diffusion resistance for divalent Ca^{2+} ions, but, presenting less resistance to monovalent Li^+ ions. However, upon performing galvanic cycling at 25 mA/g current density for 10 cycles, the charge-discharge profile for MoOHCF , as shown in Figure 3.85, was observed to indicate a pseudo capacitive behavior with Li^+ ions, as in the case of Ca^{2+} ions, with a reversible specific capacity was 25.57 mAh/g, resulting in a capacity utilization of 32.35% for Li^+ , as compared to a capacity utilization of 42.60% for Ca^{2+}

ions. This could indicate an inconsistency in symmetry as well as poorly defined symmetry in the unit cells of MoOHCF.

However, when compared to SnHCF, MoOHCF has better unit cell symmetry as observed through improved definition in x-ray diffraction peaks. This would translate into a more uniform electron density distribution across the MoOHCF unit cell as compared to SnHCF unit cells which is reflected by the higher MoO^{3+} -N stretching frequency of 231cm^{-1} as opposed to a lower Sn^{4+} -N stretching frequency of 208cm^{-1} , leading to improved specific capacity utilization in the case of both Li^+ ions and Ca^{2+} ions.

Figure 3.85. Charge-discharge profile of molybdenum oxide hexacyanoferrate in 1M $\text{Li}(\text{ClO}_4)$ in acetonitrile at a current density of 25 mA/g.

Eight metal hexacyanoferrate compounds were synthesized and were subjected to physical characterization (SEM and PXRD), electrochemical characterization (CV and GC) and optical characterization (FTIR), to identify a suitable metal hexacyanoferrate cathode(s) for non-aqueous rechargeable Ca^{2+} ion batteries. A summary of the unit cell

parameters and electrochemical data for the eight metal hexacyanoferrate compounds has been tabulated in Tables 3.1 and 3.2, respectively. The discussion and summary of the above described results will be presented in Chapter 4.

#	Compound	Unit Formula	Molar Mass (g/mole)	Unit Cell Symmetry	Unit Cell Parameters	Space Group
1	FeHCF (III, II)	$\text{Ca}_2\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$	939	Cubic	$a=b=c=10.13\text{ \AA}$ $\alpha=\beta=\gamma=90$	Pm3m
2	CoHCF (II, II)	$\text{CaCoFe}(\text{CN})_6$	310.86	Monoclinic	$a=10.76\text{ \AA}$, $b=3.92\text{ \AA}$, $c=9.59\text{ \AA}$; $\alpha=\gamma=90$; $\beta=98.91$	P2/m
3	ZnHCF (II, II)	$\text{Ca}_{0.5}\text{Zn}_{1.5}\text{Fe}(\text{CN})_6$	330	Monoclinic (major phase)	$a=9.36\text{ \AA}$, $b=12.27\text{ \AA}$, $c=7.48\text{ \AA}$; $\alpha=\gamma=90$; $\beta=98.91$	P2 ₁ /n
4	BaHCF (II, II)	$\text{Ca}_{0.5}\text{KBaFe}(\text{CN})_6$	407.94	Tetragonal	$a=b=15.22\text{ \AA}$, $c=13.43\text{ \AA}$; $\alpha=\beta=\gamma=90$	not identified
5	MoOHCF (V, II)	$\text{Ca}_{0.5}\text{MoOFe}(\text{CN})_6$	343.8	not identified	not identified	not identified
6	MnHCF (II, II)	$\text{Ca}_{0.5}\text{Mn}_{1.5}\text{Fe}(\text{CN})_6$	314.26	Triclinic	$a=7.64\text{ \AA}$, $b=6.37\text{ \AA}$, $c=13.43\text{ \AA}$; $\alpha=97.29$, $\beta=98.80$; $\gamma=96.85$	P-1
7	AlHCF (III, II)	$\text{Ca}_{0.5}\text{AlFe}(\text{CN})_6$	258.83	Cubic	$a=b=c=10.153\text{ \AA}$; $\alpha=\beta=\gamma=90$	Fm3m
8	SnHCF (IV, II)	$\text{Ca}_{0.5}\text{SnFe}(\text{CN})_6$	353.56	not identified	not identified	not identified

Table 3.1. Summary of unit cell parameters of metal hexacyanoferrate compounds under study.

#	Compound	Unit Formula	Theoretical Specific Capacity (mAh/g)		Experimental (Ca ²⁺) Reversible Specific Capacity (mAh/g)			Capacity Util (%) - Ca ²⁺ ions @ 25 mA/g	Exp (Li ⁺) Reversible Specific Capacity (mAh/g)	Capacity Util (%) - Li ⁺ ions @ 25 mA/g
			Ca ²⁺	Li ⁺	25 mA/g	50 mA/g	100 mA/g			
1	FeHCF (III, II)	Ca ₂ Fe ₄ (Fe(CN) ₆) ₃	114.6	120.44	86.56	75.12	62.25	75.54	104.93	87.12
2	CoHCF (II, II)	CaCoFe(CN) ₆	86.53	89.9	55.04	56.6	44.18	63.60	42.37	47.131
3	ZnHCF (II, II)	Ca _{0.5} Zn _{1.5} Fe(CN) ₆	81.5	84.26	39.47	35.5	30.38	48.42	51.47	61.084
4	BaHCF (II, II)	Ca _{0.5} KBaFe(CN) ₆	65.94	67.61	29.5	27.8	22.61	44.73	29	42.89
5	MoOHCF (V, II)	Ca _{0.5} MoOFe(CN) ₆	78.24	80.72	33.38	31.05	27.44	42.66	25.27	31.30
6	MnHCF (II, II)	Ca _{0.5} Mn _{1.5} Fe(CN) ₆	85.59	88.64	35.54	35.5	30.38	41.52	65.93	74.37
7	AlHCF (III, II)	Ca _{0.5} AlFe(CN) ₆	103.9	108.63	27.26	22.95	19.25	26.23	35.76	32.91
8	SnHCF (IV, II)	Ca _{0.5} SnFe(CN) ₆	76.08	78.41	13.8	11.4	9.38	18.13	13.43	17.12

Table 3.2. Summary of electrochemical measurements of metal hexacyanoferrate compounds under study.

Chapter 4. Analysis

Chapter 4 discusses and summarizes the results related to physical characterization (SEM and P-XRD), electrochemical characterization (CV and GC) and nature of the bonds (FTIR) of the metal hexacyanoferrate materials based cathodes for Ca^{2+} ion rechargeable batteries. The chapter further discusses the possible relationship between the nature of the bonds existing in metal hexacyanoferrate cathodes and specific capacity utilization ratios.

From a physical characterization point of view, it was observed from the particle size information derived from SEM imaging that the cathode materials with smaller particles and morphologies that provided large surface area to volume ratio, generally had a higher probability of demonstrating high specific capacity utilization. This is due to more access sites and reduced diffusion lengths for the intercalating cations. Synthesizing all of the materials at elevated temperatures reduced the average particle size and produced agglomeration of the particles that led to more porous films.

It was also observed from XRD measurements that materials that possessed good crystallinity and well-defined symmetry (sharp and narrow peaks) in the unit cells, had a higher probability of demonstrating high specific capacity utilization. This is most likely due to the existence of well-defined diffusion pathways for the intercalating cations. The lack of symmetry can be identified by broad and diffused peaks, resulting in increase in diffusion resistance to the intercalating cations (from the cyclic voltammetry curves) as

was observed in the case of tetravalent and pentavalent metal hexacyanoferrates, namely, SnHCF and MoOHCF, respectively.

In order to understand the effect of the valency of the metal ions coordinated to the nitrogen end of the ferrocyanide ligands on the electrochemical performance of the cathode materials, the capacity utilization of cathode materials with Ca^{2+} ions were compared to the ratio of charge to (high spin (HS)) crystal ionic radius² for the metal ions at the nitrogen end, as shown in Figure 4.1. This ratio was defined as the σ -parameter [29]. The σ -parameter reflects electric field strength exerted by the metal ion which determines its polarization power, which can be defined as the ability of the metal ion to attract the electron density towards itself. This is also reflective of the strength of the ionic/covalent bond formed by the metal ion. This parameter was plotted with reversible capacity utilization in Fig. 4.1; a reversible capacity of 50% was used as a benchmark.

Figure 4.1. Reversible capacity utilization for Ca^{2+} ion cells versus σ -parameter.

From Figure 4.1, it was observed that the top three performing materials: FeHCF, CaCoHCF and CaZnHCF had σ -parameter values between 2.55 and 4.86 that produced reversible capacities above 50%. This indicated intermediate bond strength between Fe-N, Co-N and Zn-N for the FeHCF, CaCoHCF and CaZnHCF, respectively. In order to further probe this observation, the reversible capacity utilization with Ca^{2+} ions was compared against electronegativity values for the metal ions (χ_i) [28] on the nitrogen end of the ferrocyanide, as shown in Figure 4.2. Electronegativity (χ_i) is defined as a measure of the power of a metal ion in a molecule to attract the electron density towards itself.

Figure 4.2. Reversible capacity utilization (Ca^{2+} ions) versus electronegativity values (χ_i).

From Figure 4.2, it was again observed that the metals such as Fe, Co, and Zn that had intermediate electronegativity values ranging from 1.321 to 1.556, among the tested materials, demonstrated high capacity utilization of above 50%. Based on the trends in Figures 4.1 and 4.2, it could be speculated that the amount of bond strength between the metals ions and nitrogen, as indicated by the σ -parameter and the ability of the metal ion

coordinated with the nitrogen to attract electron cloud towards itself, as indicated by electronegativity values, should be intermediate in magnitude. This would result in more balanced electron density distribution across the unit cell of the molecule, leading to reduced electrostatic interactions between the intercalation cations and the unit cell lattice, which correlates with high reversible capacity utilization.

The trends were further corroborated by comparing metal nitrogen stretch frequencies measured by FTIR in the far-IR frequency range to the σ -parameter and electronegativity values, as shown in Figure 4.3 (a) and Figure 4.3 (b). It was again observed that the compounds that had intermediate metal-nitrogen stretch frequencies such as FeHCF, CaCoHCF and CaZnHCF had high capacity utilization. From Figure 4.4, which compares σ -parameter values, metal-nitrogen stretch frequencies and the reversible capacity utilization of all the cathode materials under investigation against cation electronegativity values (χ_i), it was observed that the materials that had intermediate values of σ -parameter values, metal-nitrogen stretch frequencies and cation electronegativity (χ_i) values (FeHCF, CaCOHCF, CaZnHCF), demonstrated the highest reversible capacity utilization among the eight cathode materials under investigation.

Figure 4.3 (a).Metal-nitrogen stretch frequency versus σ -parameter. (b). Metal-Nitrogen stretch frequency versus cation electronegativity (χ_i).

Based on the results and discussion of the results, it is hypothesized that an intermediate value of bond strengths and electron cloud distribution across the unit cell lattice of the cathode materials, would result in a reasonable change in free energy for intercalated ions, while minimizing strong electrostatic interaction between the intercalating cation and unit cell lattice which would reduce ion mobility. This balance leads to improved

reversible capacity utilization of the cathode materials. Hence, these parameters can be used for screening cathode materials for intercalation type batteries.

Figure 4.4. Comparison between metal-nitrogen stretch frequency, σ -parameter and reversible capacity utilization (Ca²⁺ ions) versus cation electronegativity (χ_i).

Chapter 5. Summary and Conclusion

A study was undertaken to identify metal hexacyanoferrate cathode materials for a non-aqueous rechargeable Ca^{2+} ion battery. In order to identify suitable cathode materials, a set of eight metal hexacyanoferrate materials were synthesized with the following metal ions: Ba^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+} , Fe^{3+} , Al^{3+} , Sn^{4+} , and Mo^{5+} on the nitrogen end of the ferrocyanide. The resulting metal hexacyanoferrate materials are: K_2BaHCF , MnHCF , ZnHCF , CaCoHCF , FeHCF , CaAlHCF , SnHCF and MoOHCF , respectively. These materials allowed a study of the effect of increasing valency of the metal ion (on the nitrogen end of ferrocyanide) on the electrochemical properties of the cathode materials. Following the synthesis, the mentioned metal hexacyanoferrates powders were subjected to scanning electron microscopy imaging and X-ray diffraction to identify the particle size and morphology as well as the unit cell symmetry and unit cell parameters. Following the physical characterization, the metal hexacyanoferrate powders were used to prepare a cathode paste and subsequently, cathode electrodes. These cathodes were subjected to electrochemical characterization using cyclic voltammetry (CV) and galvanic cycling (GC). The CV technique allowed characterization of redox behavior and the reversibility of redox process of the cathode electrodes. The shape of the redox peaks, the ratio of the oxidation and reduction currents, as well as the separation of oxidation and reduction potentials identified from CV measurements, allowed us to study the kinetics associated with intercalation and de-intercalation of Ca^{2+} ions. The GC

measurement was used to test the performance of the cathode electrodes, and determine the reversible gravimetric capacity (mAh/g) at different current densities. This measurement allowed the identification of cathode materials that performed well (FeHCF, CaCoHCF and ZnHCF) over the other materials (K₂BaHCF, MnHCF, MoOHCF, CaAlHCF and SnHCF). The GC measurement also allowed the identification of the amount of resistance encountered by the diffusion of the intercalating cations within the interstitial spaces of the cathode materials.

In order to identify and understand the role of different metal ions in contributing towards the resistance encountered by the intercalating cation, FTIR measurements were performed on as synthesized metal hexacyanoferrate powders. This allowed the identification of metal-nitrogen stretching frequencies. The metal nitrogen frequencies reflect the bond strength of metal-nitrogen bonds which could also reflect the uniformity of electron cloud distribution around the metal hexacyanoferrate lattice. The metal-nitrogen stretching frequency when compared to the electronegativity values of the metal species (on the nitrogen end) and the σ -parameter, revealed an empirical trend among the eight metal hexacyanoferrates under test, where by, the metal hexacyanoferrates (FeHCF, CaCoHCF, ZnHCF) that had intermediate values for all three parameters, namely, metal-nitrogen stretching frequency (187 to 237 cm⁻¹), σ -parameter (2.55 to 4.86) and cation electronegativity (χ_i) (1.321 to 1.556), demonstrated high reversible gravimetric capacity utilization (50% or greater). The rest of the materials (K₂BHCF, MnHCF, MoOHCF, CaAlHCF, SnHCF) that had one or more parameters with an extreme value(s), demonstrated reduced gravimetric capacity utilization. This empirical trend could be

tentatively attributed to the balance in bond strength and electron cloud density across the lattice of FeHCF, CaCoHCF and ZnHCF, resulting in minimal electrostatic interaction between the intercalating Ca^{2+} ions and unit cell lattice, leading to improved reversible capacity utilization of the cathode materials. For other materials (K_2BHCF , MnHCF , MoOHCF , CaAlHCF , SnHCF), it is speculated that there could be varying degrees of electron cloud polarization (mild to severe), resulting in strong electrostatic interactions between Ca^{2+} ions and the unit cell lattice, subsequently reducing the reversible gravimetric capacity utilization.

Based on the findings of this work, a similar calculation was undertaken for other metal hexacyanoferrates, to determine the possibility of identifying materials that had a high probability of achieving high gravimetric capacity utilization with Ca^{2+} ions. The calculations (σ -parameter and cation electronegativity), revealed that copper hexacyanoferrate ($\sigma = 2.64$ and electronegativity = 1.372), nickel hexacyanoferrate ($\sigma = 2.90$ and electronegativity = 1.367) and vanadium hexacyanoferrate ($\sigma = 4.93$ and electronegativity = 1.545), could be possible candidates for measurements in order to determine whether they could demonstrate high capacity utilization. Based on a literature survey, nickel hexacyanoferrate [24] and copper hexacyanoferrate [30] have demonstrated promising results as cathode materials for Ca^{2+} and Mg^{2+} ion aqueous rechargeable batteries, indicating potential promise for non-aqueous rechargeable Ca^{2+} ion batteries. A simple five-step approach has been proposed below to identify potential metal hexacyanoferrate based cathode materials:

- (a) Identify transition metal ions with an oxidation state of either 2+ or 3+.
- (b) Calculate the σ -parameter for the metal ions under consideration.
- (c) Identify cation electronegativity (χ_i) for the metal ions under consideration.
- (d) If the σ -parameter and cation electronegativity (χ_i) values fall in the following range: σ -parameter (2.55 to 4.86) and cation electronegativity (χ_i) (1.321 to 1.556), then those materials are potential candidates for far-IR FTIR measurements to identify metal-nitrogen stretching frequency.
- (e) If the metal nitrogen stretching frequency lies in the range of 187 to 237 cm^{-1} , then the material should be treated as a potential cathode material and electrochemically characterized to determine its performance as a cathode material.

In order to confirm and further improve the accuracy of identifying potential metal hexacyanoferrate cathode materials using the above described approach, it is important to study a larger number of metal hexacyanoferrates and other metal hexacyanometallates. This will not only verify the selection method but also allow for the identification of a more accurate range of values of the above discussed parameters to be considered. The goal of identifying more efficient battery materials is becoming increasingly more important as we move to pervasive use of mobile electronics.

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