ELECTROCHEMICAL STUDIES OF HEXAVANADATES AND LITHIUM MANGANESE OXIDES FOR AQUEOUS RECHARGEABLE LITHIUM BATTERIES

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Abstract

Aqueous rechargeable lithium ion battery (ARLB) systems are potential alternative to existing rechargeable battery systems like Ni-Cd, Ni-MH, lead acid and lithium ion battery due to its advantages including rate capabilities, safety and environmental friendliness. Investigations of high energy/power, long cycle life and low-cost materials for aqueous rechargeable lithium ion batteries are of great interest especially for transportation applications such as electric (EVs) or hybrid-electric vehicles (HEVs), large-scale power storage grids and wearable electronics. ARLBs have higher power density but lower energy densities compared to lithium polymer batteries. ARLBs have much better rate capabilities (10-5000mA g\(^{-1}\)) compared to lithium ion batteries (0.1-10mA g\(^{-1}\)). This thesis focuses on the development and study of novel hexavanadate based anode and lithium manganese oxide based cathode materials for ARLBs with higher energy densities and better cycle life performances at higher rates.

In this thesis, new set of hexavanadate based materials with high theoretical capacities like Li\(_3\)V\(_6\)O\(_{16}\), Na\(_2\)V\(_6\)O\(_{16}\), K\(_2\)V\(_6\)O\(_{16}\), CaV\(_6\)O\(_{16}\) and SrV\(_6\)O\(_{16}\) from the family of metal vanadium oxides (M\(^{\frac{2x+}{x}}\)V\(_6\)O\(_{16}\); \(x = \) valency of alkali metal ion) for aqueous rechargeable lithium ion battery were synthesized by both facile hydrothermal and sol-gel method using Vanadium Oxide (V\(_2\)O\(_5\)) and hydroxide salt of the alkali metal ion (LiOH, NaOH, KOH, Ca(OH)\(_2\) and Sr(OH)\(_2\)). Similarly, different morphologies of high-voltage Spinel materials like LiMn\(_2\)O\(_4\) were explored for its suitability to develop a better full cell ARLB. Electrochemical studies show higher lithium ion insertion into M\(^{\frac{2x+}{x}}\)V\(_6\)O\(_{16}\) but with irreversible capacity loss which is the research challenge this work has aimed to study and tried to address.

As-prepared material were subjected to crystallographic X-ray diffraction (XRD analysis, mechanical properties, surface morphology (field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM)) characterization to evaluate the effect of crystal structure and morphology on its electrochemical performance. CaV\(_6\)O\(_{16}\) doped with TiO\(_2\) as anode exhibits an initial capacity of 350mAh\(^{-1}\) and retention
of 200mAh\(^{-1}\) over 100 charge/discharge cycles, at a current density of 500mAg\(^{-1}\), which is much better than any aqueous lithium-ion battery reported. LiMn\(_2\)O\(_4\) hollow microspheres as cathode displays an initial capacity of 145mAh\(^{-1}\) and a capacity retention of more than 90% of its initial capacity for over 1000 cycles at a current density of 500mAh\(^{-1}\), which proves its potential for usage in commercial applications.

Fundamental studies on the importance of different morphologies, mechanism of intercalation/de-intercalation of lithium ions in aqueous media into \(\frac{M_{2}}{x}V_{6}O_{16}\), dissolution of electrode material, effect of electrolyte’s counter-ion on rate performance, influence of annealing temperature on crystallinity and electrochemical performance were conducted to help us optimize several parameters to achieve the best performance. Further, a full-cell ARLB is constructed in a pouch cell configuration using LiMn\(_2\)O\(_4\) as cathode and Na\(_2\)V\(_6\)O\(_{16}\) and CaV\(_6\)O\(_{16}\) as Anode and evaluated for its electrochemical performance. Additionally, different energy harvesting options are explored to power a combination of two or more energy storage systems coupled to a sensor-driven smart consumption system. Finally, we demonstrate the application of an intelligent power sourcing storage and consumption system (IPSSC) through two case-studies using an ontology developed with the knowledge obtained through proper classification of the available energy harvesting systems, energy requirement of devices and their components and ambient real-time source of energy. A kinetic energy harvesting based RMS simulation tool was used to calculate the number of data packets that could be transmitted in a wireless sensor network application from the above real-time energy sources.
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Abbreviations

ARLB: Aqueous rechargeable lithium ion batteries
LIB: Lithium Ion battery
LIM: Lithium intercalated material
IOT: Internet of things
WSNs: Wireless sensor networks
EVs: Electric vehicles
HEVs: Hybrid electric vehicles
CV: Cyclic voltammetry
GCD: Galvanic charge/discharge
IPSSC: Intelligent power sourcing storage and consumption
SCE: Standard calomel electrode
SHE: Standard hydrogen electrode
Redox: Reduction and Oxidation
EDS: Energy Dispersive X-ray Spectroscopy
HRTEM: High Resolution Transmission Electron Microscopy
PXRD: Powder X-ray Diffraction
SAED: Selected Area Electron Diffraction
SEM: Scanning Electron Microscopy
SEI: Secondary Electron Images
TEM: Transmission Electron Microscopy
XRD: X-ray Diffraction
HT-XRD: High temperature X-ray Diffraction
Z: Atomic Number
Chapter 1 Introduction

Chapter 1 introduces the importance of aqueous rechargeable lithium ion batteries (ARLBs) in comparison to other energy storage options. It provides a background on different energy storage systems and how it compares with ARLBs. Motivation towards development of ARLBs in applications like wearable electronics and electric vehicles, where safety is of prime concern along with other necessities like better energy density and long cycle life with higher rate capabilities is stressed upon. In section 1.3, research gap analysis in the development of a complete ARLB system is discussed with respect to anode and cathode materials with a focus on hexavanadates and lithium manganese oxide spinels respectively. Further, research objectives and scope of the work to be done in this thesis in discussed in brief. Finally this chapter end with section 1.5, which details about the brief organization of the following thesis, chapter by chapter.
Chapter 1

Introduction

1.1 Background

Increasing energy needs and pressing global warming issues have generated the need for developing better systems for energy generation and a goal towards less dependency on fossil fuels. Extensive research have been conducted in the area of renewable energy and indisputably energy storage plays a vital role in storing energy from solar cells/wind mills and returning it back to energy grid.\(^1\)\(^-\)\(^7\) The only method to achieve the goal is to focus more on renewables. Germany’s share in renewable energy has increased from 6.3% to above 25.4% in last 13 years, which proves to the world that with further improvements in green technology the share of renewable energy could be improved and every nation could achieve carbon neutrality.\(^1\) Rechargeable batteries play a vital role in everyday life utilities like computers, mobile phones and electric vehicles (EVs). The currently used rechargeable battery systems for such applications include Lead acid, Nickel-cadmium, Nickel-Metal hydride and Lithium ion batteries. Many efforts made to explore various possibilities to improve the above systems to satisfy the technical requirements for EVs were futile \(^8\)\(^-\)\(^{12}\). Most of them have their intrinsic problems which are hard to solve. For example, lead acid and nickel cadmium have low energy density and employs environmentally harmful materials like lead and cadmium while Ni-MH batteries have large self discharge and lithium ion batteries have a high risk of safety because of the flammability of organic electrolyte and the reactivity of the electrode material with the organic electrolyte during overcharging or short-circuiting. Lithium ion battery manufacturing requires sophisticated cell assembly technologies due to necessity of having a perfectly dry environment and as the conductivity of the organic electrolyte is low, the power density and its operation at high rate is not good, thus increasing the cost of lithium ion batteries. \(^13\)\(^-\)\(^{16}\) With the storage and utilization of such large amount of energy comes along a concern about the deliverable capacity and safety of such energy storage devices. Thus, considering the above problems like high cost, safety and environmental concerns, development of a low cost, safe, high power, rechargeable green battery systems are detrimental for applications like Electric vehicles, Solar and wind mill farms. Recently, many safe and low cost water based energy storage Systems have shown promising performance with respect to cycle life and power storage. \(^17\)\(^-\)\(^{21}\)
1.2 Motivation

Lithium ion batteries have been used on a large scale in mobile devices, electric vehicles and finally it is getting widely spread to interconnected network of wireless sensors that are linked over the cloud that are make up the internet of thing(IOT). Environmental issues and increasing power demands are driving the need for high performance advanced energy storage technologies that can overcome the limits of present state of art devices. Aqueous rechargeable Lithium Ion battery(ARLB) are one of the promising candidates as energy storage devices mainly due to their safety and good rate capabilities. Theoretically, these systems possess high energy densities and long cycle life. Safety is the most critical criteria as battery systems become larger in terms of stored energy as well as physical size. Importance of battery safety is emphasized again by fire explosion in Toxco – A North American based largest lithium battery recycler and a more recent battery explosion at GM’s Warren Technical Center in Warren, Mich on 11th April 2012 both caused by lithium ion batteries.

![Figure 1-1 Market forecast of rechargeable batteries by LG Economic Research Institute. xEV includes all types of electric vehicles such as hybrid (HEV), plug-in hybrid (PHEV) and full (EV) types.](image)

The market forecast for all type of xEVs and other applications is estimated to rise steadily every year (Figure 1.1) driving the demand for higher energy/power density
LIBs and other advanced energy storage technologies. Currently the commercial LIBs employ LiCoO$_2$ cathode, graphite anode and LiPF$_6$ in a mixture of carbonate solvents as the electrolyte$^{[23]}$. One of the material challenges for developing improved LIBs for EV applications is the development of electrode materials with high energy and power density, faster discharge kinetics and better stability. The other challenge is to develop safer, cheaper, more flexible, mechanically stable and more reliable electrolytes to replace the liquid mixture of lithium salts in organic solvents$^{[24]}$. Though the current liquid electrolytes provide sufficiently high ionic conductivity and relatively stable performance, the presence of organic flammable solvents is a safety issue$^{[25]}$. Another goal of lithium rechargeable battery development is mechanical flexibility that is required for weight sensitive applications and various forms of flexible, portable electronic devices. To convert such potentials into reality, one paramount challenge that needs to be addressed is the inability of making flexible electrodes with robust mechanical property along with excellent electrochemical performance. Also, such batteries should fit to the life cycles of the applications and should be disposable or recyclable. For the flexible lithium battery, organic conducting materials such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-based polymers, sulfide-based polymer, and carbonyl-based polymers have been used$^{[26-31]}$. However, the implementation of conducting polymers leads to cells with low capacity, self-discharge, poor cycling capability, and low rate capability$^{[26,32]}$. Also, the organic materials are subjected to low potential, dissolution into liquid electrolytes, low thermal stability, and need a high amount of carbon conductor material.

Currently, wearable technology encompasses few products mainly in the healthcare/medical, and fitness/wellness application areas. In these areas, there is a greater use-case for wearable technology in order to transmit data such as vital signs, and track user performance. Dominant wearable products here include continuous glucose monitors – such as from Abbott and Medtronic, activity monitors – such as Fitbit, Addidas miCoach and Nike Fuelband, and fitness and heart-rate monitors – such as from Garmin, Polar and Suunto. The wearable technology market is growing with a rapid pace, with shipments likely to rise by more than 500 percent from 2011 to 2015. In 2011, 14 million wearable technology devices were estimated to have been shipped according to a new report from IMS research. However, by 2016, shipments will increase to 92.5 million units based on most likely forecast scenario from IMS Research presented in Figure 1.2.$^{[33]}$
These wearable technologies pose a very crucial demand in the space of batteries with high energy density and safety. Most of the devices come directly or indirectly in contact with body fluids and parts and hence, safety under any situation cannot be compromised, which makes the use of LIB a challenge. Moreover, research on lightweight flexible batteries has also been of extensive interest motivated by their potential applications in flexible electronics used for applications like wearable sports electronics and solar batteries.

This report thus focuses on the development of safe flexible rechargeable aqueous electrolyte based lithium ion battery for high energy and power density applications like performance training in Sports or tracking in manufacturing sector.

1.3 Research Gap analysis

Inherent limitation of materials that make the architecture of lithium ion batteries has limited its use in applications where high power and compactness remain a must. Most of the lithium ion batteries last for about 500-900 cycles which is approximately 30
months with an assumption of 1 charge/discharge per day, which prevents the usage of
these batteries in applications where replacement of batteries is not easy and is costly.
Most of the current lithium ion batteries are designed for certain current loads/rates.
Operating at variable current rates causes stress in the electrode material during its
operation. This stress causes irreversible capacity loss and also degrades the cycle life
of the battery. ARLBs have an inherent advantage of high rate performance due to the
high conductivity offered by aqueous electrolyte. But, to make the ARLBs competitive
with lithium ion batteries, improvements in both the cycling stability and energy density
is detrimental.

Most of the materials studied for lithium ion batteries could be directly adopted in
aqueous rechargeable lithium ion batteries but the selection of those materials are
restricted by the inherent limitation of the aqueous electrolyte which decomposes at
about 1.23 V vs. SHE to release oxygen and at around -1.3 V vs. SHE to release hydrogen
thereby limiting the cell potential and causing side-reaction that seriously impacts the
cycling performance. Hence improving the overall voltage of an ARLB would require
careful selection and probable development of new materials or electrode morphologies
that could reversibly and stably intercalate and de-intercalate lithium ions at around the
decomposition potential of water, without causing any side-reactions.

The remarkable structural superior discharge capacity, flexibility and copiousness of
vanadium oxides amongst the numerous transition metal oxides have spurred immense
interest amongst the research community to explore the possibility of using these
vanadium oxides and its derivative compounds for large scale grid-application. [13,34–37]

**For Anodes in ARLBs**

The layered structure of V$_2$O$_5$ has been studied for about half a century and the fully
lithiated compound Li$_3$V$_2$O$_5$ of the Li$_x$V$_2$O$_5$ exhibit rock salt structure and the lithium
insertion and deinsertion process involves two redox couples, V$^{5+}$/V$^{4+}$ and V$^{4+}$/V$^{3+}$,
which results in the combination of the potential difference and the structural change
makes the intercalation process uncontrollable which leads to amorphization on cycling
and thereby capacity loss.
The layered structure of LiV$_3$O$_8$ comprises of VO$_6$ octahedra and VO$_5$ tetrahedra, held together by Li$^+$ cation which cannot be extracted as it probably acts as a pillar ion in stabilizing the crystal structure. Although lithium ions can be stored at two potential sites within the crystal, the Li ions at the octahedral sites in the interlayer are immobile thus cannot participate in the intercalation/deintercalation processes but the tetrahedral site can insert two additional lithium ions leading to the formation of Li$_3$V$_3$O$_8$. This process involves one redox couple and its highly reversible but the specific capacity (200mAh$^{-1}$) is still lower than the Li$_3$V$_2$O$_5$ (290mAh$^{-1}$) in lithium ion batteries. Substituting Li ion with Na ion, K ion, Ca ion and Sr ion to form new material would open new avenues for a high capacity and better cycle life based aqueous lithium ion battery.

Sodium vanadate has been studied for its potential Li intercalated electrode materials. Hydrothermal synthesis of Na$_2$V$_6$O$_{16}$ using V$_2$O$_5$ and sodium salts have been reported by Zhou et.al [41] and Yu et.al. [42] The effect on crystallinity of Na$_{1+x}$V$_3$O$_8$ during the lithium insertion/deinsertion has been studied by Kawakita et al. [40] Many synthesis method to produce different morphologies (nanowires and nanobelts) of Na$_2$V$_6$O$_{16}$ .nH$_2$O have been reported using low temperature hydrothermal method without the use of a surfactant.[41–45] Wang et.al has studied the use of sodium hexavanadate nanowire(Na$_2$V$_6$O$_{16}$) for lithium ion battery which gave an initial specific discharge capacity of 235mAh$^{-1}$ and better cycling stability on heat treatments.[44] However, not much attempt has been focused to study the lithium intercalation/de-intercalation mechanism in such systems and so far no study has been done to evaluate the potential use of this material for aqueous rechargeable lithium ion battery. Substitution of lithium with sodium has not only improved the capacity but also the cycling stability of these hexavanadates, hence it would be interesting to see if further substitution with other cations from the alkali and alkali-earth metals could have any significant effect on the electrochemical performance of these hexavanadates.

**For Cathodes in ARLBs:**

Spinel lithium manganese oxide (LiMn$_2$O$_4$ or LMO) with a 3-D framework of face sharing tetrahedral and octahedral sites or lithium diffusion was first proposed by Thackeray as an electrochemically active material among many other manganese
oxides and it offers excellent cathode properties for Li-ion rechargeable batteries.\textsuperscript{46–48} Features such as low production cost, environmentally benign and high electric potentials of LMO makes it one of the most studied material for cathode applications. Manganese dissolution due to side reactions with water, structural transformation, loss of crystallinity, development of micro-strain, formation of two cubic phases and large polarization due to difficulty in lithium ion diffusion into bulk electrode under large current causes the decay in capacity on long cycling. Carbon coating, cation doping or nano-designing of the electrodes usually solves this. Carbon coating and Cation doping does help in stabilizing the capacity loses during cycling but at an expense of possible capacity that can be achieved.\textsuperscript{49–51} One of the strategies used for improving the rate performance is by growing the crystals in nano-dimension in a particular morphology that enables multiple pathways for Li\textsuperscript{+} ions to enter into the bulk and reduce the distance that is required for the lithium ions to travel to & from the interstitial sites for efficient intercalation/de-intercalation during the electrochemical cycling. As developing non-stoichiometric spinel or doping alternative metal ions has not been completely successful due to the compromise on capacity and hence engineering new nano-architectures that can doesn’t compromise on capacity and are able to handle structural stresses well during lithium insertion and extraction are the best available solution to date.

For electrolyte in ARLBs:

Various methods to optimize electrolyte has been performed some of which is to optimize the pH, oxygen content and mixture with organic electrolyte. The influence of counter-ion has been studied widely in lithium ion batteries but so far there are no reports of its study in ARLB systems. In this thesis, a study has been attempted to compare the rate performance of LiMn\textsubscript{2}O\textsubscript{4} micro-architectures (Cubes, Hollow spheres, Nanocubes/Microsphere hybrid) in LiCl, LiNO\textsubscript{3}, Li\textsubscript{2}SO\textsubscript{4} electrolyte to understand the effect of counter-ion with respect to morphology on the rate capabilities, which could help in better electrolyte selection for commercial development of aqueous rechargeable lithium ion batteries.
Finally, development of a flexible aqueous rechargeable lithium ion pouch battery with high power density and cycle life using hexavanadates as anodes and LMO as cathode in an optimized electrolyte system is thus the main focus.

1.4 Research Hypothesis, Objectives and Scope

Research hypothesis

Effect of pillar ions: On the basis of state-of-the-art study, it is anticipating that a substitution of the pillar ions (Li\(^+\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Sr\(^{2+}\)) with increasing ionic radii, might increase the interlayer space between V\(_6\)O\(_{16}\)\(^2-\) structure, which will help in accommodating more lithium ions during the intercalation process thereby resulting in higher capacity. In addition to these pillar ions also act as support that prevents the structure from collapse and vanadium compounds with interlayer pillar ions have better cycling stability and reduced vanadium dissolution compared to simple oxides like V\(_2\)O\(_5\), VO\(_2\), V\(_6\)O\(_{13}\). At the same time investigation is necessary to find the optimum size of pillar ion that hold the framework together and also smaller or larger interlayer space might decrease the number of lithium ion entering the material and fail to hold the structure intact during long cycling and high current operations, respectively. Hence finding the optimum pillar ion size is crucial for developing a potential electrode for any electrochemical system.

Factors such as (i) increase in the size of the pillar ion (down the periodic column) within hexavanadates should increase the crystal structure, crystal volume and size of the material, (ii) presence of water content within the molecule should influence the volume of the crystal and thereby its capacity and performance significantly. Heat treatment studies that vary the interlayer water content could be used to do perform a comparative electrochemical performance analysis. As a result of this a thermal expansion of the crystal which might or might not co-relate with loss of interlayer water molecules. Hence, it would be interesting to see how a combination of both effects thermal expansion of crystal and loss of interlayer water molecules impacts the crystal volume and thereby its electrochemical performance.
**Effect of surface area and geometry:** Increase in surface area and geometry of a microstructure affects the electrochemical performance especially the rate performance over long cycling as it impacts the kinetics of how Lithium ion inserts and de-inserts from the structure.

**Effect of lithium intercalation:** Factors that influence rate performance depends on the electrode and the electrolyte. Lithium Ion Electrolyte with same solvent and different counter ions should theoretically provide similar electrochemical performance which is not observed usually. While lithium inserts at the anode during charging and cathode during discharging the counter ion undergoes reduction and oxidation at the counter electrodes respectively. As the counter ions are in water, their motion within water shouldn't influence the kinetics of the reaction and hence it is believed that the oxidation potential of the counter ion plays a predominant role in material rate performance along with electrode's properties.

**Primary research objectives of the thesis:**

1. Investigate the impact of pillar ion (M site in $\text{M}_{\frac{x}{6}}^{x+}\text{V}_6\text{O}_{16}$) substitution within hexavanadates (hewettite group) on the structural properties and electrochemical performance.

Vanadium compounds like $\text{V}_2\text{O}_5$, $\text{V}_6\text{O}_{13}$, $\text{V}_6\text{O}_{16}$, $\text{LiV}_3\text{O}_8$ are widely studied as cathode in LIBs and anode for ARLBs due to their higher theoretical capacity (>400 mAhg⁻¹) which is due to their wide redox potential range, stable vanadium-oxygen framework, and good chemical stability which presents with unique safety characteristics that prevent oxygen release from its lattice compared to cobalt and nickel oxides as the $\text{V}^{4+/3+}$ and $\text{V}^{3+/2+}$ couples lie well above the $\text{O}^{2-}$: 2p band. Even-though the theoretical capacities of these vanadium compounds are in the range of 300-500 mAhg⁻¹, the practically achievable capacities are always lower i.e. 45 mAhg⁻¹ for $\text{V}_2\text{O}_5$ and 40-50 mAhg⁻¹ for $\text{LiV}_3\text{O}_8$, but hexavanadate compounds like $\text{Na}_2\text{V}_6\text{O}_{16}$ and $\text{Li}_3\text{V}_6\text{O}_{16}$ has shown a capacity of 120 mAhg⁻¹ and 150 mAhg⁻¹ respectively. Hence, supercell structure of hexavanadates with different pillar ions is considered for further study in this thesis to explore for the possibility to extend its practical capacity towards theoretical or near-theoretical values while also improving the electrochemical cycling...
Chapter 1

Introduction

stability of vanadium compounds. Hence, one of the major objectives of this thesis is to synthesize submicron structures of hexavanadates(\(\text{M}_{\frac{3}{2}}^{2+}\text{V}_6\text{O}_{16}\); M=Li\(^+\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Sr\(^{2+}\)) especially the hewettite mineral group for their study as potential anode material in ARLBs and study how the pillar ion substitution affects their structural property using various characterization techniques like FE-SEM, TEM, XRD and AFM and electrochemical performances using cyclic voltammetry (CV), galvanostatic cycling, XPS and electrochemical impedance studies (EIS), among others.

2. **Fundamental studies on the charge storage mechanisms in these hexavanadate structures**

In this new era, where batteries are widely used in various applications, the need to store charge faster and in large quantities have increased. Capacitors are known to store charge in the shortest possible time but the charge/energy doesn’t last long, batteries are known to store better charge/energy but the time taken to store them is higher. Supercapacitors, ultra-capacitors, and hybrid electrochemical capacitors are designed to operate in between the capacitor and battery range. The method by which energy is stored in a battery depends upon various factors like the redox potential of the material, the size, morphology, surface area, crystal structure and even lattice orientation. In this thesis, using Randles-Sevcik equation which describes the effect of scan rate on the peak current in cyclic voltammetry, the charge storage contribution due to Li-ion intercalation(bulk storage) and pseudocapacitance(surface storage) in hexavanadate submicron structures are calculated. Understanding the charge storage property of a material can provide cues for further tailoring the material to suit specific energy storage requirements.

3. **Investigate the effect of morphology on the electrochemical properties of lithium manganese oxide cathodes in ARLB system**

Developing a high power full cell ARLB requires compatible electrodes with high capacity and higher voltage window. Hexavanadates are chosen for the study as a potential anode material, while LiMn\(_2\)O\(_4\) is chosen as a potential candidate for cathode material because of its higher theoretical capacity(\(~145\)mahg\(^{-1}\)) and operational potential(\(~0\) to 1.1V vs SCE). LiMn\(_2\)O\(_4\) is also one of the most studied and reviewed cathode materials for ARLB system and the production of LiMn\(_2\)O\(_4\) can be easily scaled.
up for commercial production owing to the facile synthesis process. One of the major issues with LiMn$_2$O$_4$ is manganese dissolution which happens due to side-reactions with the electrolyte and reduced rate performance under long cycling. Different morphologies of LiMn$_2$O$_4$ has been studied for its electrochemical performance in lithium ion batteries and very few have been studied in ARLB system. Hence, designing various nano/micro architectures of LiMn$_2$O$_4$ for its electrochemical study in ARLB system is one of the another major focus in this thesis.

4. **Electrochemical studies on the effect of electrolyte’s counter-ion towards micro-architecture cathodes**
   One of the most important factor that determine the choice of the electrode is the rate at which the material can insert charge in a stable manner without any irreversible capacity loss or structural breakdown. Various efforts to tailor electrodes’ morphology, sizes and chemical make-up have been performed to improve the rate capabilities of the material. Along with the electrode, the electrolyte also determines its rate capabilities as the transport of ions into the electrode occurs through the electrolyte and through the electrode/electrolyte interface. The influence of counter-ion has been studied widely in lithium ion batteries but so far there are no reports of its study in ARLB systems. To understand the effect of counter-ion on the rate capabilities of various morphology of the electrode, comparison studies on the rate performance of LiMn$_2$O$_4$ micro-architectures(Cubes, Hollow spheres, Nanocubes/Microsphere hybrid) in LiCl, LiNO$_3$, Li$_2$SO$_4$ electrolyte are performed in an ARLB setup.

5. **To fabricate a stable, high power full cell ARLB with superior rate capabilities**
   Fundamental studies and scientific understanding of the electrochemical behaviour of hexavanadate materials as anodes and LiMn$_2$O$_4$ microarchitectures as cathode, will help in building a full cell ARLB battery in an electrolyte salt with the most appropriate counter-ion that help in better rate performance. Such a full cell ARLB has many real time application, which has been further demonstrated using an intelligent power sourcing, storage and consumption model and ontology for designing an optimum smart energy harvesting and storage module for various user-defined application.
Research Scope

To confront the research gap discussed in section 1.3 and in the literature review (chapter 2), the research scope of this thesis is to explore different alkali and alkali-earth metal hexavanadates as anodes and lithium manganese oxide microarchitectures as cathodes in a suitable electrolyte to develop a high energy/power density material for aqueous rechargeable battery with superior cycling stability.

Further, the research objective of this work is the development of full cell flexible ARLB that could be self-powered from ambient energy sources using energy harvesting components which could then fit in for a variety of applications like sports electronics, location tracking or energy monitoring. Development of this full cell battery is achieved using the best performing alkali or alkali-earth metal hexavanadates($M^{x+}_2V_6O_{16}$; $M=Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}$) as anode and lithium manganese oxide(LMO) morphology as the cathode.
Chapter 1

Introduction

A new Intelligent power sourcing storage and consumption model (IPSSC) is proposed and an ontology is developed on the concept which will allow any user to select the best combination of energy storage and harvesting components based on his choice of application and intended purpose. The sub-objectives are defined as follows:

1. **Development of stable, wide-potential-range** $\frac{M_2^{x^+}V_6O_{16}}{x}$ & **LMO as anode and cathode materials respectively.**
   a) Synthesis of nanostructured $\frac{M_2^{x^+}V_6O_{16}}{x}$ and microstructured LMO via low temperature techniques (e.g. Sol-gel and low temperature hydrothermal synthesis)
   b) Doping using transition metal oxide (e.g. Anatase and rutile TiO$_2$) to increase the cycling stability of the material.
   c) Study of electrochemical properties with $\frac{M_2^{x^+}V_6O_{16}}{x}$ & LMO as working electrode in ARLB.
   d) Full-cell electrochemical studies using Na$_2$V$_6$O$_{16}$ and CaV$_6$O$_{16}$ as anodes and LiMn$_2$O$_4$ microarchitectures as cathode.
   e) Synthesis and electrochemical study of a symmetric ARLB using Na$_2$V$_6$O$_{16}$ material that function as both cathode and anode.

1. **Fundamental studies on high-capacity - high stability** $\frac{M_2^{x^+}V_6O_{16}}{x}$ and **LMO.**
   a) Electrochemical studies on $\frac{M_2^{x^+}V_6O_{16}}{x}$ and LMO nano/micro-architected electrode materials as anode and cathode respectively in ARLBs.
   b) Investigation on the effects of counter-ion in lithium salt based aqueous electrolytes on the rate-performance in LMO cathodes.
   c) Investigations on the consequence of high temperature sintering on the crystallinity and electrochemical performance of Na$_2$V$_6$O$_{16}$ as both cathode and anode.
   d) Electrochemical studies on the effect of pillar ion substitution in $\frac{M_2^{x^+}V_6O_{16}}{x}$ on the crystal structure, morphology, redox potentials, galvanostatitic charge/discharge performance and finally on the charge storage mechanism of hexavanadate bronzes.
   e) Investigations on $\frac{M_2^{x^+}V_6O_{16}}{x}$ and LMO based electrodes using various characterisation techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray Photoelectron spectroscopy (XPS)
cyclic voltammetry (CV), galvanostatic cycling and electrochemical impedance studies (EIS), among others.

2. Investigation and the development of Intelligent power sourcing, storage and consumption model and ontology for designing an optimum smart energy harvesting and storage module for user-defined application.

   a) Optimization of flexible battery architectures for obtaining the ideal energy density along with rate capabilities in ARLB system.

   b) Developing a user-case scenario based on the cues from IPSSC ontology for the development of an optimum energy storage and harvesting system for a fitness tracking device in athletes and energy monitoring in manufacturing sector.

Thus, a brief history of the work done in this field, the technology gap analysis yet to be addressed and the study on novel material based on the insights from existing research gaps will be used to develop better ARLBs architectures with higher energy and power densities, good cycle life and rate capabilities, which will be highlighted in this report.

1.5 Thesis Organization

This thesis is organized as follows. Chapter 2 briefly introduces lithium ion batteries and addresses the need for a safe and better battery. It details about the history of aqueous rechargeable lithium ion batteries (ARLB), its kinetics and key opportunities in this system. A brief literature review is done on the existing electrode materials for ARLB with a further focus on hewettite heterostructures and LiMn$_2$O$_4$ micro-architectures and fundamental studies conducted in the literature. Chapter 3 describes the various techniques used in this thesis for material synthesis, structural and electrochemical characterization and studies. Chapter 4 details the experimental results followed by discussion in chapter 5. Chapter 6 deals with the application part of the ARLBs and batteries in general in the area of wearables electronics and energy harvesting. A short background study of existing energy harvesting, storage and consumption is also mentioned which forms the basis of section 6.1 and 6.2 in chapter 6. Finally, this section ends with a demonstration of the architecture, techniques and methods used to combine these aqueous rechargeable lithium ion batteries with an
energy harvesting system for an intelligent power sourcing, storage and consumption model to be used for a sports application co-relating it with a case study derived from an intelligent Energy harvesting ontology system.

Conclusion involving the scientific and technological contributions from this thesis is included in chapter 7 and suggestions for future work and details of the related study is presented in chapter 8.
Chapter 2 Literature Review

Increasing CO₂ emissions and associated problems like global warming has posed challenges to humanity. The world has witnessed the adverse effects of global warming like the recent Hurricane Sandy and earthquakes that occurred in various parts of the world. People have started believing climate change and what once thought as a buzz word "Global Warming" is now considered seriously. One of many areas to prevent such catastrophes is to focus on green technologies and in that respect batteries or energy storage system play a vital role. The changing policies promoting green and sustainable technology and development of new funds to encourage technologies and start-ups in the Green-Tech area is increasing day by day in US and other parts of the world. One among them is the development of a safe, low cost, high power, durable rechargeable battery with the ability to charge within few minutes for various applications like electric vehicles, solar farms, trains, ships, aircrafts, submarines, wind mills and home-appliances. Chapter 2 begins with section 2.1, which provides a brief literature review of existing energy storage devices and then compares them with ARLBs, it also discusses the current status and issues in ARLB system and in flexible batteries. Further, in section 2.2, various potential electrodes materials commercial and under research is reviewed. Finally, the chapter ends with section 2.3 and 2.4, which looks into the fundamental charge storage mechanism(CSM) based technique to understand CSM in ARLBs and presents with future challenges and opportunities in ARLB system.
2.1 Background & history of ARLB

Fundamentals of Battery Technology

Batteries are electrochemical cells that convert stored chemical energy into electrical energy. An electrochemical cell consists of cathode, anode and electrolyte. A separator that permits electrolyte and its ions but electrically non-conducting is used to separate the cathode and anode. The cell also uses a current collector that delivers current from the surface of the electrodes to and from the external circuit. In an open circuit condition, the working ion moves inside the cell, but it is not compensated by charge and hence, the anode becomes negatively charged while the cathode becomes positively charged until the electrochemical potential of cathode and anode are the same.

During discharge, electrons and ions from the anode flows to the cathode and during charge, an external potential difference forces the ions and electrons to travel from the cathode to anode. During discharge, an internal resistance $r$ to the ionic current $I_i$ reduces the output voltage $V_{dis}$ of a cell relative to the open-circuit voltage $V_{oc}$ by a polarization $\eta = I_i r$; the voltage $V_{ch}$ required to charge the cell is increased by $\eta$, which then represents an overvoltage. Therefore, the discharge and charge voltages of a cell are given by equation 2-1 and 2-2 respectively.

**Equation 2-1** $V_{dis} = V_{oc} - \eta(q, I_{dis})$

**Equation 2-2** $V_{ch} = V_{oc}(q,I_{ch}) + \eta(q,I_{ch})$

where $q$ represents the state of charge and $I_{dis}$, $I_{ch}$ are, respectively, the discharge and charge currents.

Batteries can be further divided into primary(non-rechargeable) batteries and secondary (rechargeable batteries). As the focus of this thesis is on aqueous rechargeable lithium ion batteries(ARLBs), further sections of this chapter will detail about existing and most common rechargeable system and compare them with ARLB system.

2.1.1 Comparison of ARLBs with conventional rechargeable batteries

Some of the conventional rechargeable batteries used widely are Nickel-cadmium, Nickel-metal hydride, Lead acid and lithium ion battery.
In Nickel cadmium batteries, Ni(OH)$_2$ is used as the cathode, cadmium as the anode and potassium hydroxide as the electrolyte. The nominal cell voltage of Ni-Cd batteries is 1.2V and the specific energy density is 40-60Whkg$^{-1}$. Reversible displacement reaction causes, large volume changes at the anode. One of the major issues with Ni-Cd batteries is the use of cadmium, which is considered toxic in many parts of the world.$^{[52]}$

In 1902, Wade et.al$^{[53]}$ gave the 1st comprehensive version on “rechargeable batteries”, with more focus on lead-lead oxide system, which was further supported by Barak et.al$^{[54]}$ by stating it as the “work house” among rechargeable batteries. Lead acid batteries are one of the most popular batteries used widely in variety of applications like starter batteries in vehicles and house-hold inverters. Lead acid batteries uses lead and lead oxide as the electrodes and sulphuric acid electrolyte. In the discharged state, both the electrodes become lead sulphate and most of the remaining electrolyte is water. Overcharging can cause electrolysis of water causing release of hydrogen and oxygen at the electrodes. A typical lead acid cell gives 2.0V and 15-20mAhg$^{-1}$. Acid leakage, environmental toxicity due to lead and poor cycling efficiency are some of the issues with lead acid batteries.$^{[55]}$

Compared to conventional batteries like lead acid, Ni-Metal hydride and Nickel-cadmium which were prominently used in late 90s, current research has helped us to develop much better batteries with newer chemistries and one among them which changed the way we store energy is Lithium ion batteries. Lithium ion battery typically uses metal oxides, lithium or carbon allotropes like graphite, super P, Carbon nanotubes, graphene as anode, metal oxides or phosphates as cathode(LiFePO$_4$, LiCoO$_2$, MnO$_2$, and LiMn$_2$O$_4$) and organic or ionic gel electrolyte as electrolyte(LiClO$_4$, LiPF$_6$ in ethylene carbonate and [BMIM]BF$_4$). Lithium ion batteries are small, light, have higher energy density and good cycle life. Most of the electronic devices currently use lithium ion batteries. Many electric and hybrid electric vehicles, aircrafts, Submarines & Vessels use lithium ion batteries. But, recent explosions and fire from Tesla electric vehicles$^{[56]}$, Boeing 787 aircraft$^{[57]}$, mobile phones and laptops have raised serious concerns about the future use of lithium ion batteries as a safe means of energy storage. Many of the batteries that exist today has its own benefits and shortcomings.
Further, many work was done on Nickel-metal hydride batteries using aqueous electrolyte and was widely commercialized. In Nickel metal hydride, the H$^+$ ions inserts reversibly into the O-Ni-O closed packed layers and into the 3-D interstitial sites of the metal hydride. But the issue with Nickel metal hydride batteries are self-discharge (∼5-20%), heat generation during overcharging, low energy density, reduced shelf life and poor cycling efficiency.

![Figure 2-1 Ragone plot: Power density Vs Energy density for different batteries](image)

When compared with these batteries (Figure 2.1), lithium ion rechargeable batteries are better in terms of its energy density, higher voltage and reduced size or compatibility.\textsuperscript{[13]} So to strike a balance between higher energy density and safety, ARLB system is ought to be a potential energy storage system in comparison with lithium ion, Nickel Metal hydride and lead acid batteries.

In the mid-1990s, Dahn and Li et.al proposed for the first time an aqueous electrolyte based rechargeable lithium ion batteries using VO$_2$(B)://LiMn$_2$O$_4$ as Anode//Cathode with 5M LiNO$_3$ aqueous solution as electrolyte.\textsuperscript{[13,58]} The energy density of this system was restricted due to the reduced cell potential achievable i.e. 1.5V which makes it less
attractive than lithium ion batteries but comparable to nickel cadmium and lead-acid batteries.

Practically, lithium ion batteries (LIBs) differ from ARLB only in its electrolyte type, LIBs use organic electrolytes (e.g. ethylene carbonate) while ARLBs use aqueous electrolyte (aqueous solution of LiCl, LiSO₄ or LiNO₃). ARLB systems use most of the redox active electrode materials that are used in LIBs, which are redox active within the range of 1.85V to 4.05V vs Li/Li⁺ in organic electrolyte. Some of the advantages and disadvantages of using aqueous electrolytes as compared to non-aqueous electrolytes are listed below

**Some of the advantages of using aqueous electrolyte are listed below:**

a) Superior ionic conductivities enables the use of increasing the thickness of the electrodes thereby facilitating the build-up of high capacity battery systems without the need of stacking.

b) Costly and unsafe lithium salts like LiPF₆ can be swapped by cheaper and safer salts like LiNO₃, Li₂SO₄.

c) Expensive separators like celgard can be substituted by inexpensive separators like glass-fiber separators or whatmann paper.

d) There are no safety concerns associated with aqueous electrolytes and fabrication can be done in ambient atmosphere without the need for expensive glove boxes and dry room conditions.

**ARLBs suffer from the following disadvantages:**

a) The breakdown potential of water (1.23V vs SHE), restricts the overall energy density achievable in comparison to organic electrolyte which can go upto >3.5V vs SHE.

b) Capacity fading during long cycling which also affects the rate capability.
2.1.2 Basic Principles of ARLB

Scheme 2.1 Schematic representation of a typical ARLB

Scheme 2.1 shows the schematic representation of a typical ARLB. It is a rechargeable electrochemical cell in which the conversion from chemical to electrical energy is reversible. An ARLB is composed of three main components, anode, cathode and electrolyte i.e. (i) A metal oxide (LiMn$_2$O$_4$) cathode and (ii) A metal oxide anode (TiO$_2$, and Fe$_2$O$_3$) and (iii) An aqueous electrolyte of Sodium, lithium or potassium salts.$^{[59,60]}$

The two electrodes have different chemical potentials as determined by the chemistry that occurs at each end. When the battery is charged, lithium ions are driven by external voltage, extracted from the cathode, pass through the electrolyte and inserted into the anode (intercalation/lithiation). On discharging, the lithium ions are released (deintercalation/delithiation) by the anode and follow the reverse route back to the cathode. During this process, electrons flow in the outer circuit giving rise to electrical current. Energy density (Wh/g or Wh/cm$^3$) is the product of specific capacity (Ah/g or Ah/cm$^3$) and voltage (V). Typical full cell reaction of VO$_2$(B)/LiMn$_2$O$_4$ cell$^{[58]}$:

\[
\text{LiMn}_2\text{O}_4 \Leftrightarrow \text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x\text{Li}^+ + xe^- \text{ ......Cathode}
\]

\[
\text{VO}_2\text{(B)} + x\text{Li}^+ + xe^- \Rightarrow \text{Li}_x\text{VO}_2 \text{ ......Anode}
\]
Thermodynamic stability of a compound acting as a lithium intercalation host in aqueous electrolyte should be higher for it to be used as a potential electrode in ARLBs. Binding energy of lithium ions in an electrode material is a good measure of its stability and this energy is equal to the voltage of the Li/Electrode cell, with more tightly bound lithium ion indicating a higher voltage for the cell. In ARLB, at about 3.2±0.2 eV, lithium ion can bind adequately strongly with an intercalation host without having any reaction with the water. In ARLBs, there is a possibility of proton insertion along with lithium ions but further work on these systems by Dahn and Li rejected any possibility of H\(^+\) insertion into manganese oxide and confirmed that only Li\(^+\) was inserted.\[^{61}\]

Li and Dahn studied the thermodynamic stability of various materials that are potential hosts for lithium intercalation in aqueous medium and according to them, the binding energy of lithium ions in these materials is equal to the cell voltage and is good measure of their stability, where higher cell potential resembles to more tightly bound lithium ion.\[^{61}\] The binding energies of LiOH and solid Li\(_2\)O which are the products of the reaction of lithium intercalated materials with H\(_2\)O and O\(_2\) are -2.22 and -2.91 eV (vs lithium atom). Hence, materials with voltage greater than 3.1 vs Li should be thermodynamically stable with respect to the formation of LiOH or Li\(_2\)O.

Micheal Gratzel et. al\[^{62}\] related the voltage \(V(x)\) of Li/Li\(_{(x)}\)(host) cell in the form of equation 2-3.

**Equation 2-3** \(V(x) = 3.885 - 0.118pH(V)\)

This expression is very crucial for the selection for suitable electrode material so that lithium ions can stably intercalate and de-intercalate from the material. The redox potential of these lithium intercalated material can vary based on the pH of the electrolyte and hence it is very crucial to use the knowledge from the pourbaix diagram to select the proper electrode material, the electrolyte and lithium concentration for electrochemical lithium insertion/de-insertion in aqueous electrolytes.

**2.1.3 Kinetics of ARLB**

The basic assumption behind the lithium ion kinetic studies is that lithium diffusion into the electrode is the rate controlling step for the electrochemical lithium insertion process.
Change of pH could shift the redox peaks of the material which might lead to shift in overall voltage that a cell might achieve, such anomalies can result in degradation in electrochemical performance. If the electrode material’s redox potential falls well within the oxidation and reduction potential of water, one can avoid the release of hydrogen and oxygen and hence prevent the pH change of the electrolyte.

Lee et.al proposed the lithium transport mechanism within the electrode via the change in cell-impedance. Unlike the organic electrolyte based lithium ion batteries which has an AC impedance spectrum with two semicircles, only one semicircle is observed in the case of an ARLB system. Absence of a surface film formation in aqueous electrolyte lowers the charge transfer resistance by an order of magnitude in comparison to the organic electrolyte. As there is no surface layer, charge transfer happens across the electrode/electrolyte interface easily, without any resistance from any surface layer. Fast charge transfer kinetics and high conductivity of water medium are the major reasons for the reduced $R_{cell}$ in ARLBs.

Nakayama et.al calculated the relation between the activation energy and the interfacial lithium ion transfer resistance at the LMO thin film electrode/electrolyte(aq. Solution) as per the equation 2-4,

**Equation 2-4** \[ \frac{T}{R_{ct}} = A \exp\left(\frac{-E_a}{RT}\right) \]

Where, ($E_a = \text{the activation energy}, T = \text{the absolute temperature}, R = \text{gas constant}, R_{ct} = \text{the interfacial lithium-ion transfer resistance}, A = \text{the pre-exponential factor}$)

$R_{ct}$ and $E_a$ for LiMn$_2$O$_4$ in organic electrolyte is found to be 400 $\Omega$ and 24kJ mol$^{-1}$, while it is 20 $\Omega$ and 50 kJ mol$^{-1}$ in the aqueous electrolyte respectively. As the activation energy required for the charge transfer across the electrolyte/electrode interface is lower in case of aqueous electrolyte, the rate capability in ARLB is very much enhanced.

One of the important finding is that an adsorption phenomenon occurs at the electrode surface. Charges adsorbs first to the electrode surface before getting into the bulk. This phenomena plays a crucial role in charge transfer kinetics.
2.1.4 Current status & issues in ARLBs

Current research on ARLBs are focused towards increasing the capacity, voltage window and cycle life of the battery by developing suitable electrode material and selecting suitable electrolyte to suit the overall battery architecture. There are many issues in ARLBs which are required to be solved for its potential use for EVs and wearable devices. The chemical/electrochemical processes of LIM(lithium intercalated materials) electrodes in aqueous solutions are much more complicated than those in the organic electrolytes. Reaction with water or oxygen, co-insertion of proton along with lithium ions, hydrogen or oxygen evolution and dissolution of electrode materials are the side reactions that are possible in an ARLB system.

Figure 2.2 gives the insertion voltages of common electrode materials that could potentially be used in ARLBs along with a detailed account of the evolution of hydrogen and oxygen w.r.t the change in pH. Oxygen evolution occurs at about 1.229V vs NHE, which further prevents Li deintercalation. Oxygen and hydrogen evolution varies with pH of the electrolyte.

![Figure 2-2 Pourbaix diagram of the potentials of the intercalation compounds and Stability limit of water as a function of pH](image)

Materials with a potential greater than 3.3V vs Li are basically stable as demonstrated from the above Figure. Anodes for ARLBs has their intercalation potential below 3.3 V vs Li. As ARLBs are primarily operated in air, it is vital to consider its stability in the presence of both H₂O and O₂.
Following is the reaction of lithium intercalated material (LIM) in the presence of oxygen and water:

\[ \text{LIM} + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \rightleftharpoons \text{Li}^+ + \text{OH}^- \]

The potential of a LIM, \( V(x) \) is given in the form of equation 2-5:

**Equation 2-5** \[ V(x) = -\frac{1}{e}(\mu_{\text{Li}}^{\text{int}}(x) - \mu_{\text{Li}}^0) \] \[ ^{[62]} \]

where \( \mu_{\text{Li}}^{\text{int}}(x) \) is the chemical potential of intercalated Li in LIM, \( \mu_{\text{Li}}^0 = (dG_{\text{Li}}^0 / dN) \) is the chemical potential of Li in Li metal and \( e \) is the magnitude of the electron charge.

The potential of a LIM, \( V(x) \), in equilibrium with \( \text{O}_2 \) and \( \text{H}_2\text{O} \) at a particular pH can be calculated with equation 2-6.

**Equation 2-6** \[ V(x) = 4.268 - 0.059 \text{pH} \ (\text{V}) \]

If, \( V(x) > 4.268 - 0.059 \text{pH} \ (\text{V}) \) no Li ion will de-intercalate and the material will be stable in alkaline solutions. As the pH decreases, the potential vs SHE for LIM drops.

Development of nanoelectrodes and different nano-morphologies are being considered as a potential option to solve most of the inherent problems with ARLB systems.

**Advantages:**

a) Better cycle life due to the ability to accommodate strain during lithium insertion/removal.
b) Higher charge/discharge rates due to better electrode/electrolyte contact area; and
c) Shorter path lengths for transport of electrons and lithium ions (permitting operation at higher power)

**Disadvantages:**

a) High surface area leaves to undesirable side reactions between the electrode and leading to self-discharge and poor cycle life.
b) Usually the synthesis methods are complex and hence simple one step method are required for it potential commercial scalability.

Hence, taking cues from these advantages and disadvantages, novel anode and cathode nanostructured materials are being developed.
So, the current research in ARLB is targeted towards solving the following issues:

- To reduce the dissolution of electrode materials in water, which causes rapid capacity fading and poor cycle life of the battery.
- Reduction of side reactions such as electrode–electrolyte reaction causing oxygen & hydrogen evolution and material degradation.
- Selecting a proper configuration of anode and cathode to match the rate capabilities of the overall system and to increase the voltage window. (for e.g. use of LiMn$_2$O$_4$ as cathode and TiO$_2$ nanotubes as anode has made possible the development of a 2V ARLB$^{[71]}$
- Selection of a suitable electrolyte with appropriate pH to raise the stability of ARLB and improving the cycle life thereby.
- Development of electrodes with various nano-morphologies to improve parameters like capacity retention, energy density & power density of ARLBs

2.1.5 Current status & issues in flexible rechargeable battery architectures

Form-factor of current devices are highly constrained by the design limitation of batteries which are either rectangular, coin-sized or cylindrical in geometry. Even with the superior volumetric efficiencies and compactness of current batteries, the design and flexibility has restricted them to fewer applications.

Hence, engineering better and unconventional battery designs is the key to inconspicuously accommodating them into devices and applications with vivid form factors. Some of the examples of such batteries are paper batteries, textile batteries, transparent batteries, thin and flexible batteries and microbatteries.$^{[26,72–79]}$ However, seamless assimilation of these batteries into electronic wearable devices and everyday objects remains a challenge. The advent of smart devices/objects has further generated interest in self-powered electronics$^{[75,80]}$ with integrated storage like a combination of energy harvester with batteries and supercapacitors. Such energy conversion and storage hybrids will require batteries that can be integrated directly into the object or surface of choice as well as with energy harvesting components. Printing has enabled
large-area fabrication of electronic devices (circuits, photovoltaics and displays.) on virtually any type of substrate[81].

Fully printable ARLB that can be fabricated and integrated simultaneously with household objects and commonly used materials would create a paradigm shift in the way devices are used now. Energy harvesting components like the photovoltaics, piezoelectric transducers, induction systems can then be easily integrated with these batteries to provide a standalone energy sourcing and storage capability.[81] We could easily integrate this technology into commonly used commodities like clothes, shoes, doors, window panes, walls and body part of vehicles thereby paving way for developing new, form factor independent flexible modules for advanced electronic technologies.

2.2 Materials in ARLB

Many potential materials studied for lithium ion batteries cannot be directly adopted in aqueous rechargeable lithium ion batteries due to inherent limitation of the aqueous electrolyte which decomposes at about 1.23V thereby limiting the cell potential. The decomposition potential of the water is not only limited by the redox potential of the electrode materials but also because of the pH of the electrolyte. The pH of the electrolyte depends on the type of salt which is dissolved in the water. Acidic pH of the electrolyte causes the water decomposition at a lower negative causing the release of hydrogen gas while, basic pH of the electrolyte causes the water to oxidize it at lower positive voltage causing the release of oxygen much ahead of the standard decomposition potential of water which is at 1.23V.[18]
Due to the inherent limitation of the aqueous electrolyte’s decomposition potential, only those materials which has its redox potentials occurring between -1.4V and 1.1V vs. SCE can be used in ARLB systems as anode and cathodes respectively. As per Figure 2.3 NVO or Na$_2$V$_6$O$_{16}$ has higher capacity and better voltage window compared to rest of the electrode materials currently used in ARLBs.

### 2.2.1 Anodes for ARLB

Unlike in lithium ion batteries, the reduction potential of water which results in the production of hydrogen at potentials below 1.5V vs. SCE restricts the electrode material that could be used as anodes in ARLBs. This inherent limitation posed by the reduction potential of water, has inspired in the careful selection and development of anode-type material whose redox potentials fall well within -1.5V to 0V vs. SCE. Some of the materials could have some of their redox reaction occurring beyond 0V in the cathodic region or very close to 0V vs. SCE. Such materials are also usually avoided while developing a full cell ARLB as the redox potential of anode equally affects the full cell voltage that can be attained in combination with an appropriate cathode. In a three-
electrode system, the full cell voltage is usually restricted by the reference electrode and the cell potential can never go beyond 1.2V, but the full cell is in a two-electrode configuration, the reference is set by the anode and hence with respect to the anode, the full cell potential can reach higher voltages like 1.9V to 2.4V. Table 2.1 presents some of the mostly commonly studied anodes materials for ARLB system. More detailed study of vanadium based compounds is listed in Table 2.3 as shown below

### Table 2.1 List of electrode materials commonly used as anodes in ARLB with their theoretical and practical capacities.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte Solution</th>
<th>Theoretical capacity (mAh g⁻¹)</th>
<th>Capacity in 1st cycle (mAh g⁻¹)</th>
<th>Capacity in n cycle (mAh g⁻¹)</th>
<th>Author and Reference no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₅V₃O₈</td>
<td>1M Li₂SO₄</td>
<td>381</td>
<td>40-45</td>
<td>10(400)</td>
<td>Kohler, J et.al and Zhao, M. et.al [14,77 ]</td>
</tr>
<tr>
<td>LiTi₂(PO₄)₃</td>
<td>5M LiNO₃</td>
<td>138</td>
<td>80</td>
<td>90(2)</td>
<td>Cui, Y. et.al, Wang, H. et.al and Luo, J. Y. et.al [78,16,79]</td>
</tr>
<tr>
<td>TiP₂O₇</td>
<td>5M LiNO₃</td>
<td>120.82</td>
<td>100</td>
<td>80(2)</td>
<td>Wang, H. et.al and Li, C. et.al [16,80]</td>
</tr>
<tr>
<td>TiO₂ nanotubes</td>
<td>3.5MLiCl/0.2</td>
<td>-</td>
<td>0.09mAh/cm²</td>
<td>-</td>
<td>Liu, S. et.al [65]</td>
</tr>
<tr>
<td></td>
<td>5M Li₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.1.1 Vanadium compounds as potential Anodes for ARLBs

The capacities of various oxide materials are being listed in Table 2.1. Among all the metal oxide materials, vanadium oxides have shown a very high theoretic capacity of above 400mAh\textsuperscript{−1}. Vanadium compounds are a good candidate for use in energy storage. General classification of most of the vanadium compounds studied by mineralogists are shown in Figure 2.4.\textsuperscript{[83,84]} The reason for it being, the wide redox potentials of the vanadium metals (V\textsuperscript{+1} to V\textsuperscript{+5}) which is interesting as it results in more number of electrons per redox change compared to other transition metals like Cobalt, copper, iron, manganese and Nickel. Different vanadium compounds have been studied for it application in various energy storage architectures like vanadium redox flow batteries, lithium ion batteries and super capacitors. \textit{V}_2\textit{O}_5 and LiV\textit{3}O\textit{8} have good chemical stability and presents with a unique safety characteristics that prevent oxygen release from its lattice compared to cobalt and nickel oxides as the V\textsuperscript{4+/3+} and V\textsuperscript{3+/2+} couples lie well above the O\textsuperscript{2−}: 2p band.\textsuperscript{[85]}

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>Capacity (mAh)</th>
<th>Voltage (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{V}_2\textit{O}_5</td>
<td>Sat.Li\textit{2}SO\textit{4}</td>
<td>120</td>
<td>52.5</td>
<td>Luo, J. Y. et al. [79]</td>
</tr>
<tr>
<td>\textit{Li}_2\textit{Mn}_4\textit{O}_9</td>
<td>6M LiNO\textit{3}</td>
<td>156</td>
<td>110</td>
<td>Wang, G. X. et al. [82]</td>
</tr>
<tr>
<td>\textit{Li}_4\textit{Mn}_5\textit{O}_12</td>
<td>6M LiNO\textit{3}</td>
<td>202</td>
<td>110</td>
<td>Wang, G. X. et al. [82]</td>
</tr>
</tbody>
</table>

\textit{VO}_2(B) - 100 - Corr, S. a. et al. and Zhang, M. [81,64]
2.2.1.2 Vanadium oxides: A background study

Various vanadium oxides like $V_2O_5$, $V_6O_{13}$, $V_6O_{16}$, $LiV_3O_8$ as cathode electrode have long been investigated as a potential 3V lithium ion battery.\textsuperscript{85} $V_2O_5$ is cheap, easy to synthesize and has a high energy density compared to other convention oxide materials. $V_2O_5$ is made of $VO_5$ square pyramids that share edges and corners. The apical V-O bond corresponds to a double bond that is much shorter than the other four bonds. Aside from these 2-D character, the structure of $V_2O_5$ can also be described as being distorted $VO_6$ octahedral. The very long V-O bond underlines the structural anisotropy of this material and the ability to insert guest species into the pervoskite kind of cavities.\textsuperscript{86} Lots of research has focused on improving the crystal structure of $V_2O_5$ for better Lithium ion intercalation so as to reach the theoretical capacity offered by it and also to improve the rate capabilities and cycling stability which is one of the main reason
posing as a roadblock for Vanadium based oxides to reach its full commercial potential as a better alternative for traditional battery electrode materials.

**Some of the most common methodologies/approaches followed are enlisted as below:**

- Synthesis and Drying process to obtain different physical forms of the V\textsubscript{2}O\textsubscript{5} powder (Xerogel and Aerogel)\textsuperscript{[87–92]}
- Various morphologies for enhanced Surface/bulk area ratio (Preferably nano or micro sizes of wires, belts, rods, tubes, entangled heterostructures)\textsuperscript{[36,81,84,91–94]}
- Carbon coating, conductive polymer coating, core/shell morphologies, long alkyl chain with amine group to enhance conductivity and achieve specific morphologies.\textsuperscript{[94]}
- Doping with transition and alkali metals which includes Cu, Zn, Fe, Co, Cr, Mg, Al, and also with oxides like TiO\textsubscript{2}, SnO\textsubscript{2} and SiO\textsubscript{2} \textsuperscript{[86,97–99]}
- Introduction of water, CO\textsubscript{2} and alkali ions into the layers of V\textsubscript{2}O\textsubscript{5}. \textsuperscript{[85,86,100]}

A perfect combination of the above approaches will help remove the shortcomings (capacity loss on long cycling, lower specific capacity compared to its theoretical capacity and poor rate capabilities) of Vanadium oxide materials, thereby, unleashing the full capability of vanadium oxide as a potential electrode for the development of next generation batteries.

V\textsubscript{2}O\textsubscript{5} is commonly synthesized by sol-gel process which via the precursor HVO\textsubscript{3}, which self-assembles into the V\textsubscript{2}O\textsubscript{5} hydrogels. These hydrogels of V\textsubscript{2}O\textsubscript{5} have pores which are usually filled with water that interconnects and make the bi-continuous solid network of V\textsubscript{2}O\textsubscript{5} chain.

The drying process which removes the water from these structures determine the type of solid that the vanadium pentoxide forms into. It can form into any of the following three types of solid amorphous vanadium pentoxide with the following surface area and specific capacity as shown in Table 2.2.
Table 2.2 Different forms of V\textsubscript{2}O\textsubscript{5}, its nominal surface area and specific capacity.

<table>
<thead>
<tr>
<th>No.</th>
<th>Type of V\textsubscript{2}O\textsubscript{5}</th>
<th>Nominal Surface area(m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>Specific Capacity(mAh\textsuperscript{-1}) at C/100 discharge rate</th>
<th>Author &amp; Reference no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xerogel</td>
<td>1-10</td>
<td>560</td>
<td>Owens, B.</td>
</tr>
<tr>
<td>2</td>
<td>Aerogel</td>
<td>350-450</td>
<td>560-780</td>
<td>B. et.al</td>
</tr>
<tr>
<td>3</td>
<td>Ambigels</td>
<td>100-300</td>
<td>410(2.9Li\textsuperscript{+})</td>
<td>[98,99]</td>
</tr>
</tbody>
</table>

In organic electrolyte the key factor that limits the performance of these Xerogel and Aerogel materials is their capacity dependability on the rate due to the diffusion limitations. These Xerogels of V\textsubscript{2}O\textsubscript{5} has like lamellar structure, with water occupying and enlarging the layers causing higher intercalation capacities. However moderate electrical conductivity (0.01-0.001 Scm\textsuperscript{-1}) of V\textsubscript{2}O\textsubscript{5} and lower diffusion coefficient of Lithium ions in the V\textsubscript{2}O\textsubscript{5} matrix(10\textsuperscript{-12} – 10\textsuperscript{-13} cm\textsuperscript{2}S\textsuperscript{-1}) limits the intercalation capacity and charge/discharge rate.[91,101,102]

Doping is a very common method to improve the rate capability and intercalation kinetics of the materials particularly, usually done at the precursor stage before the bi-continuous solid water filled interconnected porous structure is completely formed. Many metals like Cu, Co and Ce, interacts with the precursor to become vanadium bronzes with increased conductivities.[97,98,103] Specific capacity of adding metallic copper dopant is 170mAh\textsuperscript{-1} at 1C rate.[97]

LiV\textsubscript{3}O\textsubscript{8} is a pseudo-layered material formed by puckered sheets of V\textsubscript{3}O\textsubscript{8}\textsuperscript{-1} with the Li\textsuperscript{+} ion acts a pillar ion residing in the octahedral site. The typical capacity is about 200mAh\textsuperscript{-1} but in aqueous its capacity is usually less than 110mAh\textsuperscript{-1}.[14,104]

Particularly interesting is the introduction of water and other metal ions between the layers which allows their expansion which would allow more room and easy access for the intercalating ions thereby causing increased mobility (better rate) and enhanced distribution (long cycling and better reversible capacities) due to less stress on anyone part of the lattice triggering crystal collapse and eventual vanadium dissolution. The distance between the adjacent layers in V\textsubscript{2}O\textsubscript{5}.nH\textsubscript{2}O is 11.52Å compared to an interlayer distance of 4.56Å in orthorhombic V\textsubscript{2}O\textsubscript{5}.[105]

34
Table 2.3 Various vanadium oxide electrodes, its theoretical and practical capacities obtained in an ARLB system.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Theoretical Capacity (mAh g⁻¹)</th>
<th>Capacity in 1ˢᵗ cycle (mAh g⁻¹)</th>
<th>Capacity in n cycle(s) (mAh g⁻¹)</th>
<th>Author &amp; Reference no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₁.₁₆V₃O₈ Super Cell: Na₂.₃₂V₆O₁₆</td>
<td>176</td>
<td>152.42</td>
<td>112(100)</td>
<td>Vivek et.al [82]</td>
</tr>
<tr>
<td>Na₂V₆O₁₆.0.14H₂O</td>
<td>-</td>
<td>112</td>
<td>63.91(200)</td>
<td>Zhou, D. et.al [41]</td>
</tr>
<tr>
<td>VO₂ (B)</td>
<td>161</td>
<td>100</td>
<td>-</td>
<td>Zhang, M. and Corr, S. a. et.al [70,96]</td>
</tr>
<tr>
<td>LiₓV₃O₈</td>
<td>145</td>
<td>40-45</td>
<td>50(150)</td>
<td>Köhler, J. et.al [14]</td>
</tr>
<tr>
<td>Li₃V₆O₁₆</td>
<td>368.08</td>
<td>120</td>
<td>60(100)</td>
<td>Vivek et.al [106]</td>
</tr>
<tr>
<td>V₂O₅ Xerogel</td>
<td>75</td>
<td>69</td>
<td>61(100)</td>
<td>Stojković, I. et.al [88,89]</td>
</tr>
<tr>
<td>LiₓV₂O₅</td>
<td>75</td>
<td>80</td>
<td>5(40)</td>
<td>Wang, H. et.al [107]</td>
</tr>
</tbody>
</table>

Table 2.3 summarizes to-date, various vanadium oxides, their theoretical and practical capacities obtained in an ARLB system. Among various vanadium oxide compounds, it can be clearly seen that hexavanadates with the supercell structure present with more stable practical capacity and has a higher theoretical capacity which is a very good motivation to works towards the increment of their practical capacity to near theoretical values. Hence, further works in this thesis would focus on these hexavanadate bronzes or more commonly known as the hewettite group of mineral vanadium bronzes (Hewettites).
2.2.1.3 Introduction to heterostructures of hewettites

Evans & white in 1987 characterized and classified a group of minerals, referred to as “vanadium bronzes” and Hewettite is a member of this group. Figure 2.4, gives a general overview of the vanadium compounds especially vanadium bronzes.[83,84] Vanadium bronzes can be broadly classified as Hewettites, Straczekite and other vanadium bronzes. This division is made on the basis of the basic unit cell structure that builds these supercell structures. The description of hewettite was first given by Hillebrand et.al[108] as fibrous and lath-like crystal habit, deep red color, and tendency to lose or regain water according to conditions of temperature and humidity. On the basis of water content, the material phases came to be known as hewettite for nine water molecules and metahewettite for the dehydrated form i.e. three water molecules. Fibrous texture and softness of hewettites have always hampered its structural study. But, it is these same non-rigid, flexible, fibrous characteristics that makes it most desirable candidate for aqueous rechargeable lithium ion batteries. In this thesis, our major focus would be to study hewettite group of materials for its electrochemical property in aqueous electrolyte.

2.2.1.4 Structure of Hewettites

Scheme 2.2.a shows zigzag (V$_2$O$_6$)$_n$ double square pyramidal chain formed by lateral sharing of inclined octahedral chains joined by each VO$_6$ with a removal of one external oxygen atom. Scheme 2.2b, shows a complex chain which is a quadruple consisting of four single octahedral chains joined laterally by sharing inclined edges, forming a highly condensed (V$_4$O$_{12}$)$_n$ fibre. Both these chains are found as separate entities in two compounds NaVO$_3$.1.9H$_2$O which has the divanadate chain(V$_2$O$_6$)$_n$ and Synthetic Ag$_3$V$_4$O$_{12}$ having the tetravanadate chain(V$_4$O$_{12}$)$_n$.[84]
Scheme 2.2 Schematic step by step illustration on the Formation of a) $V_2O_6$ and b) $V_4O_{12}$

Figure 2-5 Crystal structure of Ca$\text{V}_6\text{O}_{16}$, $9\text{H}_2\text{O}$

Various vanadium bronzes as displayed in Figure 2.5 are formed depending on the manner in which these two complex chains of divanadate and tetravanadate join among themselves and/or with each other.

Hewettite ($V_6\text{O}_{16}$)$_n$ sheets in a crystallographic unit are formed by alternatively joining tetravanadate chains and divanadate chains laterally by sharing corners. (Figure 2.6). The V-O bonds in the distorted octahedra and square pyramids range in length from 1.59Å to 2.36 Å; the vanadium atoms in the latter also approach a sixth oxygen atom
in an adjacent chain at a distance of 2.86 Å, forming a weak bond. The sheets are arranged to form a monoclinic structure with a space-group symmetry of P2₁/m and characteristic dimensions within the layer of a=12.0 Å and b=3.6 Å (fiber axis). The third dimension and β angle depends on the nature and amount of interlayer cations and water molecules. [84]

### 2.2.1.5 Methodology for synthesis of Heterostructures of hewettites

Hewettites were mostly naturally obtained in 1980s and been studied by mineralogists after basic physical purification. Most of the times, these hewettites have trace impurities of other elements like sodium and magnesium.

Below table enlists all the reported synthesis methods for hewettite nano-architectures. Most of the studies for these nano-structures has been performed for its room temperature ferromagnetic semi-conductor properties and application.

**Table 2.4** Reported synthesis methodology for various hewettite heterostructures.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Li₃V₆O₁₆</td>
<td>Rods</td>
<td>CH₃COOL  i. 2H₂O with V₂O₅</td>
<td>Hydrothermal</td>
<td>48h</td>
<td>Vivek et.al [106]</td>
</tr>
<tr>
<td>2.</td>
<td>Na₁.₁₆V₃O₈ .xH₂O</td>
<td>Nanobeltts</td>
<td>NaOH + V₂O₅</td>
<td>Hydrothermal</td>
<td>48h</td>
<td>Vivek et.al [82]</td>
</tr>
<tr>
<td>3.</td>
<td>Na₂V₆O₁₆. 0.14H₂O</td>
<td>Nanowires</td>
<td>NaOH + V₂O₅</td>
<td>Hydrothermal</td>
<td>48h</td>
<td>D.Zhou et.al [41]</td>
</tr>
<tr>
<td>4.</td>
<td>Na₂V₆O₁₆. nH₂O</td>
<td>Nanowires</td>
<td>V₂O₅.nH₂ O nanoribbon s + NaOH +H₂O₂ (pH</td>
<td>Hydrothermal</td>
<td>24h</td>
<td>W.Avanasi Jr. et.al [43]</td>
</tr>
<tr>
<td>No.</td>
<td>Formula</td>
<td>Product</td>
<td>Preparation Method</td>
<td>Time</td>
<td>Authors</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>---------</td>
<td>--------------------</td>
<td>------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Na$_2$V$<em>6$O$</em>{16.3}$H$_2$O</td>
<td>Single crystal nanobelts</td>
<td>V$_2$O$_5$ + NaF</td>
<td>Hydrothermal</td>
<td>24h</td>
<td>Jiaguo Yu et al. [42]</td>
</tr>
<tr>
<td>6.</td>
<td>Na$_2$V$<em>6$O$</em>{16.3}$H$_2$O</td>
<td>Nanorings</td>
<td>Na$_2$CO$_3$ + NH$_4$VO$_3$</td>
<td>Multistep (Sol-gel + Hydrothermal)</td>
<td>24hr</td>
<td>Yan Xue et al. [45]</td>
</tr>
<tr>
<td>7.</td>
<td>K$_2$V$<em>6$O$</em>{16.1.5}$H$_2$O</td>
<td>Superlong Nanobelts</td>
<td>K$_3$VO$_4$ + HCl</td>
<td>Hydrothermal</td>
<td>24h</td>
<td>Liangfei Bai et al.</td>
</tr>
<tr>
<td>8.</td>
<td>Ca$_{0.5}$V$_3$O$_8$</td>
<td>Nanorods</td>
<td>Li$_{1.1}$V$_3$O$_8$ with Ca(NO$_3$)$_2$$\cdot$$n$H$_2$O</td>
<td>Aqueous based solution</td>
<td>~15-20 hours</td>
<td>S Jouanneau, et al. [109]</td>
</tr>
<tr>
<td>9.</td>
<td>CaV$<em>6$O$</em>{16.3}$H$_2$O</td>
<td>Nanoribbons</td>
<td>Metavanadates with Sodium dodecyl sulphonate SDS</td>
<td>Hydrothermal</td>
<td>-</td>
<td>Lingfen Kong et al. [110]</td>
</tr>
<tr>
<td>10.</td>
<td>CaV$<em>6$O$</em>{16}$</td>
<td>Flakes</td>
<td>V$_2$O$_5$(0.03) + Ca(OH)$_2$(0.02)</td>
<td>Hydrothermal</td>
<td>10 days</td>
<td>S Jouanneau, et al. [111]</td>
</tr>
<tr>
<td>11.</td>
<td>CaV$<em>6$O$</em>{16.3}$H$_2$O</td>
<td>Compressed rods</td>
<td>Calacium orthovanadate (obtained)</td>
<td>Hydrolysis</td>
<td>&gt;24 hours</td>
<td>LI Lanjie, et al. [112]</td>
</tr>
</tbody>
</table>
2.2.1 Cathodes for ARLB

Most of the commercial lithium ion batteries used nowadays use LiCoO$_2$ and LiFePO$_4$. LiMn$_2$O$_4$ batteries are the third most popular batteries explored nowadays for lots of commercial application. Table 2.5 summarizes most of the popular cathode materials used in the ARLB system along with their theoretical and practical capacities.
**Table 2.5** List of electrode materials commonly used as cathodes in ARLB with their theoretical and practical capacities

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte Solution</th>
<th>Theoretical capacity (mAh g⁻¹)</th>
<th>Capacity in 1st cycle (mAh g⁻¹)</th>
<th>Capacity in n cycle(s) (mAh g⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>5M LiNO₃</td>
<td>140</td>
<td>112</td>
<td>105(90)</td>
<td>Wang, X. et.al [113]</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>1M Li₂SO₄</td>
<td>148</td>
<td>84.6</td>
<td>50(1000)</td>
<td>Qu, Q. et. al and Yuan, G. et.al [114,115]</td>
</tr>
<tr>
<td>LiMnO₂</td>
<td>1 M Li₂SO₄</td>
<td>140</td>
<td>62</td>
<td>50(150)</td>
<td>Wu, M. S. et.al [116]</td>
</tr>
<tr>
<td>LiV₃O₈</td>
<td>1M Li₂SO₄</td>
<td>381</td>
<td>40-45</td>
<td>10(400)</td>
<td>Köhler, J. et.al [14]</td>
</tr>
</tbody>
</table>


| LiFePO\textsubscript{4} | 1M LiCl | 120 | 100 | 50(100) | Luo, J.-Y. et al [18] |

**2.2.2.1 LiMn\textsubscript{2}O\textsubscript{4} micro-architectures**

LiMn\textsubscript{2}O\textsubscript{4} spinel structure was first proposed by Mike Thackery.\textsuperscript{[46,47]} Its structure closely resembles to that of \(\alpha\)-NaFeO\textsubscript{2} layered structure with a cubic closed packing of oxygen anions. LiMn\textsubscript{2}O\textsubscript{4} belongs to the space group of Fd3m with manganese cations occupying one half of the octahedral sites(16d) and lithium ions occupying one eighth of the tetrahedral chains. The edge sharing octahedral Mn\textsubscript{2}O\textsubscript{4} framework is stable and possesses a series of intersecting tunnel formed by the face-sharing of tetrahedral lithium sites(8a) and empty octahedral sites(16c). Such a structure enables three dimensional diffusion of lithium ions into its three dimensional interstitial space formed by the face sharing of tetrahedral(8a and 48f) and octahedral(16c).

When LiMn\textsubscript{2}O\textsubscript{4} is used as a purely cathode material, lithium intercalation happens into the 8a tetrahedral sites of LiMn\textsubscript{2}O\textsubscript{4} at around \(-0.8\) to \(-0.9\) V vs. SCE and the extraction of lithium happens with concomitant oxidation of Manganese at \(-1.0\) V.\textsuperscript{[46]} On charging, Manganese gets oxidized from +3.5 to +4. After the removal of one half of the lithium ions, remaining lithium atoms orders itself at the tetrahedral sites. In this way, the cubic structure is retained as the unit cell contracts. Volume changes in this case are isotropic and hence, it doesn’t affect the structural stability during reversible insertion/extraction of lithium ions.

As a potential anode material, LiMn\textsubscript{2}O\textsubscript{4} shows redox reactions below 0V at around \(-0.2\) V to \(-0.4\) V vs NHE. This leads to Manganese to reduce from +3.5 to +3, which further leads to disproportionation reaction leading to +2 oxidation state of manganese which has increased dissolution into the electrolyte when compared to the Mn+4 oxidation state. Also, lithium insertion/extraction in the anodic voltage range results in phase transformation of LiMn\textsubscript{2}O\textsubscript{4} from cubic to tetrahedral which also results in Jahn tellar effect due to the 6.5% volume change in the unit cell due to the phase
transformation. These effects result in structural stress leading to breakdown and also increased manganese dissolution into the electrolyte which leads to serious capacity fading and hence impacts the performance during long electrochemical cycling of the material. \[50\]

Schlorb et.al\[117\] and Vivier et.al\[118\] reported proton insertion into of LiMn$_2$O$_4$ when cycled in KOH and Borate solution medium respectively, while Jayalakshmi et.al\[119\] reported dual cation insertion and de-insertion into LiMn$_2$O$_4$ using aqueous solution of LiCl, NH$_4$Cl and KCl. It was found that presence of K$^+$ and NH$_4^+$ promotes proton insertion/extraction in comparison to Li$^+$. They also for the first time have shown potassium ion insertion into the of LiMn$_2$O$_4$ framework. Hence in electrolytes with only lithium salts, the overall capacity contributions can be due to both lithium and proton dual insertion. It is difficult to determine the exact quantity of proton inserted and the capacity contribution by simple electrochemical testing methods.

When cycled between 0 to 1V vs SCE, LiMn$_2$O$_4$ should cycle well with minimal capacity decay on long cycling, but in some electrolyte with an acidic pH, there will be overlap of hydrogen evolution peak with the redox potential peaks which can cause side reaction leading to manganese dissolution. Apart from that the other causes of capacity fading in LiMn$_2$O$_4$ reported are formation of two cubic phases, loss of crystallinity and development of micro-strain. All these results in structural instability and volume changes and general solution to develop non-stoichiometric spinel or doping of alternative metal ions has not be completely successful due to the compromise in capacity and hence the only prospect of improvement that is envisioned is reduction in particle size along with engineering new nano-architectures that can handle structural stresses during lithium insertion and extraction well along with maintenance of maximum achievable capacity.

2.2.2.2 Structure of LiMn$_2$O$_4$
In LiMn$_2$O$_4$, as seen in Figure 2.6, Li$^+$ cation occupies the tetrahedral sites while Manganese ions occupy the octahedral sites in the cubic close packed arrangement of oxygen. During initial stages of charging, lithium from one 8a site moves to another 8a site through an octahedral 16c site. Even after the lithium is de-intercalated at around ~0.9V, the structure continues to maintain its cubic symmetry and the process is reversible even during discharge, thereby providing stable capacity. The edge sharing arrangement of MnO$_6$ octahedra forms the Mn$_2$O$_4$ array with three dimensional channels for lithium transport, similarly, V$_6$O$_{16}$ is formed by sharing corners laterally joining V$_2$O$_6$ and V$_4$O$_{12}$.

**Methodology for synthesis of LiMn$_2$O$_4$**

Table 2.6 compiles most of the different methodologies used for the synthesis of different LiMn$_2$O$_4$ morphology and their electrochemical performance in lithium ion batteries (LIBs) along with the possible scientific reasoning for its specific electrochemical behavior.
Table 2.6 Synthesis methodology for various LiMn$_2$O$_4$ morphologies along with their electrochemical performance outcomes

<table>
<thead>
<tr>
<th>No.</th>
<th>LiMn$_2$O$_4$ Morphology (size)</th>
<th>Technique/synthesis method</th>
<th>Electrochemical performance (in general LIBs)</th>
<th>Author &amp;/or Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nanochain (beads: 100nm in dia)</td>
<td>Starch-assisted Sol-gel</td>
<td>Better rate capability and cycling stability.</td>
<td>W. Tang et.al [120]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Interconnected nanocrystalline morphology, facilitated faster lithium ion transport</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Spheres (10-nm)</td>
<td>Ultrasonic spray pyrolysis</td>
<td>No capacity fading at 3V region for 50 cycles.</td>
<td>Park et.al [121]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sustains volume changes by inducing phase transitions to occur in random directions</td>
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</tr>
<tr>
<td>3.</td>
<td>nanoparticles</td>
<td>Flame spray pyrolysis</td>
<td>Non-aggregation and hence better performance during cycling</td>
<td>Patey et.al [122]</td>
</tr>
<tr>
<td>4.</td>
<td>1-D nanorods</td>
<td>Hydrothermal using 1-D MnO₂ nanostructures as template</td>
<td>Large surface-to-volume ration allows better material-electrolyte contact, efficient 1-D transport of electrons and superficial strain slackening during cycling</td>
<td>Tang et.al, Yang et.al and Luo et.al [123–125]</td>
</tr>
<tr>
<td>5.</td>
<td>1-D nanowires</td>
<td>Hydrothermal using 1-D Na₀.₄₄MnO₂ nanowires &amp; α-MnO₂ nanowires as self-template</td>
<td>Excellent rate capability and cycling stability. Reduced diffusion lengths of both lithium and electrons</td>
<td>Honso et.al, Zhou et.al [126,127]</td>
</tr>
<tr>
<td>6.</td>
<td>1-D nanotubes</td>
<td>MnO₂ nanotubes as sel-template assisted growth</td>
<td>Poor cycling stability and rate capabilities compared to nanowires due to</td>
<td>Ding et.al [128]</td>
</tr>
<tr>
<td></td>
<td>Random heterostructures</td>
<td>Hydrothermal (complex and requires many reactants)</td>
<td>Requires calcination at higher temperature to counter the oxygen-deficiency.</td>
<td>Wu et.al, Liddle et.al and Jiang et.al [129–131]</td>
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</tr>
<tr>
<td>7.</td>
<td>Nanoparticles(50-100nm) and porous structure</td>
<td>One-pot resorcinol-formaldehyde route</td>
<td>Better cycling due to reduced Mn dissolution and stabilized surface</td>
<td>Shaju et.al and Chen et.al [132,133]</td>
</tr>
<tr>
<td>8.</td>
<td>2-D sheets</td>
<td>Sol-gel using MnO₂ nanosheets with solution of diethyl ether and lithium methide</td>
<td>Higher discharge capacity in comparison with LiMn₂O₄ powders made with solid state synthesis due to nanoporous structure, high crystallinity and exposed {1,1,1} facets that improved</td>
<td>Sun et.al [134]</td>
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<tr>
<td><strong>10.</strong></td>
<td>3-D porous microspheres (50-200nm)</td>
<td>$\alpha$-MnO$_2$ urchin or biomimetic nanostructures of MnCO$_3$ as self-template assisted synthesis. Tunning between spherical and rhombohedral can be done using different agar contents.</td>
<td>Stable at high current cycling</td>
<td>Xi. Et.al and Uchiyama et.al $^{[135,136]}$</td>
</tr>
<tr>
<td><strong>11.</strong></td>
<td>Nanorods, nanothorn microspheres and hollow nanospheres</td>
<td>Simple sol-gel growth Using corresponding MnO$_2$ as templates</td>
<td>LiMn$_2$O$_4$ hollow nanospheres has better interface areas between electrode and electrolyte, better particle size and higher inter-space for lithium transport into the bulk</td>
<td>Luo et.al $^{[125]}$</td>
</tr>
</tbody>
</table>
At 3.0V vs. Li, Jahn-Teller distortion occurs within the LiMn$_2$O$_4$ crystal which leads to a phase transition in LiMn$_2$O$_4$ from cubic to tetrahedral results in development of stress within structure due to a volume increase of approximately 6.6%, which leads to a structural collapse during lithium insertion and extraction during galvanic cycling. At 3V vs. Li, disproportionation reaction also occurs, which increases manganese dissolution and hence capacity fading during the charge/discharge.

As LiMn$_2$O$_4$ is intended to be used as a cathode material in ARLBs, effects of Jahn-Teller distortion will be minimal as the material will be cycled only in the 4V vs. Li or 1.1V vs. SCE region.$^{[46]}$ Here, manganese dissolution can happen if oxygen evolution happens during the galvanic cycling due to improper electrode-electrolyte side-reactions. One of the reasons for this is choice of right electrolyte and its optimum pH.$^{[18]}$ Effect of counter-ion in rate capabilities and performance in such system is also vital which will studied in detail in this thesis.

### 2.3 Fundamental studies on charge storage mechanism and lithium intercalation

Even-though vanadium oxides and their bronzes provide with very high theoretical capacities, actual practical capacities obtained from them is very low <10-30% of their theoretical capacities in ARLB systems. Various materials engineering techniques like nano-designing of various morphologies, carbon coating or metal-ion doping has helped improve the capacities in these vanadium compounds during the initial few charge/discharge cycles but the capacity falls rapidly thereafter, for the rest of electrochemical cycling. It is assumed that vanadium dissolution and structural collapse are the major reasons for such behaviour. But the real mechanism by which the structural breakdown is initiated during the lithium intercalation/de-intercalation and the electrochemical reactions that leads to vanadium dissolution into the electrolyte is unknown.

It is the electrode surface that comes in contact first with the electrolyte and it is the region where the electrochemical reaction begin and the charge accumulation process begins. Even, the oxidation and reduction process of water occurs at the surface leading to the erosion of material and its eventual dissolution. X-ray photoelectron spectroscopy
(XPS) is an interesting study that can give an idea of the possible electrochemical reactions occurring at the surface.

Very few studies in the ARLB systems have employed XPS to study the degradation of capacity in vanadium compounds. This works uses XPS to under the mechanism by which lithium intercalation causes irreversible capacity losses in calcium meta-hewettite during the electrochemical cycling and how addition of an additive like TiO$_2$ influences the volumetric stress caused during lithium insertion and extraction upon long cycling.

Oxygen-deficient vacancies help certain compounds in exhibiting room temperature ferromagnetic semiconductor type properties but it can also help in electrochemical redox reaction to occur even in compounds with vanadium at its maximum oxidation state. XPS studies on potassium hexavanadates has been performed to understand how such oxygen deficient vacancies are caused and how it could have helped in its electrochemical performance.

Materials with open layered structure could present an avenue for co-insertion of proton along with lithium ions, but the chances of this is highly reduced when the pH of the solution is neutral and the electrode material is operated well within the redox potential of water. Oxygen evolution at 1.23V vs SHE could cause side reaction along with rapid proton insertion within the material thereby providing with very high capacity and a flat charge/discharge plateau at $\approx$1.23V vs SHE but this could also cause volumetric stress within the crystal and hence could result in collapse of the structure and thereby rapid capacity fading during subsequent cycling.

In some case, it could also increase the pH of the solution causing a shift in the redox potential of the material and hence the charge/discharge potential which can cause serious detrimental effect during the electrochemical cycling with variable peak voltage at every cycle. In this thesis all the materials have undergone electrochemical testing in a neutral pH electrolyte and well within the redox potential of water, thereby minimizing any chances of proton insertion. Hence one can avoid any charge contribution due to proton insertion.

As discussed in section 2.1.2, absence of a surface film formation in aqueous electrolyte lowers the charge transfer resistance by an order of magnitude in comparison to the organic electrolyte. As the conductivity of water is higher than organic electrolyte it does help in presenting the ions at the electrode surface i.e. at the electrolyte//electrode border easily, and if the material allows insertion of the lithium ions into the bulk of it.
i.e. into the interstitial sites or within the interlayer and provides with enough energy to hold them within those sites, it will present with a higher energy density but if the material allows slower insertion into the bulk but faster accumulation of charge at the surface, it will present with higher power density and lower energy density. The simplest method to study the mechanism by which charge is stored in a material is by doing a voltage sweep cyclic voltammetric experiment at various scan rates and then using the Randles-Sercik equation to determine the contribution of individual charge storage mechanism i.e. bulk storage and surface capacitance.

Charge Storage mechanism by Randles-Sercik equation\[^{[137]}\]:

The Randles-Sevcik equation describes the effect of scan rate on the peak current in cyclic voltammetry.

Cyclic voltammetry can be used to study the relation between current and scan rate as given by equations 2-7 and 2-8.

Equation 2-7  \[ i = \frac{dV}{dt} * C_\phi \]

Equation 2-8  \[ i = 0.4958nFAC(D\alpha nF\nu/RT)^{1/2} \]

where \(C_\phi\) is surface capacitance, \(\nu\) is scan rate, \(n\) is the number of electrons, \(F\) is the Faraday constant, \(A\) is the electrode area, \(c\) is the concentration of \(\text{Li}^+\), \(D\) is the diffusion coefficient, \(\alpha\) is the transfer coefficient, \(R\) is the gas constant and \(T\) is the temperature. In equation 2-7, the current is linear with the scan rate which describes the capacitive current due to the surface redox reactions whereas, while equation 2-8 describes current due to normal diffusion limited faradaic \(\text{Li}^+\) insertion process where the current follows a linear relationship with the square root of scan rate.

Therefore, by combining equations 2-7 and 2-8, we get equation 2-9.

Equation 2-9  \[ i(V) = k_1\nu + k_2\nu^{1/2} \]

where, \(k_1\nu\) = surface capacitance, \(k_2\nu^{1/2}\) = intercalation capacity

Hence, by determining the slope (\(k_1\)) and intercept (\(k_2\)), one can quantify, at specific peak potentials, the fraction of the current due to each of these contributions and can
also calculate the diffusion coefficient of Li\(^+\) for the material during the charge / discharge process.

### 2.4 Future challenges & Opportunity

Despite various efforts to develop an alternative safer energy storage in comparison to lithium ion batteries, it has not been entirely successful. ARLBs provides an efficient viable safer alternative to lithium ion batteries. Aqueous offer various benefits like safety, high conductivity but has the problem of very small voltage window of oxidation and reduction i.e. -1.2 to 1.23V vs SHE, which limits the overall cell potential of am ARLB system. Various efforts to develop high voltage, high capacity and cycling-stable electrodes are in progress.

Out of them vanadium compounds provides the highest potential as a viable anode material for ARLBs and lithium manganese oxide spinel as a cathode for the ARLBs. Strategies to push the capacity of these materials to their near theoretically has been carried out for long and this thesis focuses on some of those efforts and studies the inherent mechanism behind their electrochemical behaviour and uses them to develop a complete ARLB system using hewettite compound as anode and lithium manganese heterostructures as the cathode.

Charge storage mechanisms’ study of the various hexavanadates with different alkali and alkali earth metal cation as the pillar ions were performed. Understanding the charge storage mechanism within a material can help one design electrodes that can cater the needs of a particular application. Various factors can influence such behaviour within a material like surface area to volume ratio, morphology, crystal structure, current density and the concentration of lithium ions within the electrolyte. Understanding the electrochemical and structural changes occurring during the cycling with XPS will help in developing approaches that would prevent irreversible capacity loss during cycling. Such studies and analytical techniques may be used to provide insights into the mechanism of lithium ion storage within such ARLB systems that can help engineer various electrode chemistries and designs approaches towards the development of next generation materials for an aqueous rechargeable energy storage system with better cycle life, high rate capability, higher voltage and superior safety.
Further, such ARLB systems are used in applications where these systems are combined with energy harvesting sources and with an intelligent IC that monitors the health and prolongs the life cycle of these ARLBs by power management approaches by optimizing the usage with intelligent feedback.
Chapter 3  Methods & Materials

Chapter 3 starts with the details of different methods used to synthesize various vanadium bronzes and different morphologies of lithium manganese oxides to be used as anode and cathode respectively in aqueous rechargeable lithium ion battery. Further, various characterization methods and techniques used to study the physical, chemical, structural, thermal and electrochemical properties of these materials are discussed in detail.
3.1 Material Synthesis

This section deals with the various synthesis approach used to synthesize the hewettites and lithium manganese oxides to be used as electrode materials in ARLB system for this thesis.

3.1.1 Hydrothermal

Hydrothermal processes are the techniques used to crystallize chemical compounds at high vapour pressures and high temperatures in an aqueous solution.

**Procedure:**

It is a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is executed in an apparatus consisting of a steel pressure vessel called autoclave, in which a precursor is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the precursor and the cooler end causes seeds to take additional growth.

**Hydrothermal synthesis has several advantages over conventional synthetic methods such as:**

1. Compounds with elements in oxidation states that are difficult to attain, especially important for transition metal compounds, can be obtained in closed systems by hydrothermal synthesis.
2. The product is produced in one step; it is very pure, since the only other reaction product is oxygen, and it forms uniform crystals.
3. This method can produce crystalline phases that are not stable at the melting point. It can also synthesize materials that have a high vapour pressure near their melting points.
4. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition.

Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.
Thus considering the unique advantages offered by this method, like nano-architectures and crystallinity, hydrothermal synthesis has been used to produce \( \text{Na}_2\text{V}_6\text{O}_{16} \) and \( \text{K}_2\text{V}_6\text{O}_{16} \). This study reports the synthesis of a belt-type morphology for \( \text{Na}_2\text{V}_6\text{O}_{16} \) and \( \text{K}_2\text{V}_6\text{O}_{16} \). A comparative study has been reported between the half-cell performances of the \( \text{Na}_2\text{V}_6\text{O}_{16} \) and \( \text{K}_2\text{V}_6\text{O}_{16} \) to identify the best performing material to be used as a potential anode material in combination with different morphologies of \( \text{LiMn}_2\text{O}_4 \) cathode in a full ARLB system.

![Scheme 3.1 Schematic illustration of the synthesis of alkali and alkali-earth metal ion hexavanadates](image)

### 3.1.1.1. Preparation of 2-dimensional (\( \text{Na}_2\text{V}_6\text{O}_{16} \cdot 0.14\text{H}_2\text{O} \)) NVO belts

Analytically-pure vanadium pentoxide (\( \text{V}_2\text{O}_5 \), 98%. Sigma Aldrich) and sodium hydroxide (\( \text{NaOH} \), Sigma Aldrich) was used as received. 0.01 moles \( \text{NaOH} \) was mixed with 0.01 moles of \( \text{V}_2\text{O}_5 \) in deionized (DI) water and stirred overnight to obtain an orange brown solution which was transferred to a 50ml Teflon-lined stainless steel autoclave and heated at 180°C for 48 h. Resulting precipitate mixture was filtered, washed, and dried at 80°C for 4 h to obtain the as-synthesized \( \text{Na}_2\text{V}_6\text{O}_{16} \) powder (NVO). To study the effect of heat-treatment on the structural and electrochemical properties of NVO, further heat treatment was carried out for 2 h at 200°C, 300°C and
400°C and the respective samples are denoted as NVO-200, NVO-300 and NVO-400 respectively.

Following sequential reactions occur when NaOH and V₂O₅ are mixed and autoclaved to yield Na₂V₆O₁₆ hydrothermally: Na⁺ inserts into the V₃O₈⁻ layers forming the Na₂V₆O₁₆.⁴³

\[
\begin{align*}
V₂O₅ + 2 NaOH & = 2 VO₃Na + H₂O \\
VO₃Na + V₂O₅ & = V₃O₈Na \\
2V₃O₈Na + NaOH & = Na₂V₆O₁₆ + Na⁺ + OH⁻ + H₂O(excess)
\end{align*}
\]

ΔH\text{calculated} for the reaction is -2.659 eV (-257 kJ mol\(^{-1}\))

### 3.1.1.2 Preparation of 1-D (K₂V₆O₁₆) KVO fibers

0.01 moles of KOH was dissolved in 100 ml of deionized water along with 0.01 moles of V₂O₅. When all chemical completely dissolved, 10 ml of 30 percent hydrogen peroxide was added into the above solution (till pH : 9) and neutralized(pH:7) with 1M HCl. During this process, the color of the solution changed from bisque, orange, sepia to brown. Then, the solution is kept at 100°C for 24 hours till the entire water is evaporated. Finally, the brown powder is filtered and dried at 80°C to remove any surface water on the sample.

We expect that the formation of KVO occur in these steps leading to the insertion of K⁺ into the V₃O₈⁻ puckered layers forming KVOₓH₂O

\[
\begin{align*}
V₂O₅ + 2KOH & = 2VO₃K + H₂O \\
VO₃K + V₂O₅ & = V₃O₈K \\
2V₃O₈K + KOH & = K₂V₆O₈ₓH₂O + K⁺ + OH⁻ + H₂O(excess)
\end{align*}
\]

### 3.1.2 Sol-gel

Sol-gel is one of the most commonly used technique to prepare various electrode materials for lithium ion batteries. Preparation of various oxide is easily achieved by this technique.
This method when properly optimized could also result in various nano-architectures. This method can be performed in a water medium or other medium like alcohol, acetone or any organic liquids.

Li$_3$V$_6$O$_{16}$, Na$_2$V$_6$O$_{16}$, 0.14H$_2$O, K$_2$V$_6$O$_{16}$, CaV$_6$O$_{16}$,7H$_2$O and SrV$_6$O$_{16}$ were synthesized in a simple single step sol-gel synthesis. Analytically-pure vanadium pentoxide(V$_2$O$_5$, 98% Sigma Aldrich) and lithium acetate(CH$_3$COOLi.2H$_2$O, Sigma Aldrich) or sodium hydroxide (NaOH, Sigma Aldrich) or potassium hydroxide(KOH, sigma Aldrich) or calcium hydroxide (Ca(OH)$_2$, Sigma Aldrich) or Strontium hydroxide(Sr(OH)$_2$, Sigma Aldrich) was used as received.

Quantities in which the precursors were added is as follows:

**Table 3.1** Precursors and their concentration for the synthesis of hewettites

<table>
<thead>
<tr>
<th>Materials</th>
<th>Main salt(moles)</th>
<th>Reacting chemical(moles)</th>
<th>After dissolution H$_2$O$_2$ added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$V$<em>6$O$</em>{16}$</td>
<td>V$_2$O$_5$(0.01)</td>
<td>CH$_3$COOLi.2H$_2$O (0.025)</td>
<td>10ml 30%</td>
</tr>
<tr>
<td>Na$_2$V$<em>6$O$</em>{16}$</td>
<td>V$_2$O$_5$(0.01)</td>
<td>NaOH(0.01)</td>
<td>10ml 30%</td>
</tr>
<tr>
<td>K$_2$V$<em>6$O$</em>{16}$</td>
<td>V$_2$O$_5$(0.01)</td>
<td>KOH(0.01)</td>
<td>10ml 30%</td>
</tr>
<tr>
<td>CaV$<em>6$O$</em>{16}$</td>
<td>V$_2$O$_5$(0.03)</td>
<td>Ca(OH)$_2$(0.02)</td>
<td>10ml 95%</td>
</tr>
<tr>
<td>SrV$<em>6$O$</em>{16}$</td>
<td>V$_2$O$_5$(0.03)</td>
<td>Sr(OH)$_2$(0.02)</td>
<td>10ml 95%</td>
</tr>
</tbody>
</table>

It can be observed that the materials synthesized by hydrothermal and sol-gel process are exactly same both in terms of crystallinity and morphology. Hence, we can conclude that the processes conducted via hydrothermal could be replicated in a sol-gel synthesis in the case of hewettite structures.
3.1.2.1 Preparation of crystalline LVO rods

LVO is synthesized by a facile one step synthesis method, 0.4487g of CH$_3$COOLi·2H$_2$O was dissolved in 60 ml of deionized water along with 1.0000 g V$_2$O$_5$. When all chemical completely dissolved, 10 ml of 30 percent hydrogen peroxide was added into the above solution (till pH : 9) and neutralized(pH:7) with 1M HCl. During this process, the color of the solution changed from bisque, orange, sepia to brown. Meanwhile, there will be some bubbles generated from the solution. Then, the gel precursor was dried at 110 ºC for 24 h in air. After that, the gel precursor was ground into power. The resultant precursor was calcinated at 400 ºC for 2 h in air. After that it is cooled down to room temperature, the produced material is ground for an hour using mortal and pestle. Then, it is calcinated at 550 ºC for 6 h in air. After it is cooled down to room temperature, brown product is obtained(Figure 4.3.a). These brown products are further ground for another 10~20 min.

3.1.2.2 Preparation of 3-Dimensional (CaV$_6$O$_{16}.x$H$_2$O)CVO heterostructures

0.02 moles(1.4818g) Ca(OH)$_2$ was mixed with 0.03 moles(5.4564g) of V$_2$O$_5$ in deionized (DI) water and stirred overnight to obtain an orange yellow solution, after which,10ml 95% H$_2$O$_2$ was added to it and heated at 120 ºC for 24 hours. The colour of the solution will change from Orange yellow to red and finally water will be completely evaporated to obtain a reddish brown colour powder. Resulting precipitate mixture was vacuum dried at 80 ºC for 4 h to obtain the as-synthesized CaV$_6$O$_{16}.x$H$_2$O powder (CVO).

The reaction that occur during the formation of CaV$_6$O$_{16}.x$H$_2$O can be classified into the following steps.

When Ca(OH)$_2$ and V$_2$O$_5$ are mixed and heated in solution phase to yield CaV$_6$O$_{16}.x$H$_2$O: Ca$^{2+}$ inserts into the V$_3$O$_8$ layers forming the CaV$_6$O$_{16}.x$H$_2$O.

\[
\text{V}_2\text{O}_5 + \text{Ca(OH)}_2 = (\text{VO}_3)_2\text{Ca} + \text{H}_2\text{O}
\]

\[(\text{VO}_3)_2\text{Ca} + 2\text{V}_2\text{O}_5 = (\text{V}_3\text{O}_8)_2\text{Ca}\]

\[(\text{V}_3\text{O}_8)_2\text{Ca} + \text{Ca(OH)}_2 = \text{CaV}_6\text{O}_{16} + \text{Ca}^{2+} + 2\text{OH}^- + \text{H}_2\text{O(}\text{excess})\]

Finally,

\[3\text{V}_2\text{O}_5 + 2\text{Ca(OH)}_2 = \text{CaV}_6\text{O}_{16}.x\text{H}_2\text{O}\]
3.1.2.3 Preparation of 3-Dimensional (SrV$_6$O$_{16}.x$H$_2$O) SVO network

0.02 moles (2.4326g) Sr(OH)$_2$ was mixed with 0.03 moles (5.4564g) of V$_2$O$_5$ in deionized (DI) water and stirred overnight to obtain an orange solution, after which, 10ml 95% H$_2$O$_2$ was added to it and heated at 120$^\circ$C for 24 hours. The colour of the solution will change from Orange yellow to red and finally water will be completely evaporated to obtain a reddish brown colour powder. Resulting precipitate mixture was vacuum dried at 80$^\circ$C for 4 h to obtain the as-synthesized SrV$_6$O$_{16}.x$H$_2$O powder (SVO).

The reaction that occur during the formation of SrV$_6$O$_{16}.x$H$_2$O can be classified into the following steps.

When Sr(OH)$_2$ and V$_2$O$_5$ are mixed and heated in solution phase to yield SrV$_6$O$_{16}.x$H$_2$O: Sr$^{2+}$ inserts into the V$_3$O$_8^-$ layers forming the SrV$_6$O$_{16}.x$H$_2$O.

\[
V_2O_5 + Sr(OH)_2 = (VO_3)_2Sr + H_2O
\]
\[
(VO_3)_2Ca + 2V_2O_5 = (V_3O_8)_2Sr
\]
\[
(V_3O_8)_2Sr + Sr(OH)_2 = SrV_6O_{16} + Sr^{2+} + 2OH^- + H_2O(\text{excess})
\]

Finally,
\[
3V_2O_5 + 2Sr(OH)_2 = SrV_6O_{16}.xH_2O
\]

3.1.3 Solution-based Synthesis of LiMn$_2$O$_4$ micro-architectures

LiMn$_2$O$_4$ sphere morphologies are usually grown by a typical template assisted growth method, where the MnO$_2$ spherical morphology acts as the seed template for the growth. Scheme 3.2 summarizes the synthesis method for LiMn2O4 microarchitectures studied in this thesis. Analytically-pure MnSO$_4$.H$_2$O (MnSO$_4$.H$_2$O, 98%, Sigma Aldrich) and NH$_4$HCO$_3$ (NH$_4$HCO$_3$, Sigma Aldrich) was used as received. 10 mmol MnSO$_4$.H$_2$O was mixed with 100 mmol of NH$_4$HCO$_3$ in 1 litre of deionized (DI) water and then 100 mL 99% ethanol was added into the above solution under vigorous stirring for an hour. After that, the solution was centrifuged, washed with DI water and ethanol to obtain MnCO$_3$ solid microspheres, which was later dried at 80$^\circ$C. MnCO$_3$ hollow microspheres were prepared by adding 50 mmol of (NH$_4$)$_2$SO$_4$ to the above mixture of
MnSO$_4$.H$_2$O and NH$_4$HCO$_3$ while microcubes were obtained by adding 100mmol of (NH$_4$)$_2$SO$_4$ to the above mixture of NH$_4$HCO$_3$ and MnSO$_4$.H$_2$O. Further, the three samples (MnCO$_3$ solid microspheres, hollow microspheres and microcubes) was calcinatned at 400$^\circ$C to obtain MnO$_2$ and ground to obtain fine powder. Finally, the obtained MnO$_2$ powders were mixed with LiOH.H$_2$O in a ratio of 2:1.05 respectively and further subjected to heat treatment at 750$^\circ$C for 10 hours to obtain fine LiMn$_2$O$_4$ powder.

**Scheme 3.2** Schematic illustration of the Synthesis of LiMn$_2$O$_4$ micro-architectures

### 3.2 Characterization Methodologies

This section details the various characterization methods employed to study the physical, structural, thermal and electrochemical properties of the materials so as to optimize them for its potential use as electrode in aqueous rechargeable lithium ion battery.

#### 3.2.1 Microscopy Methods

**3.2.1.1 Field emission scanning electron microscope (FE-SEM)**

Morphological studies of all samples were conducted using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6340F and JEOL 7600F) at an accelerating voltage of 5kV. Sample preparation was done by spreading the sample over a carbon
tape sticker fixed on an aluminium sample holder and coated with ~10-15 nm of platinum using a sputtering coater (JEOL JFC-1600).

3.2.1.2 Transmission electron microscope (TEM)

Transmission electron microscopy (TEM, JEOL 2100F) at an accelerating voltage of 200kV. TEM is performed to study the morphology and crystallography of the material. Operation of TEM at higher voltage than FESEM enables shorter wavelength of electron beams to hit the samples, thereby enabling capture of images at much higher resolution by interfering with the thin crystals within the samples and bringing about an electron interference patterns at a fitting defect-of-focus, which can be directly inferred as projected potential of the crystal structure. This helps not only in structural determination but also to understand atomic anomalies and investigations at atomic scale.

3.2.1.3 Atomic force microscopy (AFM)

The surface topology and features were studied using atomic force microscope (AFM) was carried out using a non-conductive silicon nitride tip using an Agilent 5500 AFM tool operated in contact mode.

3.2.2 Diffraction Studies

3.2.2.1 Powder x-ray diffraction (XRD)

Phase purity and crystal structure of all materials were examined by a Bruker X-ray diffractometer D8 Powder (Cu-Kα radiation, with step scanning (0.01°, 0.6s dwell time, 40kV). The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld phase analysis within the Topas V3 (Bruker-AXS), using fundamental parameters approach.

3.2.2.2 High temperature x-ray diffraction (HT-XRD)

Hewettites were study of their structural instability on water loses from their crystal samples using a Siemen D5005 High temperature X-ray powder diffraction machine.
Cu-Kα radiation, with step scanning (0.02°, 0.6s dwell time, 20kV). The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld phase analysis within the Topas V3, using fundamental parameters approach.

### 3.2.2.3 Selected area electron diffraction (SAED)

SAED was conducted inside TEM column (Section 3.2.1.2). The principle of electron diffraction in this technique is similar with XRD by adhering to Bragg’s law. Due to the extremely short wavelength of highly coherent electron beam in TEM chamber (0.0251 Å), the wave-like electron passes through the lattice plane within the crystal which serve as diffraction grating, eventually resulting in diffraction. This technique provides information of crystal orientation relationships between grains, and it is able to identify the lattice metrics of the crystals. Samples for SAED were prepared by grinding under ethanol and drops of the resulting suspension deposited on copper-grids, and fitted with a low-background Gatan double tilt holder.

### 3.2.3 Spectroscopy studies

#### 3.2.3.1 Energy dispersive x-ray spectroscopy (EDS)

Where required, scanning electron microscope (SEM, JEOL-JSM 5310) attached with energy dispersive spectroscopy (EDS) was used to analyze the elemental compositions of the samples. For EDS-FESEM, working distance of 15 cm and accelerating voltage of 20 kV were selected and scanned on an area of ~50 μm x 50 μm for 10 min to obtain the spectrum. After irradiated by a focused electron beam, ground state electrons in energy level bounded to nucleus absorb the incident energy and escape away from the orbital, leaving behind empty holes. An electron from higher energy shell subsequently fills up the hole and releases the energy difference between these two discrete shells in the form of a characteristic x-ray. Hence, energy-dispersive spectrometer analyzes the amount and energy values of characteristic x-ray and reveals the elemental composition of a sample.
3.2.3.2 X-ray photoelectron spectroscopy (XPS)

In order to understand the redox processes, ex-situ X-ray photoelectron spectroscopy (XPS) data were collected from PerkinElmer PHI 5100 system using Al Kα X-ray source with passing energy of 20 eV. Samples were sputtered with argon inside the XPS chamber to remove surface contaminants. Analysis were performed using CasaXPS software (Version 2.3.15). XPS analysis of all the hewettites were done to study their chemical constituents. XPS analyses were carried out on after-cycled samples of CVO to study the loss of capacity during long-cycling.

3.2.3.3 Raman Spectroscopy (RS)

The Raman spectra were recorded with a RENISHAW in Via Raman microscope. The source laser wave length was 633nm. Raman spectra of the samples was done for hewettites and their original precursors to understand how the peaks co-relate. Inter-comparison of hewettites is done to understand on how the interlayer variation in pillar ion changes the Raman spectral and to find particular signatures of the same.

3.2.4 Thermal Analysis: To determine the water-content in Hewettites

To study the water content in various samples of hewettites, two approaches were followed.
Crystal volume: The lattice parameters obtained after Topas refinement were used to calculate the crystal volume. Once the unit cell is known, the (Sub)cell will have 6 vanadium atoms per layer in the hewettite-group minerals. These vanadium counts will establish the unit cell formula and its volume should be consistent with the volume of the layer which is 275Å³ for a hewettite V₆O₁₆ layer plus interlayer materials like H₂O(23 Å³) and/or for alkali/alkali earth metals like Calcium(10Å³). Hence by knowing the crystal volume of the sample via TOPAS refinement, and with the above cell volume values of V₆O₁₆, for alkali/alkali earth metals and water, one can easily calculate the amount of water in the crystal which forms the water of crystallization in these hewettites.
3.2.4.1 Thermogravimetric analysis (TGA)

Another approach which can be used to study the water content in these hewettites is by using thermal gravimetric (TG) analysis, which is done using TA-TGA Q500 instrument under N₂ atmosphere. The amount of water which has evaporated from the sample after heating it to a particular temperature divided by the molar mass of the water will give the number of water molecules attached to the crystal. The type of attachment of H₂O to the crystal can also be studied to an extent with TGA. There could be three kinds of water within a crystal, they are, free water, hydrogen bonded water and metal-coordinated water.

3.3 Electrochemical characterization

3.3.1 Cell Fabrication

Electrodes were prepared by mixing the active material, binder (Kynar 2801), and Super P Li carbon (Timcal) in the weight ratio of 75:15:10, using 1-methyl-2-pyrrolidinone (NMP, anhydrous) as solvent to form slurry. This viscous slurry was coated onto a 1cm² area of graphite paper and dried in a convection oven at 80°C to form the electrodes.

3.3.2 Pouch Cell fabrication

Screen printing like painting is a process to coat the electrode materials, the current collectors and the electrolyte on a substrate which can be a transparent and flexible one like PET or on any material like cloth. Figure 3.1 illustrates anode and cathode electrodes coated over a graphite paper as a substrate and a nickel tab as the current collector.

Screen printing can also be effectively used to so series and parallel combination of battery to increase their voltage and capacity, thus making it suitable for various device configurations.

Screen printing has been sought as an important technique to fabricate different battery architecture to satisfy the power demands of various sports electronic device.
3.3.3 Electrochemical Impedance Spectroscopy

EIS is one of the most common methods used to study the electrochemical process and understand the kinetics of the electrochemical Li insertion/de-insertion process. EIS enables in qualitative comparison of diffusion-controlled and charge transfer reactions occurring before and after the charge/discharge process. It can also be used to do a comparative study among different materials. It can give the conductivity values of various materials which can be helpful in tuning the conductivity of such material by the addition of other materials like carbon or silver. The vertically inclined line in the low frequency refers to the lithium diffusion related kinetics & is usually denoted as Warburg element in the equivalent circuit. By fitting EIS with an appropriate equivalent circuit one can gain insights to the effects of various morphologies, conductivity, grain size of material on its electrochemical performance like rate, capacity and cycling. In this thesis, EIS studies were carried out on various hewettite materials to understand the effect on conductivity of these materials upon the change of alkali metal ion between the V$_6$O$_{16}$ layers. Also EIS was conducted on half cell electrodes of hewettite material and also on the full cell before and after cycling to understand the charge-transfer kinetics occurring in the system. The study was done by applying an A.C. amplitude of 10mV over the frequency range of 100kHz to 5MHz in room temperature. The Nyquist plots of $Z''$ vs. $Z'$ were erived & analysed using Zplot & Zview software (version 2.3 Scribner Associates Inc. USA)
3.3.4 Cyclic Voltammetry

Cyclic voltammetry is carried out by applying a certain voltage sweep (mVs\(^{-1}\)) across a voltage range (say -1.0V to 0V) and measure the current (mostly in mA). The peak current at a particular voltage indicates the redox reaction at that voltage which also indicates the voltage at which the lithium ion inserts and de-inserts into the material. Cyclic voltammetry is the basic measurement performed to understand the voltage range in which the material is electrochemically active. It also can provide information about the charge storage mechanism, the current and power output, the redox reactions, structural changes and side reaction occurring within the material as a result of lithium insertion and de-insertion during the process. Cyclic voltammetry (CV) of the half cells were carried out in a three-electrode configuration, in an aqueous lithium-salt based electrolyte solution (for e.g. like 3M lithium nitrate (LiNO\(_3\)) or 3M Lithium chloride (LiCl) or 3M Lithium Sulphate(Li\(_2\)SO\(_4\))), with platinum foil and a standard calomel electrode (SCE) as the counter and reference electrodes, using a computer-controlled potentiostat (Solartron, 1470E) at room temperature, in a particular voltage range vs. SCE. \(^{[137]}\)

3.3.5 Galvanostatic cycling

Galvanostatic cycling is usually performed by applying a constant current (positive or negative depending on charge or discharge) from a cell’s open circuit voltage to a pre-set voltage and the time taken to completion is measured. From the time taken for a complete charge and discharge, the charge capacity and discharge capacity are calculated in mAh. Dividing the capacity by the weight of the active material provides the specific capacity of that material. Galvanostatic cycling experiment is performed in a three cell configuration (Working electrode, counter electrode and reference electrode) to evaluate the material’s capacity, changes in capacity occurring during the charge/discharge process (cycle life) and the columbic efficiency. The pre-set upper-limit voltage for a material is determined from its cyclic voltammetric profile and redox peak potential in a half-cell configuration. To elucidate the electrochemical performance of a material, galvanostatic charge / discharge of the half cells were carried
out in a three-electrode configuration, in an aqueous solution of lithium salt, with platinum foil and a standard calomel electrode (SCE) as the counter and reference electrodes respectively, using a computer-controlled potentiostat (Solartron, 1470E) at room temperature, in a particular voltage range vs. SCE. Galvanostatic cycling in half cell configuration is required to obtain the stable specific capacity of the material, which is necessary for mass optimization during the assembly of a full cell battery. During galvanostatic cycling of batteries, the charge and discharge current are often expressed as a C-rate, which is a measure of the rate at which a battery is charged or discharged relatively to its theoretical capacity. 1 C rate is the necessary current applied or drained from the battery to completely charge or discharge it in one hour. Theoretical capacity of a material is calculated from the following formula:

\[
\text{Specific capacity} = \frac{\text{charge stored}}{\text{mass}}
\]

For one mole of a cathode material, assuming it provides "x" moles of electrons:

**Equation 3-1**  
\[
\text{Specific Capacity} = x \times \text{Na} \times \text{Q}_e / M_w
\]

Where,

\[\text{Na} = \text{Avogadro’s number}\]
\[\text{Q}_e = \text{Charge of an electron (in coulombs)}\]
\[M_w = \text{Formula mass of cathode material}\]

This value is in coulombs per gram.  
(To convert it to mAh g\(^{-1}\), it is divided by 3.6)

Galvanostatic cycling in full cell configuration is usually performed in a two electrode configuration to study the electrochemical performance of a full cell battery. It is carried out in an aqueous solution of lithium salt, with anode as the counter and cathode as the working electrodes, using a computer-controlled potentiostat (Solartron, 1470E) at room temperature, in a particular voltage range obtained by combing the standard reduction potential of both then anode and cathode half cell reactions.
The galvanostatic experiment plots are shown in three different graphs. The first graph shows the simple charge and discharge plot which is expressed as Potential vs Specific capacity. The nature of the plot can explain various types of charge storage mechanism and redox reaction occurring during the process. The area under the curve for the plot also gives the energy density of the cell.

The second graph is called the cycling profile, which provides information about the performance of the battery on long cycling. During long cycling, the performance of the battery can changes, depending on the charge storage mechanisms and its accompanied redox reactions, the cycling performance can improve or decrease or even remain stable without any change for a long number of cycles. The third graph is usually the coloumbic efficiency plot, which is obtained by plotting the coloumbic efficiency Vs the cycle number. Coloumbic efficiency of the cell is obtained by taking the percentage of the ratio obtained by dividing the discharge capacity with the charge capacity at every cycle. It provides information about the irreversible capacity loss occurring the charge discharge process which usually occurs when the material cannot deintercalate the same number of lithium ions which it intercalates during the cycling process. In simple words it also provides the energy output of a system with respect to the energy input over long charge/discharge cycling.

### 3.4 Summary

Alkali and Alkali-earth metal oxide hexavanadates (hewettites) structures are synthesized by simple one-step hydrothermal and sol-gel methods, while lithium manganese oxide microstructures were synthesized using a solution-based template assisted growth method. The synthesis method followed for the synthesis are environmental friendly, industrially scalable, results in high volume production and does not require sophisticated set-up unlike other traditional nano-material manufacturing processes. Various characterization techniques like physical, chemical, structural and electrochemical that are used to study the hewettites and lithium managanese oxides structures in chapter 4 are discussed in detail. Thus, chapter 3 of this thesis covers the synthesis of materials along with the characterization techniques that would be used in
further chapter to understand the various structural and electrochemical properties of these materials.
Chapter 4 Results

This chapter details the results of various experiments undertaken in this thesis. It starts with the justification of using hydrothermal and sol-gel method for the synthesis of these vanadium oxide bronzes specifically called as hewettites and studies these various vanadium oxides bronzes by dividing them into two major classes based on the group of metal ion i.e. alkali or alkali-earth metal cation that intercalates within the $V_6O_{16}$ pseudo-layered structure. Various techniques used to improve the irreversible capacity loss in CVO has been discussed in detail after a proper scientific analysis of the redox reactions and lithium intercalation mechanism occurring within the system during the long cycling. Further, this chapter also details the study of LiMn$_2$O$_4$ micro-architectures as cathode materials for aqueous rechargeable lithium ion battery. Finally, the best performing LiMn$_2$O$_4$ morphology as cathode is combined with the best performing anode from both the classes (alkali and alkali-earth) based vanadium oxide bronzes (hewettites) to study them in a full cell configuration. Further in the section 6 of application, these full cell batteries in pouch cell architectures are combined with flexible solar cells and RFID tags for various wearable electronic applications. A small case-study based application on the IPSC Ontology model is performed using the flexible Solar battery with RFID.
4.1 Justification for Hydrothermal & sol-gel synthesis in ARLB

Vanadium based pseudo-layered oxides with tunable interlayer distances (C-axis) by varying different pillar ions that stabilize the layers are a potential electrode material for aqueous rechargeable lithium ion batteries. Hewettites are naturally occurring minerals and can be obtained at very low cost. Figure 4.1, shows the as-prepared colour and texture of various hewettites which are the major focus of study in this thesis.

Hewettites are safe for usage and has very high theoretical capacity of upto 440mAh$^{-1}$ due to its insertion of higher number of lithium ion (>10) into it pseudo-layered supercell structure.

But practically, only upto 140mAh$^{-1}$ was only extractable out of NVO – barnesite one of compounds out of the hewettite family.  Another issue notable with vanadium based materials are their poor cycling life owing to many factors like low conductivity, reduced ion diffusivity and vanadium dissolution.  

Figure 4-1 Naked-eye view of hewettite heterostructures (Hexavanadate bronzes)
The pre-cursor for the synthesis of Hewettites are $V_2O_5$, which exhibits theoretical capacity of $\sim400\text{mAh}^{-1}$ due to their capability to intercalate nearly 3 Li ions per mole of active material

$$ (V_2O_5 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_xV_2O_5) $$

On the other hand, performance of conventional bulk $V_2O_5$ powders is limited by slow lithium diffusion rate ($\sim10^{-12}\text{ cm}^2\text{S}^{-1}$) in the lattice, structural instability with lithium intercalation/de-intercalation and low electronic conductivity ($10^{-2} - 10^{-3}\text{ S cm}^{-1}$)\[85\], leading to inferior battery performance such as low initial capacity and poor rate capability and capacity degradation on long cycling. Some of the methods, mostly commonly used to improve the electrochemical performance of $V_2O_5$ is fabrication of nanoarchitectures by electrospinning or insertion of alkali metal ions like $\text{Li}^+$ chemically during synthesis to prevent structural collapse.\[139\] Studies have shown that nanofibers of vanadium oxides like $V_2O_5$ and $\text{LiV}_3\text{O}_8$ exhibits better electrochemical performance compared to their bulk forms due to their morphology, shorter diffusion pathways for lithium ion during charging and discharging.\[139,140\]

In our study we employ both the strategies using simple hydrothermal and sol-gel methods, both resulting in very similar outputs.

Hydrothermal methods are commonly used to synthesize various nano-architectures of materials due to their ease of synthesis. In Hydrothermal method, stoichiometric amounts of the reactants are dissolved in water according to the requirement and size of the hydrothermal bomb. Type of architecture and size of material can be controlled by controlling the time of reaction and also by the temperature of the reaction. In sol-gel method also, the materials are synthesized in the same way as in Hydrothermal, the only difference being, the process takes additional 6 hours more for the solvent/water to evaporate completely before the dry powder can be used, while in Hydrothermal, the powder and the water would be in separate form, making it easier for them to extract and further dry them.

For simplicity, hewettites are further divided into alkali metal ion based hewettites(section 4.2) and alkali-earth metal ion based hewettites(section 4.3) on the basis of the kind of the cation occupying the interstitial site between the $V_6O_{16}^{2-}$ puckered layers.
4.2 Alkali metal ion hexavanadates

Alkali metal ion hexavanadates, LVO, NVO and KVO from the group of alkali metals are chosen for study in this thesis due to their simplicity in synthesis and natural abundance (Figure 4.2). The valency of the pillar ions in this case is +1 and the only parameter that would influence the variation in these alkali-metal oxide hexavanadates (LVO, NVO and KVO) is their ion size. The alkali metal ions (Li⁺, Na⁺, K⁺) are also known as pillar–ions hold the layers intact and prevents the structure from collapse during stress caused during the electrochemical process of lithium insertion and de-insertion. Further in this section, three different alkali metal ion hexavanadates: Li₃V₆O₁₆, Na₂.₃2V₆O₁₆, K₂V₆O₁₆ would be studied in detail for their physical, structural and electrochemical properties. Synthesis of these compounds were detailed in section 3.1.1 and 3.1.2.
4.2.1 \( \text{Li}_3\text{V}_6\text{O}_{16} \) (LVO)

Practical capacities of various vanadium oxides like \( \text{LiV}_2\text{O}_5 \), \( \text{LiV}_3\text{O}_8 \), and \( \text{VO}_2\text{(B)} \) studied for ARLBs are 47m Ah\(^{-1}\), 45m Ah\(^{-1}\) and 100m Ah\(^{-1}\) respectively with only half their initial capacity at the end of 100 cycles.

In aqueous electrolyte, \( \text{LiV}_3\text{O}_8 \) shows a capacity less than 45m Ah\(^{-1}\) and very high capacity fading due to breakdown of crystal structure and inherent vanadium dissolution. To develop a complete aqueous rechargeable lithium ion battery, it is necessary to develop an anode which has a stable redox peaks at much higher negative potential along with higher capacity at least in the range of typical cathodes like \( \text{LiMn}_2\text{O}_4 \) which is \( \sim \)125-140m Ah\(^{-1}\).

Vivek et.al has studied this holotype synthetic bronze : \( \text{Li}_3\text{V}_6\text{O}_{16} \) (herewith, referred as LVO) with wide operating potential -1.1V- 0 V vs SCE in an aqueous solution of lithium chloride.

![Figure 4-3 LVO: a) Actual powder, b) HR-TEM image, c) lattice fringe obtained from selected area, d) SAED pattern, e) FE-SEM image and f) AFM image. ([103]-Reproduced by permission of The Royal Society of Chemistry)](image-url)
As obtained brown powder of LVO (Figure 4.3.a) was studied using FE-SEM, as seen in image(Figure 4.3.e), LVO shows rod-type morphology with an average diameter of \(~0.5\mu m\) and length of \(\leq 5\mu m\), hence providing an aspect ratio of \(~20\). From HR-TEM (Figure 4.3.b) the obtained lattice fringe pattern (Figure 4.3.c) and selected area electron diffraction (Figure 4.3.d) of LVO rods divulges several layers of lamellar crystals. Higher surface area in LVO renders it usefulness for more rapid charge-discharge in ARLBs and LIBs. Similarly, the rod like appearance of AFM image (Figure 4.3.f) confirms with the FE-SEM and TEM images.

![Image of a diagram showing X-ray diffraction (XRD) pattern of LVO rods.](image)

**Figure 4.4** Rietveld refinement of X-ray diffraction (XRD) pattern of LVO rods. ([103]-Reproduced by permission of The Royal Society of Chemistry)

The XRD patterns as shown in Figure 4.4 can be fully indexed to the crystal structure of Li\(_3\)V\(_6\)O\(_{16}\) (P\(_{121}/m1\), PDF 4-0417) via Rietveld refinement(R factor <0.06), without the presence of any impurity peaks. The XRD data shown in Figure 4.4 for LVO can be reasonably indexed to the observed selected area diffraction pattern in Figure 4.3.d.
Figure 4-5 Crystal structure obtained from LVO cif file showing only 2 lithium ions(a) and energy minimized structure showing all the three lithium ions present within the crystal(b).

The atomic co-ordinates of the structure (Li$_2$V$_6$O$_{16}$) were studied by DFT calculations. Starting with initial structure as reported in (PDF 4-0417), the fractional co-ordinates and lattice parameters were optimized. It is noted that the location of 3rd and subsequent Li ions are not reported in the crystallographic information file. This study has helped in the prediction of the position of 3rd Li in the lattice. The optimized structure of Li$_2$V$_6$O$_{16}$ is shown in Figure 4.5.a. Additional Li ions were introduced in the lattice and the fractional co-ordinates were optimized subsequently. The location of the 3rd ion was predicted in as shown in the Figure 4.5.b. The 3rd ion is located in an octahedral site in the lattice. Thus, by energy minimization studies, it was able to find the location of the third lithium, which was not mentioned in the crystallographic information file of the LVO base structure.

The X-ray Photoelectron Spectroscopy (XPS) survey spectrum (Figure 4.6) reveals the presence of Lithium, Vanadium and Oxygen without any impurities. The high resolution spectrum of V2p$^{3/2}$ and V2p$^{1/2}$ centered at 516.1 and 523.6 eV respectively indicates the presence of V$^{5+}$ species (Figure 4.7.a). Similarly for the Li 1s region, the
core level is as 54.85eV with the dominant Li signal assigned to Li⁺ (Figure 4.7.b). Hence we prove the monoclinic nature of Li₃V₆O₁₆ with no evident impurities detected.

**Figure 4-6** XPS survey spectrum of LVO-1 (before charge/discharge).

**Figure 4-7** High resolution XPS spectrum of LVO-1 a) V2p region b) Li⁺ region. ([103]-Reproduced by permission of The Royal Society of Chemistry)

Vanadium exists in a stable tetrahedral co-ordination in its +5 oxidation state, while, vanadium in square pyramidal coordination is found in both the V⁵⁺ and V⁴⁺ forms. Nevertheless, octahedral vanadium is found in all oxidation states with some
distortion in various compounds. Hence, we can conclude that the vanadium compounds that are electrochemically active exist in octahedral coordination.

**Figure 4.8** a) Cyclic voltammograms of LVO as anode in three electron configuration (vs SCE) from -1.2 to 0V at scan rate of 0.5 mVs\(^{-1}\) and 2 mVs\(^{-1}\). b) Galvanostatic discharge/charge profiles of LVO in 3M LiNO\(_3\) aqueous solution, in three electrode configuration (vs SCE) from -1.2 to 0V, at current density of 0.5 mA g\(^{-1}\). ([103]-Reproduced by permission of The Royal Society of Chemistry)

Cyclic voltammetry (CV) and galvanostatic charge/discharge of the half cells were carried out in a three-electrode configuration using 3M lithium nitrate (LiNO\(_3\)) aqueous solution as electrolyte, with platinum foil and a SCE as the counter and reference electrodes respectively at room temperature, in the voltage range of -1.2 to 0V vs. SCE using a Solartron 1470E equipment. In order to investigate the phase transformations and the charge storage mechanism occurring during the electrochemical processes cyclic voltammetric tests (Figure 4.8.a) of the LVO rods as anode was carried out in three-electrode configuration within the potential range of -1.2 to 0.0V at a scan rate of 0.5 mVs\(^{-1}\) and 2 mVs\(^{-1}\). CV of LVO shows two main reduction peaks at -0.4V and -0.6V while a faint reduction peak can be observed at -0.3V vs. SCE and two main oxidation peaks at -0.425V and -0.275V vs. SCE respectively.

Anodic LVO gave an initial charge capacity of 110 mAh g\(^{-1}\) and discharge capacity of 120 mAh g\(^{-1}\) (Figure 4.8.b). In comparison to other commonly used anode materials like LiTi\(_2\)(PO\(_4\))\(_3\), LiT\(_2\)(PO\(_4\))\(_3\) and LiV\(_3\)O\(_8\) in ARLBs, LVO displays a slightly higher anode
capacity at a higher negative voltage. Multi-lithium ion intercalation/de-intercalation process is the reason why a flat discharge plateau is absent in this material.[25]

![Figure 4-9](image)

**Figure 4-9** a) Cycling performance and columbic efficiency of LVO as anode in ARLB at a current density of 0.5 mA g\(^{-1}\) and b) Rate performance of LVO for 10 cycles each at current densities of 0.1mA/g, 0.5mA/g, 1.6mA/g, 3.2mA/g and 6.4mA/g in the cut-off voltage window of -1.2V to 0V vs. SCE. ([103]-Reproduced by permission of The Royal Society of Chemistry)

At the end of 100 cycles, LVO rods gave a discharge capacity of 62.5mAh g\(^{-1}\) which is ~52% of its initial capacity. At a high current density of 0.5A g\(^{-1}\), decent columbic efficiency of 99-86% was achieved over the cycles from 1-100 (Figure 4.9.a). At varying current densities, LVO was cycled for 10 cycles each to study its capacity degradation during the cycling. (Figure 4.9.b)

After cycling effect on LVO as an anode electrode was examined using XPS (Figure 4.10). The spectrum of V2p region displays new peaks in both V2p\(_{3/2}\) and V2p\(_{1/2}\) orbital that can be observed along with the peaks corresponding to V\(^{5+}\) species. Charging of LVO results in the reduction of vanadium from +5 to +4 which is evident from these new peaks corresponding to V\(^{4+}\) species.
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Figure 4-10 Evidence of vanadium in the V+5/+4 oxidation states after charge/discharge using a high-resolution XPS spectra of LVO at the V2P region. ([103]-Reproduced by permission of The Royal Society of Chemistry)

The overall capacity of LVO has relative contributions of both surface capacitive and diffusion controlled bulk intercalation processes which can be studied by fitting the voltammetric currents at various sweep rates (Figure 4.11) to appropriate power law relationships given in section 2.3. Two lithium ions present in the octahedral pockets of the structure holds the layers together in LVO rods.

Figure 4-11 a) Cyclic voltammetric response of LVO rods at sweep rates of 4mVs\(^{-1}\) (a), 2mVs\(^{-1}\) (b), 1mVs\(^{-1}\) (c), 0.5mVs\(^{-1}\) (d) and 0.25mVs\(^{-1}\) (e) respectively. ; b) Charge storage mechanism using inverse power law with peak currents corresponding to cycles a, b, c, d & e as shown in Figure 4.9a. ([103]-Reproduced by permission of The Royal Society of Chemistry)
Surface capacitance and intercalation based capacity contribution of LVO at 4mVs\(^{-1}\) was computed to be ~22.22% and ~77.83% respectively. Bulk storage mechanism helps in higher capacity and hence increased energy density while surface-capacitance based energy storage behaviour supports stable operation at faster insertion/extraction kinetics therefore higher power density.

The two faradaic charge storage mechanisms gives us an opportunity to design energy storage devices of desired property i.e. faster storage, higher capacity, high voltage, and different rate capabilities. which is crucial considering the functionality for different applications. One of the most sorted approach that can help tune this charge storage property along with helping to achieve a higher capacity is the replacement of the pillar ions with a bigger size and higher oxidation state which will be explored in further sections.

### 4.2.2 \(\text{Na}_{2.32}\text{V}_6\text{O}_{16}\) (NVO)

\(\text{Na}_{2.32}\text{V}_6\text{O}_{16}\cdot n\text{H}_2\text{O}\) or Barnesite as it is commonly known among mineralogist is a mineral found mainly in Colorado mines as a bright reddish brown fibers.\(^{[141]}\) After this mineral has been studied for its crystal properties by the mineralogists in 1980s, not much studies were made until early 2011, when this material was reported to have ‘Superconducting behaviour’ and also electrochemical properties both in organic and aqueous lithium ion batteries. In NVO, Sodium ion due to its bigger size would have resulted in increasing the interlayer distances and helping to accommodate more lithium ions during intercalation thereby helping in achieving higher capacity compared to LVO.

Under naked eye, NVO looks like an orange brown coloured powder. (Figure 4.12.a) When observed under FE-SEM(Figure 4.12.e) and TEM(Figure 4.12.b) to study the morphology of NVO, one can observe ~0.5-0.7µm long rod with a width of 50-60nm. HR-TEM image(Figure 4.12.c) shows very clear lattice fringes which proves that the material is highly crystalline in nature. Each rods appears to be well bundled(Figure 4.12.f) which is confirmed using an AFM. SAED pattern shown in Figure 4.12.d reveals the presence of several layers of lamellar crystals that build up to form a rod type of morphology in NVO. Aspect ratio of NVO nano-rods is 10-14,which is lower compared to most other hewettites discussed further in this thesis.
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Figure 4-12 NVO: a) Actual powder, b) HR-TEM image, c) lattice fringe obtained from selected area, d) SAED pattern, e) FE-SEM image and f) AFM image.

Higher aspect ratio does help in faster conduction of electrons and charge across them but smaller aspect ratio has its own advantages which will be discussed further in this section. Nanostructured morphology are well known to provide shorter diffusion pathways for insertion/de-insertion of lithium ions into the materials, while higher surface area provides more number of channels for the lithium intercalation and de-intercalation process. Thus providing better rate capabilities.

Further, powder XRD patterns of NVO was collected and evaluated using rietveld refinement to study the crystal structure. The XRD patterns (Figure 4.13.a) can be fully indexed to the crystal structure (Figure 4.13.b) of $\text{Na}_{2.32} \text{V}_6 \text{O}_{16}$ ($P1_2_1/m1$, PDF 16-4514) via Rietveld refinement, without the presence of any impurity peaks.
Figure 4-13  a) Rietveld refinement of X-ray diffraction (XRD) pattern of NVO rods and b) crystal structure of NVO.

From, the sharp peak intensity of the XRD patterns, it can be clearly seen that NVO is highly crystalline in nature. To investigate the redox reactions occurring in NVO, cyclic voltammetric(CV) experiments were carried in three electrode configuration using platinum as the counter electrode and Standard calomel electrode(SCE) as the reference electrode, the results of which are shown in Figure 4.14.a.

Figure 4-14 (a) Cyclic voltammograms (CV) of NVO rods at 0.25mVs$^{-1}$, 0.5mVs$^{-1}$, 1mVs$^{-1}$, 2mVs$^{-1}$, 4mVs$^{-1}$ in three-electrode configuration (vs. SCE) from -1.0 to 0.0V. (b) Galvanostatic charge-discharge profiles of NVO rods in three-electrode configuration(vs SCE) from -1.0V to 0.0V in 3M aqueous solution of LiCl, with platinum wire as the counter electrode at a current density of 0.5Ag$^{-1}$.
NVO has its reduction peak at -0.6V vs SCE and oxidation peaks at approximately -0.4V vs. SCE. The reduction peak indicates the potential of lithium intercalation into the material and oxidation peak indicates the potential of lithium de-intercalation from the material.

Further, the electrochemical charge/discharge performance of NVO as anode is evaluated using galvanostatic charge/discharge cycling as shown in Figure.4.14.b. using three electrode configuration at a current density of 0.5mAhg⁻¹. NVO as anode gave an initial charge capacity of 130mAhg⁻¹ and discharge capacity of 120mAhg⁻¹ (All the specific capacity values are calculated with respect to the mass of the active material). When compared to other commonly used anode materials like Ti₂P₂O₇, LiT₂(PO₄)₃ and LiV₃O₈ in ARLBs which gives a discharge capacity of 100mAhg⁻¹, 80mAhg⁻¹ and 40mAhg⁻¹ respectively[14,16,142,143], NVO rods displays a slightly higher anode capacity at a higher negative voltage window.

![Figure 4-15 Specific capacity vs. cycle number and coulombic efficiency of NVO rods as anode in 3M LiCl aqueous solution, in three-electrode configuration from -1.0 to 0.0V vs. SCE, at current density of 0.5Ag⁻¹](image)

**Figure 4-15** Specific capacity vs. cycle number and coulombic efficiency of NVO rods as anode in 3M LiCl aqueous solution, in three-electrode configuration from -1.0 to 0.0V vs. SCE, at current density of 0.5Ag⁻¹
When cycled for 100 cycles, the capacity of NVO rods falls from ~155 mAh g\(^{-1}\) to 115 mAh g\(^{-1}\) which is ~74% of its initial capacity after 100 cycles. Columbic efficiency is fairly stable at ~98%. (Figure 4.15) Shorter length of carbon nanotubes are preferred as filler for composites compared to the longer ones because they are very good at handling stress within the composite matrix. Lithium insertion and extraction imparts a similar kind of volumetric stress on materials and hence nanostructured materials with lower aspect ratios help in buffering the stress across the bundle of nano-rods thereby maintaining the structural intact during long cycling.

![Figure 4-16 Peak current vs square root of scan rate with peaks a, b as labelled in Cyclic voltammetric plot shown as inset.](image)

Very little is known about the charge storage mechanism that occurs in NVO, hence by fitting voltammetrix currents to various sweep rates to appropriate power law realtionship given in «Eq.1-2», we can approximately find out the individual contributions of surface-capacitance and bulk lithium intercalation.
By determining the slope ($K_1$) and intercept ($K_2$), one can quantify, at specific peak potentials, the fraction of the current due to each of these contributions and can also calculate the diffusion coefficient of Li-ion within the material.

\[ k_1 \times v = \text{Surface capacitance} \] .............. (1)
\[ K_2 \times v^{1/2} = \text{Intercalation capacity} \] .............. (2)

From Figure 4.16 it is clear that the charge storage mechanism is predominantly bulk intercalation but there is also significant contribution of surface capacitance (~28%), which helps in stable operations during faster charge-discharge and thereby better power densities. It is this pseudocapacitive charging which facilitates low energy Li$^+$ pathways from surface to the subsurface $V_6O_{16}^-$ interlayer sites, which increases the rate capabilities of NVO rods. These properties of NVO rods make it very much suitable as a potential anode material in ARLB systems.

**4.2.3 $K_2V_6O_{16}$ (KVO)**

Vanadium oxides and its bronzes are widely studied in ARBs due to its ability to intercalate and de-intercalate lithium ions in an aqueous solution of lithium salt. Even though, vanadium oxides have a very high theoretical capacity, its practical capacity has always been lower (<45 mAhg$^{-1}$) and has very high capacity fading during long charge/discharge cycles. $K_2V_6O_{16}.nH_2O$ is one of the material least studied among the vanadium oxide bronzes family for its electrochemical properties. $K_2V_6O_{16}.1.5H_2O$ has been studied for its room temperature magnetic semiconductor properties.$^{144}$ Wu et.al. and Xue et.al. reported the synthesis of $K_2V_6O_{16}.1.5H_2O$ by hydrothermal method using potassium orthovanadate as the precursor and studied the obtained the 1D $K_2V_6O_{16}.1.5H_2O$ nanobelts for its room-temperature ferromagnetism.$^{[45,99,144]}$ Room-temperature magnetic semiconductor materials have great interests due its potential applications in the field of sensors, spin-polarized LEDs, photovoltaics and optoelectronics. Liangfei et.al reported the electro-conductivity of the synthetic product at 300K as $1.9 \times 10^{-1}$ Scm$^{-1}$ which is that of a typical semiconductor and has a band gap of 1.95eV.$^{[144]}$ The bulk of $K_2V_6O_{16}.1.5H_2O$ was found to have a direct band-gap
diamagnetic semiconductor with vanadium existing in $V^{+5}$ oxidation state, which has no unpaired electron spins. Room temperature ferromagnetism can arise in a pure compounds without any doped ions or impurities or other phases co-existing in them, if they have cation defect sites or oxygen defect vacancies. $\text{V}_2\text{O}_5$, $\text{TiO}_2$ and $\text{CeO}_2$ has ferromagnetism due to the oxygen vacancies and this would be the same reason for ferromagnetism in $\text{K}_2\text{V}_6\text{O}_{16}.1.5\text{H}_2\text{O}$ as both Vanadium and potassium are in high valance states.[144]

This section reports for the first time reports the electrochemical studies including the charge storage mechanism of $\text{K}_2\text{V}_6\text{O}_{16}.2.24\text{H}_2\text{O}$ in aqueous rechargeable batteries as a potential anode material for an aqueous rechargeable lithium ion battery. $\text{K}_2\text{V}_6\text{O}_{16}.2.24\text{H}_2\text{O}$ displays a modest capacity of $72\text{mAh}^{-1}$ during its 1st cycle and maintains a fairly stable capacity of $\sim60\text{mAh}^{-1}$ at the end of 200 cycles. KVO is synthesized by a novel one-step sol-gel method using vanadium oxide as the precursor as detailed in section 3.1.1.2. One of the main advantages of using $\text{K}_2\text{V}_6\text{O}_{16}.1.5\text{H}_2\text{O}$ belts as a potential anode material is its facile synthesis procedure, which can easily be scaled up for large scale cost-effective production.

Figure 4-17 KVO: a) Actual powder, b) HR-TEM image, c) FE-SEM image, d) TEM image, e) SAED pattern and f) lattice fringe obtained from selected area.
Figure 4.17 provides information about the physical appearance and morphology of KVO. With naked eyes, KVO looks like an orange brown powder (Figure 4.17.a) and when observed under a transmission electron microscope and field emission scanning electron microscope, KVO looks like a 2-D belts with length >10 µm and a width of ~0.5µm.(Figure 4.17.b, Figure 4.17.c and Figure 4.17.d). The aspect nature of these KVO belts are higher than 20. From the HR-TEM image (Figure 4.17.d) the obtained lattice fringe pattern (Figure 4.17.f) and selected area electron diffraction (Figure 4.17.e) of the KVO belts reveal the presence of several layers of lamellar crystals, which lead to the formation of an extended belt type of morphology. Micro-structured crystalline belt morphologies are quite rare in materials which make them very much suitable as electrodes in batteries due to their higher surface areas making them useful for high rate applications. [82,94,100,106,139,145]

**Figure 4-18** Rietveld refinement of X-ray diffraction (XRD) pattern of KVO belts

Further, powder XRD patterns of KVO was collected and evaluated using rietveld refinement to study the crystal structure. All the reflection peaks of the XRD patterns
(Figure 4.18) can be fully indexed to the monoclinic crystal structure of KVO\((P12_1/m1,\) JCPDS card No. 51-0379) \textit{via} Rietveld refinement, without the presence of any impurity peaks. From, the sharp peak intensity of the XRD patterns, it can be clearly seen that KVO belts are highly crystalline in nature.

\textbf{Figure 4-19} (a) Thermo-gravimetric analysis(TGA) of KVO (b) XPS spectra of the O\textsubscript{sp} peak in K\textsubscript{2}V\textsubscript{6}O\textsubscript{16}.2.24H\textsubscript{2}O(KVO) belts. Inset: Red dash line shows the XPS for O\textsuperscript{2−} in the K\textsubscript{2}V\textsubscript{6}O\textsubscript{16}.2.24H\textsubscript{2}O nanobelts. Blue dotted lines shows the XPS for O\textsuperscript{2−} ions in the oxygen-deficient regions.

From TGA(Figure 4.19.a) one can observe that most of the water content from KVO is removed at around 100°C which can be seen as a rapid loss in weight of KVO from 30°C to 100°C. Beyond 200°C, there is small loses of water molecule from the structure which continues till 800°C. The total percentage of water loss from the structure is 5.927\%, which gives the molecular formula of KVO as K\textsubscript{2}V\textsubscript{6}O\textsubscript{16}.2.24H\textsubscript{2}O.

The oxidation state of vanadium according to the formula of KVO is +5 making further oxidation difficult in KVO. Oxygen defect vacancies are known to present in KVO, which is confirmed, with a multicomponent peak fitting using a guasssian simulation of the O1s peaks obtained from the XPS of KVO compound obtained from the sol-gel synthesis. Figure 4.19.b shows the presence of fitted peaks where the lowest binding energy peak at 528.7eV represents the one for O\textsuperscript{2−} ions in KVO while the other peak at higher binding energy of 531.3eV represent the O\textsuperscript{2−} ions in the oxygen defect vacancies.
within the KVO belts. Two electrons from the oxygen vacancy can occupy the 4d orbitals of the two vanadium atoms causing them to be in a partially reduced state, making them electrochemically active. As there are 8 kinds of oxygen atoms in a unit cell(Figure 4.18), there is a possibility of 8 type of oxygen vacancies in the super cell. The 24 hours heating at 100°C during the synthesis could be reason for inducing oxygen vacancy in the system. The same reason which makes KVO a room temperature ferromagnetic material is also responsible to some extent for its electrochemical activity.

**Figure 4-20** (a) Cyclic voltammograms (CV) of KVO belts at 0.25mVs⁻¹, 0.5mVs⁻¹, 1mVs⁻¹, 2mVs⁻¹, 4mVs⁻¹ in three-electrode configuration (vs. SCE) from -1.0 to 0.0 V. (b)Galvanostatic charge-discharge profiles of KVO belts in three-electrode configuration(vs SCE) from -1.0V to 0.0V in 3M aqueous solution of LiCl, with platinum wire as the counter electrode at a current density of 0.5Ag⁻¹

KVO has its reduction peak at -0.3V vs SCE and oxidation peaks at approximately -0.15V vs SCE.(Figure 4.20.a) Lithium intercalation occurs during the reduction reaction while lithium deintercalation occurs during the oxidation process. At the redox peaks, maximum lithium inserts and de-inserts to and from the material resulting in higher number of electrons at those potential and hence one can observe a flat curve at that peak potential during the corresponding galvanostatic cycling.(Figure 4.20.b)
Further, the galvanostatic charge/discharge performance of KVO as anode is shown in Figure 4.20.b. using three electrode configuration at a current density of 0.5A g⁻¹. KVO as anode gave an initial charge capacity of 65mAh g⁻¹ and discharge capacity of 72mAh g⁻¹. (All the specific capacity values are calculated with respect to the mass of the active material). When compared to other commonly used anode materials, KVO displays a slightly higher capacity compared to LiV₃O₈ (40mAh g⁻¹) and lower capacity compared to LiTi₂(PO₄)₃ and LiT₂(PO₄)₃ in ARLBs which gives a discharge capacity of 100mAh g⁻¹ and 80mAh g⁻¹ respectively. [22-24].

![Graph](image)

**Figure 4-21** Peak current vs square root of scan rate with peaks a, b as labelled in Cyclic voltammetric plot shown in Figure 4.a.

By fitting voltammetric currents to various sweep rates to appropriate power law relationship given in «Eq.1-3», we can approximately find out the individual contributions of surface-capacitance and bulk lithium intercalation.

From Figure 4.21 it is clear that the charge storage mechanism is predominantly surface capacitance (~88%) but there is also some significant contribution of bulk
intercalation (~12%), which helps in stable operations during faster charge-discharge and thereby higher power densities. It is this pseudocapacitive charging which facilitates low energy Li\(^+\) pathways from surface to the subsurface \(V_6O_{16}^-\) interlayer sites, which increases the rate capabilities of KVO belts.

![Image](image.png)

**Figure 4-22** Specific capacity vs. cycle number of KVO belts as anode in 3M LiCl aqueous solution, in three-electrode configuration from -1.0 to 0.0V vs SCE, at current density of 0.5A g\(^{-1}\).

Even though the capacity falls during the first 20 cycles to 65mAh\(^{-1}\), it gets stabilized after that and maintains a stable capacity. It maintains a capacity of ~92.3\% at the end of 200 cycles from the 20\(^{th}\) cycle and a capacity of 83.3\% from its 1\(^{st}\) cycle. (Figure 4.22) This unique stability of KVO towards long cycling at high rate of 500mA g\(^{-1}\) can be attributed to its ability to its pseudo-capacitive charge storage mechanism and its belt type of morphology, which opens up multiple lithium ion pathways for insertion into the material.\(^{146}\) The exact role of oxygen defect vacancies in preventing the structure from collapse and vanadium dissolution needs to be ascertained yet, but these defects in structures helps in higher number of lithium ions to intercalate and de-intercalate into the structure, thereby helping in achieving higher capacities even-though majority of
KVO’s charge storage happens through surface capacitance which limits the maximum capacity achievable for the material at the compromise of high rate performance and stability.

Half cell electrochemical studies of KVO belts, carried out in 3M LiCl aqueous solution, gave a discharge capacity of 72mA\(^{-1}\) and an cycling efficiency of 83.3% at the end of 200 cycles at an operational current density of 500mA\(^{-1}\). Such stable performance for long cycles at high current densities is attributed to its pseudo-capacitive behaviour as observed in the charge storage mechanism study. Surface capacitance usually have the advantage of higher power density and stable performance for long cycles but at a compromise of energy density. Oxygen deficient vacancies in KVO have not only made it electrochemically active but also have contributed to its slightly higher capacity. Such combination of modest capacity with stable performance even at high current rates makes KVO an ideal candidate as anode for faster high performance aqueous rechargeable batteries. Further defect induced studies on KVO which involves creating proton-compensated cation vacancies or schottky defects might help in achieving the theoretically possible capacities in these materials.

4.3 Alkali-earth metal ion hexavanadates

Alkali-earth metal ion hexavanadates, CVO and SVO from the group of alkali earth metals are chosen for study in section(Figure 4.23). The name for the hewettite family comes from CVO which is named as hewettite for CVO.9H\(_2\)O and metahewettite for CVO.3H\(_2\)O. CVO is found in natural abundance while SVO is synthetically prepared. CVO and SVO : the alkai-earth metal ion hexavanadates studied in this section are both synthesized in laboratory and the details of the synthesis are mentioned in section 3.1.2.2 and 3.1.2.3. The valency of the pillar ions in this case is +2, as compared to +1 in case of alkali metal ion hexavanadates. The alkali-earth metal ions(Ca\(^{+}\) and Sr\(^{+}\)) are also known as pillar–ions hold the layers intact and prevents the structure from collapse during stress caused during the electrochemical process of lithium insertion and de-insertion. Further in this section, three different alkali metal ion hexavanadates : CaV\(_6\)O\(_{16}\) and SrV\(_6\)O\(_{16}\) would be studied in detail for their physical, structural and electrochemical properties.
4.3.1 CaV$_6$O$_{16}$ (CVO)

Various vanadium compounds like V$_2$O$_5$\cite{88,92}, VO$_2$(B)\cite{96}, LiV$_3$O$_8$\cite{14,95,104}, Na$_2$V$_6$O$_{16}$nH$_2$O\cite{41,44}, K$_2$V$_6$O$_{16}$\cite{147,148}, Li$_3$V$_6$O$_{16}$\cite{106} has been of immense interests as cathodes in Lithium ion batteries and anodes in aqueous rechargeable lithium ion batteries due their open structure, the high valence state of vanadium and the ability to withstand stress during high rate operation. Even though the theoretical capacities of these vanadium compounds are in the range of 300-500mAh g$^{-1}$, the practically achievable capacities are always lower i.e. 45mAh g$^{-1}$ for V$_2$O$_5$, 120mAh g$^{-1}$ for LVO and 130mAh g$^{-1}$ for NVO. Also, these vanadium compounds typically lose almost 50% of their initial capacity at the end of 100cycles due to the inherent structural stability issue and the vanadium dissolution. In hewettite/hexavanadates structures, chains of VO$_6$ octahedra and linked by opposite corners imparting fibrous nature to these compounds. The (VO$_5$)$_n$ chains are joined laterally or by sharing inclined octahedral edges forming highly distorted structure with V-O bond varying in distances from 1.55Å to 2.7Å, sometimes giving them an appearance of a five-fold square pyramid. Open channels are left between the sheets of V$_6$O$_{16}^-$ or in the V-oxide networks, which are
occupied by cations and water molecules. The cations occupying these channels act as pillars and also help stabilize the charge formed in the Vanadium-Oxide framework.\[^{84}\]

By varying the pillar ions, one can tweak various properties of these materials like the morphology, crystal structure, interstitial distances, aid in creating defect vacancies which lead to different electrochemical performances. It can be clearly seen that by replacing sodium ion with the lithium ion, NVO performs slightly better in terms of capacity and cycling stability compared to LVO, which replacing the sodium ions with a potassium ion in the structure results in lower capacity but with higher cycling stability. This could be because of increased interstitial volume resulting in increased separation of oxygen anions within the V-O framework from the inserted lithium during the charge/discharge process resulting in higher energy required by these lithium ions to intercalate. The present study extrapolates the study further by changing these alkali-metal ion (Li\(^+\) and Na\(^+\)) with a divalent alkali-earth metal ion (Ca\(^{2+}\)) to understand the changes in crystal structure, morphology and electrochemical performance.

CaV\(_6\)O\(_{16}\).\(n\)H\(_2\)O (CVO) – calcium hexavanadate or more commonly known as hewettite for its structure with nine molecules of water in the crystal and metahewettite with three molecules of water in its formula unit. Its is a very commonly found, naturally occurring mineral, vanadium oxide bronze found in mining sites at Colorado plateau, South Africa and in Utah salt lake. In its natural form it appears as bright reddish brown in colour and looks fibrous. The fibrous character of this mineral can be attributes to the chains of VO\(_6\) octahedra linked by opposite edges. The distance between the opposite vertices of the VO\(_6\) octahedron is 3.6\(\text{Å}\) which is the fiber period. Other forms of hexavanadates like barnasite(NVO), potassium hexavanadate also occur commonly with this mineral CVO and is came to known as hewettites group of minerals.

Various methods for the synthesis of calcium hexavanadates have been reported so far, below table describes the approaches and methods used for the synthesis of CVO.
<table>
<thead>
<tr>
<th>No.</th>
<th>Materials</th>
<th>Reactants</th>
<th>Synthesis method</th>
<th>Author &amp; Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca$_{0.5}$V$_3$O$_8$ rods</td>
<td>Li$_{1.1}$V$_3$O$_8$ with Ca(NO$_3$)$_2$•nH$_2$O</td>
<td>Aqueous based solution (~15-20 hours)</td>
<td>S Jouanneau, et al $^{[109]}$</td>
</tr>
<tr>
<td>2</td>
<td>CaV$<em>6$O$</em>{16}$•3H$_2$O nanoribbons</td>
<td>Metavanadates with Sodium dodecyl sulphonate SDS</td>
<td>Hydrothermal</td>
<td>Lingfen Kong et al $^{[110]}$</td>
</tr>
<tr>
<td>3</td>
<td>CaV$<em>6$O$</em>{16}$ flakes</td>
<td>V$_2$O$_5$(0.03) + Ca(OH)$_2$(0.02)</td>
<td>Hydrothermal(10 days)</td>
<td>S Jouanneau, et al $^{[111]}$</td>
</tr>
<tr>
<td>4</td>
<td>CaV$<em>6$O$</em>{16}$•3H$_2$O compressed rods</td>
<td>Calacium orthovanadate(obtained by calcification of sodium orthovanadate) with HCl</td>
<td>Hydrolysis(&gt;24 hours)</td>
<td>LI Lanjie, et al $^{[112]}$</td>
</tr>
</tbody>
</table>

In this thesis, CaV$_6$O$_{16}$•nH$_2$O is synthesized as per the procedure mentioned in section 3.1.2.2. The reaction that occur during the formation of CaV$_6$O$_{16}$•nH$_2$O can be classified into the following steps. When Ca(OH)$_2$ and V$_2$O$_5$ are mixed and heated in solution phase to yield CaV$_6$O$_{16}$•nH$_2$O: Ca$^{2+}$ inserts into the V$_3$O$_8$- layers forming the CaV$_6$O$_{16}$•nH$_2$O.

Figure 4.24 provides information about the physical appearance and morphology of CVO. Physically, CVO looks like a orange brown powder(Figure 4.24.a) and when observed under a transmission electron microscope and field emission scanning electron microscope, CVO looks like a bundled 2-D belts with lateral alignment and has a length >3 µm and a width of ~150nm.(Figure 4.24.b and Figure 4.24.e).
The aspect nature of these CVO belts are higher than 20. From the HR-TEM image (Figure 4.24.b) the obtained lattice fringe pattern (Figure 4.24.c) and selected area electron diffraction (Figure 4.24.d) of the CVO bundled lamellar belts(blb) reveal the presence of several layers of lamellar crystals, which lead to the formation of an extended belt type of morphology. The bundled lamellar belt(blb) morphology was further confirmed using an AFM (Figure 4.24.f). Micro-structured crystalline belt morphologies are quite rare in materials which make them very much suitable as electrodes in batteries due to their higher surface areas making them useful for high rate applications.
The XRD patterns (Figure 4.25.a) can be fully indexed to the crystal structure of CaV$_6$O$_{16}$ ($P_{12_1}/m_1$, JCPDS 33-317) via Rietveld refinement (R factor <0.05), without the presence of any impurity peaks. The XRD data shown in Figure 4.25.a for CVO can be reasonably indexed to the observed selected area diffraction pattern in Figure 4.24.d. The sheets arrange to form a monoclinic layer structure with a space-group symmetry of $P_{12_1}/m_1$ and the characteristic dimensions of the layers are $a=12.167\text{Å}$ and $b=3.505\text{Å}$ (fiber axis) can be clearly seen as shown on the SAED pattern. The third “C” dimension and $b$ angle will depend primarily on the nature and amount of interlayer cations and water molecules. In this case the $c$ axis has a value of 11.24Å and $\beta$ angle has a value of 96.418°. Figure 4.25.b. shows the crystal structure of CVO drawn from the refined XRD pattern of CVO.
Thermal Analysis: To study the water content within CVO

To study the water content in various samples of hewettites, two approaches were followed.

Crystal volume: The lattice parameters obtained after Topas refinement were used to calculate the crystal volume. Once the unit cell is known, the (Sub)cell will have 6 vanadium atoms per layer in the hewettite-group minerals. These vanadium counts will establish the unit cell formula and its volume should be consistent with the volume of the layer which is $275\text{Å}^3$ for a hewettite $\text{V}_6\text{O}_{16}$ layer plus interlayer materials like $\text{H}_2\text{O}(23\text{Å}^3)$ and/or for alkali/alkali earth metals like Calcium$(10\text{Å}^3)$. Hence by knowing the crystal volume of the sample via TOPAS refinement, and with the above cell
volume values of V₆O₁₆, for alkali/alkali earth metals and water, one can easily calculate the amount of water in the crystal which forms the water of crystallization in these hewettites.

In our case, the crystal volume is 476.4365 Å³. Hence, by calculation, the total number of all water molecule is Total volume of cell(476.4365 Å³) – volume of V₆O₁₆ layer(275 Å³) – volume of calcium ion(10 Å³) / 23 = 8.3. Thereby, the total water molecule is 8.3 and the formula of the compound is CaV₆O₁₆. 8.3H₂O, which is similar to that of a hydrated hewettite(CaV₆O₁₆.9H₂O) under room temperature.

To study the conversion of hewettite to meta-hewettite, CVO was dehydrated by heating at 100°C for 24 hours in vacuum conditions before performing TGA, to determine the water content left in the structure.

**Thermal gravimetric (TG) analysis:**

Thermal gravimetric (TG) analysis is done using TA-TGA Q500 instrument under N₂ atmosphere. The amount of water which has evaporated from the sample after heating it to a particular temperature divided by the molar mass of the water will give the number of moles of water. The ratio of this moles of water to the moles of CVO(weight of CVO left after the evaporation of water divided by the CVO’s molar mass) will give the number of water molecules attached to a formula unit of CVO crystal. The type of attachment of H₂O to the crystal can also be studied to an extent with TGA. There could be three kinds of water within a crystal, they are, free water, hydrogen bonded water and metal-coordinated water.

Initial samples after de-hydration in vacuum and before performing TGA had a mass of 11.737mg and after the TGA(Figure 4.26.a) one can observe a reduction in weight by 13.14% which is of water molecule and hence from the calculations, it can be seen that CVO has 5.053 molecules of water per CVO sample. Thereby the formula of CVO obtained is CaV₆O₁₆.5.05H₂O.

To get further information about the surface composition and to understand the redox processes, ex-situ X-ray photoelectron spectroscopy (XPS) data were collected from PerkinElmer PHI 5100 system using Al Kα X-ray source with passing energy of 20 eV. Samples were sputtered with argon inside the XPS chamber to remove surface contaminants. Analysis were performed using CasaXPS software (Version 2.3.15).
XPS analysis of all the hewettites were done to study their chemical constituents. XPS analyses were also carried out on after-cycled samples of CVO and CVO:TiO$_2$ composites to study the loss of capacity during long-cycling.

**Figure 4-27** a) XPS spectra of the O$_2$p peak in CaV$_6$O$_{16}$·5.05H$_2$O (CVO-1) belts. Inset: Red dash line shows the XPS for O$_2^-$ in the CaV$_6$O$_{16}$·5.05H$_2$O nanobelts. Blue dotted lines shows the XPS for O$_2^-$ ions in the oxygen-deficient regions. b) Raman Spectroscopy for CVO, V$_2$O$_5$ and Ca(OH)$_2$

The XPS measurements further confirm the formation of CaV$_6$O$_{16}$·5.05H$_2$O. Figure 4.26.b shows a survey spectrum of the sample and a typical high-resolution spectrum of Ca(2p). No obvious impurities could be detected in the sample. In the survey spectrum (Figure 4.26.b), the binding energy values 347.2 eV, 531.0 eV and 517.6 eV are for Ca(2p), O(1s) and V(2p), respectively. In Figure 4.26.d, the binding energy values 344.5 eV and 350.6 eV are for Ca$^{2+p_{3/2}}$ and Ca$^{2+p_{1/2}}$; respectively. The binding energy values 346.6 eV and 350 eV as seen in Figure 4.26.c, corresponds to the vanadium peaks in CVO. Quantification of the XPS peak intensities gives that the sample’s surface stoichiometry of Ca:V:O is about 1:6.09:20.26, which is consistent with the formation of the CVO phase. A multicomponent peak fitting using a guasssian simulation of the O1s peaks(Figure 4.27.a) obtained from the XPS of CVO compound is used to study the oxygen deficiency in the CVO crystal structure. The red dash line from Figure 4.27.a shows the presence of fitted peaks where the lowest binding energy peak at 528.7 eV represents the one for O$_2^-$ ions in CVO while the other peak (Blue dotted line) at higher binding energy of 531.3 eV represent the O$_2^-$ ions in the oxygen
defect vacancies within the CVO. Two electrons from the oxygen vacancy can occupy the 4d orbitals of the two vanadium atoms causing them to be in a partially reduced state, making them electrochemically active. As there are 8 kinds of oxygen atoms in a unit cell, there is a possibility of 8 type of oxygen vacancies in the super cell. Also from Figure 4.27.b, it can be seen that there is a shift in the peak in the case of CVO in comparison to V$_2$O$_5$.

Figure 4-28 (a) Cyclic voltammograms (CV) of CVO BLBs at 2mVs$^{-1}$ in three-electrode configuration (vs SCE) from -1.0 to 0.0 V. (b)Galvanostatic charge-discharge profiles of CVO BLBs in three-electrode configuration(vs SCE) from -1.0V to 0.0V in 3M aqueous solution of LiCl, with platinum wire as the counter electrode at a current density of 0.5A g$^{-1}$

CVO has its reduction peak at -0.4V vs SCE and oxidation peaks at approximately -0.3V vs SCE.(Figure 4.28.a) Lithium intercalation occurs during the reduction reaction while lithium deintercalation occurs during the oxidation process. At the redox peaks, maximum lithium inserts and de-inserts to and from the material resulting in higher number of electrons at those potential and hence one can observe a flat curve at that peak potential during the corresponding galvanostatic cycling.(Figure 4.28.b)

Further, the galvanaostatic charge/discharge performance of CVO as anode is shown in Figure 4.28.b. using three electrode configuration at a current density of 0.5Ag$^{-1}$. CVO as anode gave an initial charge capacity of 180mAh g$^{-1}$ and discharge capacity of 240mAh g$^{-1}$(All the specific capacity values are calculated with respect to the mass of the active material). When compared to other commonly used anode materials, CVO
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displays a much higher capacity compared to LiV$_3$O$_8$, TiP$_2$O$_7$ and LiT$_2$(PO$_4$)$_3$ in ARLBs which gives a discharge capacity of 40mAh$^{-1}$, 100mAh$^{-1}$ and 80mAh g$^{-1}$ respectively.$^{[14,16,142,143]}$ The capacity displayed by CVO is so far the highest capacities reported for an anode material in aqueous rechargeable lithium ion battery.

Further, galvanostatic cycling was performed to study if CVO is able to maintain this high capacity displayed during its initial cycle during the long cycling. The columbic efficiency of CVO is $\sim$90%.(Figure 4.29). During the initial 30 cycles, the capacity of CVO falls rapidly to 140mAh$^{-1}$ (30th cycle) from 240mAh$^{-1}$ (1st cycle). At the end of 100 cycles CVO displays a capacity of $\sim$120mAh$^{-1}$, which is almost 50% of its capacity at the 1st cycle. This fall in capacity of CVO has been investigated using XPS, XRD and FE-SEM to understand the underlying mechanism that happens during the galvanostatic cycling. Also, charge storage mechanism occurring within the CVO is studied using Randles-Sevcik equation.

Figure 4-29 Cycling performance and columbic efficiency of CVO as anode in ARLB at a current density of 0.5 mA g$^{-1}$
From Figure 4.30 it is clear that the charge storage mechanism is predominantly bulk storage (\(~88\%\)) but there is also some significant contribution of surface capacitance (\(~12\%\)), which helps in stable operations during faster charge-discharge and thereby higher power densities.

**Figure 4-30** Peak current vs square root of scan rate with peaks a and b as labeled in Cyclic voltammetric plot shown in the inset.

Higher bulk storage indicates lower energy required by lithium ions to intercalate within the interstitial sites within the crystal while pseduocapacitive behaviour helps in faster movement within the ion channels to reach specific interstitial sites via hoping mechanism of lithium ions which swings via the medium of negatively charged oxygen ions within the V-oxide framework created due the oxygen deficient vacancies confirmed by V-O XPS plot shown in Figure 4.27.a.

It is this pseudocapacitive charging which facilitates low energy \(\text{Li}^+\) pathways from surface to the subsurface \(\text{V}_6\text{O}_{16}^-\) interlayer sites, which increases the rate capabilities of CVO BLBs.\(^{146,149}\) Higher contribution from bulk storage indicates that it is a very good battery material with better rate capabilities.
4.3.1.1 Addition of TiO$_2$ Nanofibers & Nanopowder into CVO

V$_2$O$_5$ is the precursor material which is used to synthesize CVO and even though insertion of calcium and control of water molecules within the layers have significantly improved the intercalation capacity of the compound in comparison to V$_2$O$_5$, the cycling stability is still an issue.

For commercial level application, it is very crucial that the material maintains a reasonably stable capacity on long cycling. Even though, CVO has a very high initial capacity, the capacity fading that occurs on long cycling and the sudden drop in capacity during the initial 30 cycles poses a challenge for its direct use as anode in ARLBs. Hence, it is decisive to understand in detail the capacity fading that occurs in CVO and prevent it. It is proven that addition of TiO$_2$ into orthorhombic V$_2$O$_5$ improves its lithium ion intercalation performance and cyclic stability. Lee and Cao have performed a detailed study on the preparation and intercalation properties of V$_2$O$_5$/TiO$_2$ mixture.$^{[150]}$ Also, various studies on the technique by which TiO$_2$ is incorporated within the V$_2$O$_5$ is explored and it has been attributed that such enhancement in cycling stability is due to the changes in microstructure, crystallinity, lattice structure and intercalation forces between adjacent layers in V$_2$O$_5$.\cite{151} But the real mechanism by which TiO$_2$ addition aids in the Li-intercalation property of is still V$_2$O$_5$ not clear and is in debate.

Hence, deriving the inspiration from studies performed by Lee, Cao and others, TiO$_2$ addition into CVO has been attempted to study its influence on CVO’s cycling performance. Also, an endeavour to understand the in-depth mechanism that occurs within the CVO’s crystal during the charge/discharge cycling that causes the irreversible capacity loss and how TiO$_2$ addition influences the lithium insertion behaviour by preventing the capacity fading within the CVO metahewettite crystal has been made.
Figure 4-31 Galvanostatic cycling of CVO and CVO-TiO$_2$ mixtures for 100 cycles in 3M LiCl at 0.5Ag$^{-1}$ with platinum electrode and SCE as counter and reference electrode. (Inset: 30th cycle FE-SEM images of CVO and CVO-20% nano-powder TiO$_2$

Anatase nano-powder(NP) TiO$_2$ and rutile TiO$_2$ is used for the study. Commercial form of anatase NP is obtained from Sigma-Aldrich(100nm). Rutile form of the material is obtained by heat-treating the anatase NP TiO$_2$ at 650C. 10% and 20% of both Anatase NP and rutile TiO$_2$ are physically mixed with CVO, respectively and grinded using a mortar and pestle for an hour so that a proper mixture of the materials are formed. After which electrodes are prepared using these mixtures in the standard electrode preparation methods as mentioned in section 3.3.1. A galvanostatic cycling experiment was performed in half cell configuration as per the experiment set-up mentioned in section 3.3.6.
Figure 4.31 shows the galvanic cycling of anatase nano-powder TiO$_2$, rutile TiO$_2$, CVO-anatase TiO$_2$(10%), CVO-anatase TiO$_2$(20%), CVO-rutile TiO$_2$(10%), CVO-rutile TiO$_2$(20%) and CVO. It can clearly be seen that addition of 10% anatase TiO$_2$ nanopowder improves the cycling stability of CVO but the initial capacity drops to $\sim 225\text{mAh}^{-1}$ from $\sim 240\text{mAh}^{-1}$(CVO-blank). This decrease in capacity can be accounted for the reduced interlayer space due to the steric hindrance caused by TiO$_2$. Anatase and rutile TiO$_2$ by itself has very less capacities and doesn’t account for the bulk storage based capacities in the CVO-TiO$_2$ mixtures.

Addition of 10% rutile TiO$_2$ into CVO gives a cycling efficiency to about 55% at the end of 100 cycles from its initial capacity of 200mAh$^{-1}$, but the initial capacity of this mixture is $\sim 16$% lower compared to the initial capacity offered by blank CVO($\sim 240$mAh$^{-1}$). Increasing the amount of rutile TiO$_2$ to 20% further decreases the initial capacity to 175mAh$^{-1}$ but cycling efficiency improves to $\sim 64$% at the end of 100$^{th}$ cycle compared to its initial capacity.

Addition of 10% anatase TiO$_2$, gives an initial capacity of 225mAh$^{-1}$ which is $\sim 6.25$% lower than the capacity of blank CVO($\sim 240$mAh$^{-1}$) but the cycling efficiency is 72% at the end of 100 cycles, whereas the cycling efficiency of CVO(blank) is 45%, which is a good indication that anatase TiO$_2$ helps in stabilizing the capacity of CVO. Addition of 20% anatase TiO$_2$ nanopowder gives an initial capacity of 200mAh$^{-1}$ and cycling efficiency of 54.5% at the end of 100 cycles with respect to the 1$^{st}$ cycle and the cycling efficiency is practically 100% from 20$^{th}$ cycle to the 100$^{th}$ cycle.

The inset FESEM images shown in Figure 4.31, indicates that there is a significant impact of cycling on the morphology and structure of CVO. At 30$^{th}$ cycle, the morphology of the CVO bundled belts have significantly undergone a collapse while for the TiO$_2$ mixed CVO has maintained an intact morphology even at 30$^{th}$ cycle, which clearly shows that TiO$_2$ plays a significant role in maintaining the structural stability during repeated charge/discharge cycles. Hence, it can be concluded that optimum addition of 10% anatase TiO$_2$ nanopowder greatly improves the cycling efficiency and helps maintain an overall stable higher capacity during long cycling.
4.3.1.2 Fundamental studies on CVO & CVO-TiO\textsubscript{2} composite using XPS to understand the decrease in electrochemical performance on cycling.

**Figure 4-32** XPS plot for Calcium ion within the CVO samples after 1st cycles, 25th cycle and for the 50th cycle of CVO-TiO\textsubscript{2} sample.

Movement of lithium ions in and out of the V\textsubscript{6}O\textsubscript{16} framework, creates stress within the crystal due to frequent volume changes, the calcium ions also move out of the crystal along with the lithium transport. This starts from 1\textsuperscript{st} cycle and hence, one can observe a slight decrease in calcium intensity peaks from Figure 4.32. As seen clearly from Figure 4.32, after 30 cycles, most of the calcium ion which acts as a pillar ion between the layers of V\textsubscript{6}O\textsubscript{16} is removed from CVO crystal which leads to the collapse of CVO’s structure leading to cycling instability and accelerating the vanadium dissolution. But in CVO-TiO\textsubscript{2} sample one can see that calcium ion is preserved even at the end of 50 cycles and the intensity of the calcium peak in CVO-TiO\textsubscript{2} is higher compared to that of after 1\textsuperscript{st} cycle CVO sample, which indicate that TiO\textsubscript{2} plays a major role in helping buffer the stress during the lithium diffusion and hence prevent calcium flushing out.
Figure 4-33 XPS plot for V-O within the CVO samples after 1st cycles, 25th cycle, 50th cycle, 75th cycle and for the 50th cycle of CVO-TiO₂ sample.

From Figure 4.33, it can be seen that vanadium dissolution starts from 1st cycle onwards along with the calcium release from the structure and at 100th cycle most of the vanadium is flushed out of the CVO material and gets dissolved into the electrolyte. While in CVO-TiO₂, the vanadium dissolution is heavily reduced and its intensity peak at the end of 50th cycle is comparable to that of blank CVO’s 1st cycle. Hence, it clearly shows that addition of TiO₂ into CVO reduces bleaching out of calcium ions from the V-O framework and thereby inhibiting vanadium dissolution and maintaining an intact structure during long galvanic cycling, which ultimately results in a better galvanic cycling efficiency.

4.3.2 SrV₆O₁₆ (SVO)

From our earlier background studies on finding a potential anode material for ARLBs, we found that vanadium oxides shows greater promise in terms of theoretically achievable capacities and faster insertion and extraction of lithium due to the layered and pseudo-layered structure of its compounds and bronzes. Among them, LiV₃O₈ is
one of the most studied once where it can store lithium in both its tetrahedral and octahedral sites. The lithium ions within the interlayer at the octahedral sites are immobile, only the ones at the tetrahedral sites between the inter-layers participate in the insertion/extraction process. This is one of the motivation behind the replacement of Li$^+$ from LiV$_3$O$_8$ and its similar supercell structures with other cations like Na$^+$, K$^+$ and Ca$^{2+}$ to develop new anode material for ARLB and as a cathode material LIB systems.

Various electrochemical studies on Li$_{1+x}$V$_3$O$_8$, Na$_{1+x}$V$_3$O$_8$, KV$_3$O$_8$, CaV$_3$O$_8$ and their super-cells were done in lithium ion batteries to understand the mechanism of lithium intercalation and de-intercalation in these materials and to develop them as a potential cathode material.\[40,82,99,109,147,152–154\]

Na$_2$V$_6$O$_{16}$ and CaV$_6$O$_{16}$ has been widely studied by mineralogists as a very interesting vanadium bronze material which has a natural fibre like structure and had bright reddish appearance. Many researchers have reported both the synthesis and physical characterization of Li$_3$V$_6$O$_{16}$, Na$_2$V$_6$O$_{16}$, K$_2$V$_6$O$_{16}$, CaV$_6$O$_{16}$. (Section 2.2.1.4). Various morphologies of Na$_2$V$_6$O$_{16}$ and K$_2$V$_6$O$_{16}$ have been studied for its potential application as room temperature ferromagnetic semi-conductors.\[45,144\]

Vivek et.al\[82\] has demonstrated that the use of Na$_{1.16}$V$_3$O$_8$ as a potential anode and cathode material in ARLB system and developed a full cell out of them which gave a capacity of $\sim$152.42mAh$^{-1}$ at 5Ag$^{-1}$, while Zhou et.al\[41\] has demonstrated the use of Na$_2$V$_6$O$_{16}$,0.14H$_2$O as an anode material in the ARLB system with a capacity of 122.7mAh$^{-1}$ at 60mA$^{-1}$. Vivek et.al\[106\] reported the synthesis and electrochemical performance of Li$_3$V$_6$O$_{16}$ in ARLBs as a potential anode material which gave a capacity of 120mAh$^{-1}$ at a current density of 500mA$^{-1}$. Replacing Li$^+$ from the $\frac{M^{2+}_x V_6 O_{16}}{x}$ framework to sodium ion, not only increased the capacity but also increased its rate capability.\[44,82\]This is one of the motivation that led us to further explore replacement with other cations like K$^+$, Ca$^{2+}$ and Sr$^{2+}$ into $\frac{M^{2+}_x V_6 O_{16}}{x}$ to understand the variation in maximum capacity achievable, cycling stability and rate performance. The results of the electrochemical performance of K$_2$V$_6$O$_{16}$ (KVO) and CaV$_6$O$_{16}$(CVO) has been presented in section 4.2.3 and 4.3.1 respectively. KVO has better cycling stability in comparison to CVO while CVO presents with a much higher capacity ($\sim$3X) in comparison to KVO. Further charge storage mechanisms of both the compounds were
performed to method by which KVO and CVO stores charge which co-related with its electrochemical behavior. Hence, it is explicit that replacement of pillar ion within \( \frac{M_2^{x^+}}{V_6O_{16}} \) gives a definite enhancement or suppression of certain electrochemical properties. Proper knowledge of this could help anyone design specific anode materials by tuning the interlayer cation for user-specific application.

Further in our pursuit to study the effect of cation replacement into \( \frac{M_2^{x^+}}{V_6O_{16}} \), we replace the interlayer cation with strontium ions to form \( SrV_6O_{16} \). While synthesis of various hexavanadates like \( Li_3V_6O_{16} \), \( Na_2V_6O_{16} \), \( K_2V_6O_{16} \), \( CaV_6O_{16} \) has been reported in various research articles\(^{[42-45,106,109,144]}\), there has been so far no reports on the synthesis of \( SrV_6O_{16} \) as per our knowledge.(section 2.2.1.4). We hereby report for the first time the synthesis of \( SrV_6O_{16} \) 3-D network of fibers as per the details mentioned in section 3.1.2.3.

Figure 4.34 SVO: a) Actual powder, b) HR-TEM image, c) lattice fringe obtained from selected area, d) SAED pattern, e) and f) FE-SEM image.

Figure 4.34 provides information about the physical appearance and morphology of SVO. With naked eyes, SVO looks like a reddish brown powder(Figure 4.34.a) and when observed under a transmission electron microscope and field emission scanning
electron microscope, SVO looks like a 3-D network of long fibers with length >35 µm and a width of ~0.14 µm. (Figure 4.34.b, Figure 4.34.e and Figure 4.34.f). The aspect nature of these SVO belts are higher than 250, which are higher than any other hewettite materials reported so far. From the HR-TEM image (Figure 4.34.b) the obtained lattice fringe pattern (Figure 4.34.c) and selected area electron diffraction (Figure 4.34.d) of the SVO fibers reveal the presence of several layers of lamellar crystals, which lead to the formation of long fibrous morphology. Usually such micrometres long fibers are produced by electrospinning, while in this work, we have grown crystalline bundled fibers via simple chemical sol-gel method with diameters in nano-dimension and lengths in micro-dimensions. Such fibrous materials has high applications as electrodes in batteries due to their higher surface area to volume ratios, making electrode/electrolyte contact better and help in faster transport of lithium ions and electrons through them making them useful for high rate applications. [82,94,100,106,139,145]

Better connectivity due to the bundled nature of the fibers and 3-D interconnectivity also ensures its ability to buffer the stress produced in them due to volume changes during the cycling process, thereby preventing structural collapse and ensure stable performance on long cycles of charge/discharge.

Figure 4-35 (a) Rietveld refinement of X-ray diffraction (XRD) pattern; (b) crystal structure of KVO belts

Further, powder XRD pattern of SVO was collected and evaluated using rietveld refinement to study the crystal structure. As SVO has been studied for the first time...
here, there are no reference structures for SVO, hence CVO was used as the base reference structure with its calcium ions replaced by strontium. All the reflection peaks of the XRD patterns (Figure 4.35.a) can be fully indexed to the monoclinic crystal structure of “Sr-replaced” CVO compound (P121/m1, JCPDS 33-317) via Rietveld refinement, without the presence of any impurity peaks, thus confirming our prediction that CVO and SVO shares a similar structure. From, the sharp peak intensity of the XRD patterns, it can be clearly seen that SVO fibers are highly crystalline in nature. Further single crystal XRD studies will help in better understanding the lattice parameters and crystal cell structure of SVO(Figure 4.35.b).

**Figure 4-36** a) Cyclic voltammograms of SVO as anode in three electrode configuration (vs SCE) from -1.2 to 0V at scan rate of 0.5mVs⁻¹ and 2mVs⁻¹. b) Galvanostatic discharge/charge profiles of LVO in 3M LiCl aqueous solution, in three electrode configuration (vs SCE) from -1.2 to 0V, at current density of 0.5 mA g⁻¹.

SVO has its reduction peak at -0.6V vs SCE and oxidation peaks at approximately -0.3V vs SCE.(Figue 4.36.a), which is better than KVO by atleast ~0.25V, hence making SVO a more suitable as a high voltage anode material in comparison to KVO. Lithium intercalation occurs during the reduction anode reaction while lithium deintercalation occurs during the oxidation process.

Further, the galvanostatic charge/discharge performance of SVO as anode is shown in Figure 4.36.b. using three electrode configuration at a current density of 0.5Ag⁻¹.
SVO as anode gave an initial charge capacity of \( \approx 40 \text{mAh}^{-1} \) and discharge capacity of \( 62 \text{mAh}^{-1} \) (All the specific capacity values are calculated with respect to the mass of the active material). When compared to other commonly used anode materials, SVO displays a slightly higher capacity than LiV\(_3\)O\(_8\) (40mAh\(^{-1}\)) and lower capacity compared to KVO, LVO, CVO, NVO, LiTi\(_2\)(PO\(_4\))\(_3\) and LiT\(_2\)(PO\(_4\))\(_3\) in ARLBs which gives a discharge capacity of 72mAh\(^{-1}\), 122mAh\(^{-1}\), 242mAh\(^{-1}\), 152.7mAh\(^{-1}\), 100mAh\(^{-1}\) and 80mAh g\(^{-1}\) respectively.\(^{[22-24]}\) Even though SVO displays a well-defined redox peaks in it cyclic voltammetric experiments, the galvanic charge/discharge curves looks similar to a supercapacitor material.

**Figure 4-37** Peak current vs square root of scan rate with peaks a,b as labelled in Cyclic voltammetric plot shown in the inset.

By fitting voltammetric currents to various sweep rates to appropriate power law relationship given in «Eq.1-3», we can approximately find out the individual contributions of surface-capacitance and bulk lithium intercalation.

From Figure 4.37 it is clear that the charge storage mechanism is very similar to that of KVO which is predominantly surface capacitance (\( \approx 88\% \)) but there is also some
significant contribution of bulk intercalation (~12%), which helps in stable operations during faster charge-discharge and thereby higher power densities. It is this pseudocapacitive charging which facilitates low energy Li\(^+\) pathways from surface to the subsurface \(V_6O_{16}^-\) interlayer sites, which increases the rate capabilities of SVO fibers.

![Graph](image)

**Figure 4-38** a) Cycling performance and columbic efficiency of LVO-1 as anode in ARLB at a current density of 0.5 mA\(g\)^{-1}

Even though the columbic efficiency of SVO is very poor, there is no or very less loss of capacity from its initial 62 mAh\(g\)^{-1}. It maintains a capacity of ~99.8% at the end of 100 cycles from its 1\(^{st}\) cycle. (Figure 4.38)

This unique stability of SVO towards long cycling at high rate of 500 mA\(g\)^{-1} can be attributed to its 3-D interconnected fiber type of morphology along with its pseudocapacitive charge storage mechanism, which opens up multiple lithium ion pathways for insertion into the material.\(^{[146]}\) SVO 3-D network of fibers were synthesized by a single step sol-gel method using vanadium pentoxide(\(V_2O_5\)) as the precursor. Field-emission scanning electron analysis of the materials confirms the formation of 3-D interconnected fibrous morphology with an aspect ratio >250. Half cell electrochemical
studies of SVO, carried out in 3M LiCl aqueous solution, gave a discharge capacity of 62 mA g\(^{-1}\) and an cycling efficiency of \(\sim 99.8\%\) at the end of 200 cycles at an operational current density of 500 mA g\(^{-1}\). Such stable performance for long cycles at high current densities is attributed to its 3-D fibrous network architecture and the pseudo-capacitive behaviour as observed in the charge storage mechanism study. Surface capacitance usually have the advantage of higher power density and stable performance for long cycles but at a compromise of energy density. Such combination of modest capacity with highly stable performance even at high current rates makes SVO an ideal candidate as anode for faster high performance aqueous rechargeable batteries. Further studies like doping of other transition metals into SVO or composite of two or more similar hewettite materials like CVO, NVO with SVO, might help in achieving the theoretically possible capacities in these materials along with providing this superior stability due its ability to handle stress within the structure preventing structural collapse that leads to vanadium dissolution. Such strategies might help in providing cycling stability which is one of the issues in other similar hexavanadates like LVO, CVO and NVO.

4.4 LiMn\(_2\)O\(_4\) Micro-architecture

Spinel lithium manganese oxide (LiMn\(_2\)O\(_4\) or LMO) offers excellent cathode properties for Li-ion rechargeable batteries.\(^{[50]}\) Features such as low production cost, environmentally benign and high electric potentials of LMO makes it one of the most studied material for cathode applications. Various morphological states of LMO’s such as nanoparticles, nanowires and nanorods were investigated previously.\(^{[123,125,127,131]}\) Jayaram et.al\(^{[155]}\) reported extraordinary lithium storage properties of porous LMO hollow nanofibers for Li-ion batteries. Analysis of previous studies elucidate the dependence of morphology, dimensions and porosity on electrode performance of LMO’s in rechargeable batteries.\(^{[156]}\)

When comparing the first generation ARLB’s, the cyclic and rate capabilities have been improved significantly.\(^{[13]}\) In LMO based ARLB’s, different methods like nano-structuring, doping, intermixing with conductive substrates, increasing crystalline nature, changing counter ion of the electrolyte salt (LiCl, Li\(_2\)SO\(_4\), LiNO\(_3\)) can be used for increasing the rate capabilities. In an effort to increase charge capability, Tang et. al reported LMO nanotube as cathodes in ARLB’s which delivers a high capacity of
100 mAh/g at 4.5C with a fair capacity retention.\[157\] Similarly in another study, ARLB’s using two-dimensional LMO sheets with voids delivers a reversible capacity up to 118 mAh/g with less than 7% loss after 10000 cycles.\[114\] For ARLB applications, progress in structural and functional balance such as

a) Particle size optimization and

b) Intact surface morphology could be achieved for LMO in order to improve performance or match performance related to commercially available batteries. Hence achieving sub-micrometer sized hollow nanocrystalline morphology of LiMn$_2$O$_4$ is advantageous which could be expected to shorten Li$^+$ diffusion distance and boost Li$^+$ migration in aqueous electrolytes.

### 4.4.1 LiMn$_2$O$_4$ Microspheres/Nanocubes secondary hybrid structure

Synthesis of spinel LiMn$_2$O$_4$ was achieved by simple multi-step sol-gel synthesis. As synthesized LiMn$_2$O$_4$ displays a hybrid structure in which smaller nano-cubical structures of side lengths less than 100nm have closely packed itself to form a larger micro-spherical structure of diameter greater than 2µm. But small nano-gaps of approximately 10-20nm could be seen in the microspheres due to the inefficient packing of cubes to form the sphere. But the voids are not uniform throughout the sphere and is of non-uniform dimensions throughout the sphere. But all the sphere are of uniform dimension and so are the cubes that form them. Electrochemical performance of LiMn$_2$O$_4$ hybrid structures as cathode are evaluated using an ARLB system in a three electrode configuration with 3M LiCl aqueous solution.

LMO hybrid secondary structure of Nanocubes/Microspheres would be referred as LMO-SNM from herein for the ease of depiction. Preparation of LMO-SNM is performed as described in section 3.1.3.

Figure 4.39 shows the FE-SEM image of as prepared LMO-SNM. Figure 4.39.a shows the LMO-SNM at lower magnification, where one can observe uniform microspheres of approximately 2µm in diameter (Figure 4.39.b). When looked more closely into the individual microspheres at higher magnification (Figure 4.39.c and 4.39.d), one can observe nanocubes of uniform dimensions closely packed to form the cubes.
Figure 4-39  FE-SEM images of LMO-SNM (a), (b): Microspheres; (c) and (d) Nanocubes that build the Microspheres.

The sides of each cubes measure ~100nm in length. Hence roughly one can calculate how many nanocubes would have formed the bulk of the microspheres.

**Equation 4-1**  Volume of spheres \( \cong \) number of cubes(n) \( \times \) volume of individual cubes

\[
\frac{4}{3} \pi \times 1 \times 10^{-18} = n \times 10^{-21}
\]

\[
\therefore n \cong 4186.66
\]
Hence from equation 4-1, it can be seen that the number of nanocubes that form a microsphere is \( \sim 4187 \). This calculation neglects any void spaces created due to inefficient packing of the cubes to form the sphere.

Such hierarchial growth of nanocubes to form the sphere helps in extracting the benefits of both the nano-dimension of cubes which usually helps in insertion of lithium ions in a three dimensional way seamlessly, while the micro-sized spherical morphology helps in withstanding strains caused by volume expansions during electrochemical cycling easily. \(^{[158]}\)

![Rietveld refined X-Ray Diffraction pattern of LMO-SNM](image)

**Figure 4-40** Rietveld refined X-Ray Diffraction pattern of LMO-SNM

Figure 4.40 shows the Rietveld refined XRD pattern of LMO-SNM. The patterns can be fully indexed to the crystal structure of LiMn\(_2\)O\(_4\) (Fd-3mZ, ICSD 50415) via Rietveld refinement (R-Bragg<0.2), without the presence of any impurity peaks. LMO-SNM can be perfectly indexed to crystal structure of LiMn\(_2\)O\(_4\) as shown in Figure 4.40 thereby confirming the formation of pure single phase LiMn\(_2\)O\(_4\).
Figure 4-41 Cyclic voltammetry of LMO-SNM carried out at 0.5 and 2mVs\(^{-1}\) in 3M LiCl in a three electrode configuration with platinum electrode and SCE as counter and reference electrode respectively.

Below table 4.2 lists the potentials(V vs SCE) at which reduction(insertion of lithium ions) and oxidation(deinsertion of lithium ions) occurs during the cyclic voltaammetric experiments of LMO-SNM as seen from Figure 4.41.

**Table 4.2** Redox potential values for LMO-SNM

<table>
<thead>
<tr>
<th>Peak</th>
<th>LMO-SNM [Potential (V vs. SCE)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction (appx.)</td>
<td>0.75</td>
</tr>
<tr>
<td>Oxidation (appx.)</td>
<td>0.85</td>
</tr>
</tbody>
</table>

LMO-SNM delivers a charge capacity of 122mAh\(^{-1}\) and a discharge capacity of 113mAh\(^{-1}\) in an ARLB system.(Figure 4.42)
Figure 4-42 Galvanic charge-discharge of LMO-SNM in 3M LiCl(aq solution) at 500mA g⁻¹ in a three electrode configuration with a potential range of 0-1.1V vs. SCE.

LMO-SNM has a much flat discharge plateau between 1.0V and 0.6V, thereby indicating a much higher energy density (≈78.6Wh/kg) in comparison with LiMn₂O₄ of other morphologies reported for ARLB system. [67,119,123,159]

Figure 4-43 Rate study with Galvanic charge-discharge of LMO-SNM in 3M LiCl(aq solution) at 1C in a three electrode configuration with a potential range of 0-1.1V vs. SCE


LMO-SNM shows good stability during 1000 cycles of charge and discharge at a higher current density of 500 mAg\(^{-1}\). From Figure 4.42 it can be seen that there is only 5% decrease in capacity from its 1\(^{st}\) and 100\(^{th}\) cycle, which proves the commercial viability of using LMO-NMS as a potential cathode material in ARLB system.

It is believed that the hierarchical arrangement of nanocubes to form the microsphere would have resulted in better electrode/electrolyte contact, the nano-gaps from the defects that would have resulted during the close packing of nanocubes gives room for the electrolyte to seep into the bulk of material, thereby giving better diffusion of Lithium ions, also the secondary microsphere architecture constructed by smaller building blocks of the nanocubes helps buffer strain from volume variation that arises during the Li insertion/deinsertion.

Further, a rate study for LMO-NMS is done in 3 electrolytes with anions of different sizes to study the impact of counter-ions on the rate performance of LMO-NMS electrodes. From Figure 4.43 it can be clearly seen that LMO-NMS shows good rate performance in 3M LiNO\(_3\) in comparison with 3M LiCl and 3M Li\(_2\)SO\(_4\). Various factors could have played a role in this behaviour of LMO-NMS in three different electrolytes. Size of an anion and its affinity to the electrode surface area could play a significant role in diffusion of Lithium ions which can affect the rate performance.\(^{[159]}\) Even though the thermochemical radii of SO\(_4^{2-}\) is higher than Cl\(^-\) and NO\(_3^-\). LMO-NMS rate performance in LiNO\(_3\) is better than Li\(_2\)SO\(_4\) and LiCl. The susceptibility of oxidation of a counter ion near the oxidation potential of the LMO-NMS could also play a role in causing side-reactions which might accelerate corrosion of the electrode which may leads to dissolution of manganese and hence decrease accelerate the capacity loses during high current operation. Hence, it is clear that one single factor could not explain the finding and a combination of factors are responsible for such behaviour. Further studies in section 5.3, will discuss and compare the rate performance of LiMn\(_2\)O\(_4\) micro-architectures in three different lithium salt electrolyte to study the affect of counter-ion with respect to morphology on the rate capabilities in ARLB architecture.
4.4.2 LiMn$_2$O$_4$ Hollow Microspheres

![Scheme 4.1](image-url) Schematic representation of LiMn$_2$O$_4$ Hollow microspheres and its electrochemical performance in ARLB system.

Generally, LiMn$_2$O$_4$ (LMO) shows better current response and reversible redox behaviors in organic electrolytes. Herein this chapter, the design and preparation of crystalline porous LMO microspheres (henceforth LMO-HμS) are discussed and demonstrated as a cathode material in ARLB’s with high round trip efficiency with excellent rate and cycling performances in aqueous rechargeable batteries (ARLB’s) as seen in Scheme 4.1. LMO-HμS cathodes in ARLB’s shows initial discharge capacity of 138 mAh g$^{-1}$ at 500 mA g$^{-1}$. Half-cell ARLBs with LMO-HμS as cathodes materials deliver a higher round trip efficiency at the end of 1200 cycles at a current density of 500 mA g$^{-1}$. ARLBs with LMO-HμS as cathodes exhibited excellent rate and cycling performances.

Based on the previous literatures we follow self-template method using MnCO$_3$ microsphere as a sacrificial template for the preparation of LMO-HμS. In a typical experiment 50 mmol of (NH$_4$)$_2$SO$_4$ was added to a mixture of MnSO$_4$.H$_2$O (10 mmol) and NH$_4$HCO$_3$ (100 mmol) in water under stirring to get MnCO$_3$ followed by calcination at 400°C for 5hr to obtain MnO$_2$ microspheres. As prepared MnO$_2$ powder were mixed with LiOH•H$_2$O in a ratio of 2:1.05 respectively in ethanol and allowed the solvent to slowly evaporate. The obtained mixture was then calcinated at 750°C for 10 hours to obtain LMO-HμS.
The readily prepared LMO-HμS was then analyzed using field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS). Figure 4.44.a shows panoramic view of FE-SEM image of LMO-HμS. The formation of porous microspheres of LMO with size ranging from 3.5-5 μm is evident from this image. A high resolution image of LMO-HμS shows spherical morphology and highly porous features. SEM-EDS analysis reveals the presence of elements Mn and O from the surface of LMO-HμS.

Figure 4.45 shows the Rietveld refined XRD pattern of LMO-HμS. Apparently the formation of phase pure cubic spinel structure and characteristic peaks of planes such as [111], [311], [222], [331], [551], [440], [530] and [533] is identified. The patterns can be fully indexed to the crystal structure of LiMn$_2$O$_4$ (Fd-3mZ, ICSD 50415) via Rietveld refinement (R factor<0.055), without the presence of any impurity peaks.
The lattice parameters calculated by the Topas software is 8.1929887 Å, with an average crystal size ~8.19 nm. LMO-HμS can be perfectly indexed to crystal structure of LiMn$_2$O$_4$ as shown in Figure 4.45 thereby confirming the formation of pure single phase LiMn$_2$O$_4$.

**Figure 4-45** Rietveld refined X-ray Diffraction pattern of as-prepared LMO-HμS.

**Figure 4-46** a) Charge storage mechanism using the inverse power law with the peak currents corresponding to the cycles a-d as shown in Figure 3.b; b) Cyclic voltammetric response of LMO-HμS at sweep rates of 0.25, 0.5, 1, 2 and 4 mVs$^{-1}$. 
Cyclic voltammetry (CV) of annealed LMO-HμS as cathode was carried out in three-electrode configuration within the potential range of 0.0V to 1.1V vs. SCE respectively, at a scan rate of 0.25mVs⁻¹, 0.5mVs⁻¹, 1mVs⁻¹, 2mVs⁻¹ and 4mVs⁻¹ to study the redox reactions occurring during the electrochemical processes and is presented in Figure 4.46.b. The redox peak positions of porous microspheres are presented in table 5.7. From the CV, one can observe sharp peaks at redox potentials for LMO-HμS. Therefore, it is estimated higher specific capacity is expected for LMO-HμS.

As shown in Figure 4.47.a, half-cell electrochemical performance of LMO-HμS as cathode was further studied using galvanostatic charge/discharge cycles, in three electrode configuration, at 3C rate. LMO-HμS gave an initial charge capacity of 138mAh⁻¹ and discharge capacity of 132mAh⁻¹. All the specific capacity values are calculated with respect to the mass of the active material. LMO-HμS shows higher reversible capacity of ~132mAh⁻¹ in aqueous solution compared to traditional ARLB based cathode materials, LiFePO₄, LiCoO₂ and LiMnO₂, which delivered a discharge capacity of 94mAh⁻¹, 100mAh⁻¹ and 60mAh⁻¹ respectively.

To elucidate the rate stability of porous microspheres, LMO-HμS were cycled for 10 cycles each at different C rates of 0.1C, 0.2C, 0.4C, 0.8C and 1.6C. Evidently, an increase in C rates from 0.1C to 1.6C, LMO-HμS (Figure 4.47.b) shows good stability. This indicates better rate capabilities for LMO-HμS compared to other morphologies of LiMn₂O₄ reported so far. The observed better kinetics from LMO-HμS may be attributed to the highly organized pores of LiMn₂O₄ microspheres, which can be seen
in Figure 4.44, has resulted in multiple channels for the lithium ion to enter into the material during charge/discharge thereby preventing any stress on the material during operation at different rates. Further long cycling (Figure 4.47c) shows more than 60% capacity retention at the end of 1200 cycles. Such higher capacity retention is because of the ability of the material to handle stress during long cycles of charge and discharge.

Furthermore the overall capacity of LMO-HμS possesses relative contributions from surface capacity and bulk Li-intercalation process. This could be differentiated by fitting voltammetric current at various sweep rates (Figure 4.46a). Based on Randles-Sevcik equation (See Section 2.3), total charge depends exclusively on both capacitance and intercalation process. From Figure S4, the surface capacitance contribution of LMO-HμS was estimated to be ~32% and intercalation was ~68%. Thus the sub-micrometer sized LMO-HμS based ARLBs shows superior performance when compared to previous reports.[114] Even though the intercalation and deintercalation characteristics of LiMn_2O_4 remains similar in both aqueous and non-aqueous electrolytes, well organized crystalline sub-micrometer pores efficiently prevents structure collapse during long cycles of charge and discharge. This renders short Li-ion diffusion pathway which facilitate intercalation process and reduce the polarization.[160]

In conclusion sub-micrometer sized hollow spheres of LiMn_2O_4 (LMO-HμS) were synthesized by sol-gel synthesis followed by heat-treatment. FE-SEM and TEM analysis of the materials confirms the formation spheres of LMO-PμS of approximately 2 micron radii. The new LMO-HμS exhibits high initial capacity of >138 mAhg⁻¹ at high current rate of 500mAg⁻¹. Approximately more than 60% of initial capacity was retained at the end of 1200 cycles even after cycling at a high current density of 500mAg⁻¹. Studies tailoring various porous and nano/micro architectures of LiMn_2O_4 could improve the stability of the structure on long cycling thereby helping in capacity retention.[50,160] We believe that the techniques used in this work could be helpful to develop ARLB systems.
4.4.3 LiMn$_2$O$_4$ Cubes

LiMn$_2$O$_4$ spinel with a 3-D framework of face sharing tetrahedral and octahedral sites or lithium diffusion is a very interesting material proposed by Thackery and is probably the best cathode material for the ARLB system due to its stability during lithium intercalation and de-intercalation.$^{[46,47]}$ Details on the crystal structure for LiMn$_2$O$_4$ is provided in section 2.2.2.2 and various synthesis method for various LiMn$_2$O$_4$ nanostructures are presented in section 2.2.2.3.

Some of the issues that inspire nano-engineering of different LiMn$_2$O$_4$ architectures are:

1. Side reaction with water leading to manganese dissolution.
2. Formation of two cubic phases,
3. Loss of crystallinity and

The above issues causes structural instability and volume changes. The most common solution is to develop non-stoichiometric spinel or doping alternative metal ions, which has not be completely successful due to the compromise in capacity. Therefore, engineering new nano-architectures that can doesn’t compromise on capacity and is able to handle structural stresses well during lithium insertion and extraction are the best available solution to date.

In earlier sections of 4.4.1 and 4.4.2, a hybrid secondary morphology of nanocubes/microspheres and hollow microspheres are discussed. Hence, it would be interesting to learn how micro-cubical structure would influence the electrochemical process of lithium insertion and extraction.
Figure 4-48  FE-SEM images of the as-prepared LMO microcubes

Figure 4.48 shows the FE-SEM image of as prepared LMO. Figure 4.48 shows the LMO at lower magnification, where one can observe uniform micro-cubes of approximately 1µm in side-length. Cubes have assembled to form clusters, hence this morphology should be addressed as clusters of micro-cubes (LMO-CµC) rather than individual cubes. Each cube will have an approximately volume of $1 \times 10^{-18} \text{m}^3$.

Figure 4-49  Rietveld refined X-ray Diffraction pattern of as-prepared LMO-CµC.
Chapter 4

Results

Figure 4.49 shows the Rietveld refined XRD pattern of LMO-µC. The patterns can be fully indexed to the crystal structure of LiMn$_2$O$_4$ (Fd-3mZ, ICSD 50415) via Reitveld refinement, without the presence of any impurity peaks. The lattice parameters calculated by the Topas software is 8.1725 Å, with average crystal volume ~545.84067 Å$^3$.

The cyclic voltammetric plot as shown in the Figure 4.50, shows two redox peaks at approximately 0.82 and 0.98 V vs. SCE respectively. There is a shift of the redox peaks towards the right by 0.15 V when the voltage sweep rate is decreased from 2 mVs$^{-1}$ to 0.5 mVs$^{-1}$.

![Cyclic Voltammetry](image)

**Figure 4-50** Cyclic voltammetry of LMO-ÇµC carried out at 0.5 and 2 mVs$^{-1}$ in 3M LiCl in a three electrode configuration with platinum electrode and SCE as counter and reference electrode respectively.

Repeated cycling for 3 cycles shows some decrease in current for 2 mVs$^{-1}$ but less for 0.5 mVs$^{-1}$. Probably voltage sweep at low rate leads to stabilized redox reaction and hence more stable current than at high voltage sweep rates.
Figure 4-51 Galvanic charge-discharge of LMO-CµC in 3M LiCl(aq solution) at 1C in a three electrode configuration with a potential range of 0-1.1V vs SCE.

Galvanic Charge/discharge curves of LMO-CµC, gives an approximate capacity \( \sim 110 \text{mAh}^{-1} \) (Figure 4.51). The open circuit voltage of the cell is 0.3V vs. SCE. Most of the lithium insertion and extraction happens around 0.6V to 1V vs. SCE, as seen explicitly by a more flatter curve in that region, which is as expected from the cyclic voltammetric plots as in Figure 4.50. From the area under the discharge curve, one can determine the approximate energy density of such a cell. In this the calculated energy density is \( \sim 82 \text{Watt-hour per kilogram} \).
Figure 4-52  Rate study with Galvanic charge-discharge of LMO- CuC in 3M LiCl (aq solution) at 1C in a three electrode configuration with a potential range of 0-1.1V vs SCE.

One of the most important factors that determine the choice of the electrode is its rate capability or the current-density limits till which the material can insert charge stably without any irreversible capacity loss or structural collapse. Along with the electrode, the electrolyte also determines its rate capabilities as the transport of ions into the electrode occurs through the electrolyte and through the electrode/electrolyte interface. The influence of counter-ion of the electrolyte salt has been studied widely in lithium ion batteries but so far there are no reports of its study in ARLB systems. Rate performance study of LMO-CuC in an electrolyte with lithium salt of three different counter-ion (Cl-, NO3-, SO42-) was performed at 0.1C, 0.2C, 0.4C, 0.8C and 1.6C. From Figure 4.52 it can be clearly seen that rate performance of LMO-CuC in Li2SO4 outperform in comparison with LiNO3 and LiCl. This shows that the counter-ion plays a significant role in rate performance of electrode material. Cl- has a possibility to form Cl2 at around 1V vs SCE at higher currents, which could corrode the electrode surface thereby causing a degradation in capacity while cycling at those currents. It is well-known in lithium ion battery chemistries that ionic gel electrolytes with bulkier counter-ions have the best lithium ion transfer co-efficient and hence the conductivity. As the thermochemical radii of NO3-, is lower than the SO42-, the counter-flow of these ions
During the insertion and extraction of lithium restricts its transport, hence the rate performance of $SO_4^{2-}$ is seen to be better than $NO_3^-$ . Hence, proper choice of electrolyte salt is also crucial along with the appropriate electrode to develop a high rate, high capacity and long-cycling stable ARLB system. Various factors are essential to explain the factors responsible for such a behaviour. Further discussion in section 5.3, will compare the rate performance of LiMn$_2$O$_4$ micro-architectures (Cubes, Hollow spheres, Nanocubes/Microsphere hybrid) in LiCl, LiNO$_3$, Li$_2$SO$_4$ electrolyte to study the effect of counter-ion with respect to morphology on the rate capabilities in ARLBs.

4.5 Electrochemical performance of Hewettite heterostructures with LiMn$_2$O$_4$ microarchitectures in full cell ARLB

4.5.1 NVO LMO Full cell

Aqueous rechargeable batteries are sought out as one of the safest and high power energy storage system, which can be used in areas where safety and faster storage and retrieval of power is important. LiMn$_2$O$_4$ has been studied widely as a potential cathode material in ARLB systems. It gives a stable capacity of (~84.6mAh/g) and a cycle efficiency of ~60% at the end of 1000 cycle at 100mA$^{-1}$ current density.$^{[16,18]}$ Recent studies on lithium insertion materials have paid focus on different morphologies which are in nano and micro-dimensions.$^{[17-20]}$ Section 2.4 & 4.2 of this thesis details about the synthesis different morphologies of LiMn$_2$O$_4$ synthesized by a facile chemical method and its electrochemical properties respectively, the inference from which has been the primary motivation to use LiMn$_2$O$_4$ micro-spheres as a suitable cathode for a full cell ARLB system. Similarly, from the study of various hewettites detailed in section 4.1, it is clear that NVO crystalline rods synthesized by one step hydrothermal method using $V_2O_5$ and NaOH has the highest practically achievable capacity with better cycle stability among the alkali-metal vanadium oxide bronzes. Hence, Na$_{2.32}$V$_6$O$_{16}$ has been selected as the anode electrode for the complete cell ARLB architecture.

As Na$_{2.32}$V$_6$O$_{16}$ is cycled between -1.2V to 0V vs SCE, it can be coupled with LiMn$_2$O$_4$ which has an operating voltage window of 0 to 1.1V vs SCE, to operate between 0 to
2.3 V in the full cell configuration, thereby delivering an energy density of ~240Wh/kg at better rate capabilities with aqueous electrolyte which is comparable to the energy densities offered by current lithium ion battery which uses flammable organic electrolytes. Scheme 4.2 shows the schematic representation of the NVO//LMO full cell battery and the pouch cell form of the complete cell. The battery delivers a round trip efficiency of ~50% at the end of 100 cycles at a current density of 500mA g⁻¹.

Scheme 4.2 Schematic representation of the NVO//LMO full cell ARLB with an inset showing the flexibility of the pouch cell

Further, the charge storage mechanism in Na₂.₃₂V₆O₁₆ rods are studied to evaluate its suitability as a potential anode material for aqueous rechargeable lithium ion batteries. Synthesis of Na₂.₃₂V₆O₁₆ rods and LiMn₂O₄ micro-spheres are done as per the synthesis procedure mentioned in section 2.4 and 2.5

All the material, physical characterizations like FE-SEM, TEM and XRD and electrochemical characterizations like Cyclic voltammetry and galvanostatic measurements are done as mentioned in section 4.2 and 4.1

Electrochemical charge/discharge performance of NVO as anode evaluated using galvanostatic charge/discharge cycling (shown in Figure 4.14.a. using three electrode configuration at a current density of 0.5mAh g⁻¹ gave an initial charge capacity of 130mAh g⁻¹ and discharge capacity of 120mAh g⁻¹ (All the specific capacity values are calculated with respect to the mass of the active material). When compared to other commonly used anode materials like TiP₂O₇, LiT₂(PO₄)₃ and LiV₃O₈ in ARLBs which gives a discharge capacity of 100mAh g⁻¹, 80mAh g⁻¹ and 40mAh g⁻¹
respectively\textsuperscript{[14,142,143]}, NVO rods displays a slightly higher anode capacity at a higher negative voltage window. As shown in Figure 4.42. LiMn\textsubscript{2}O\textsubscript{4} microspheres shows slightly higher reversible capacity of \(\sim\)113mAh\textsuperscript{-1} in aqueous solution compared to traditional ARLB based cathode materials, LiFePO\textsubscript{4}, LiCoO\textsubscript{2} and LiMnO\textsubscript{2}, which delivered a discharge capacity of 94mAh\textsuperscript{-1}, 100mAh\textsuperscript{-1} and 60mAh\textsuperscript{-1} respectively.\textsuperscript{[18,116,161]} Similar specific capacities of LiMn\textsubscript{2}O\textsubscript{4} microspheres as cathode and NVO rods as anode makes it an ideal combination for building a complete ARLB.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure453.png}
\caption{(a) Galvanostatic charge-discharge profiles and (b) Specific capacity vs. cycle number of NVO rods as anode and LiMn\textsubscript{2}O\textsubscript{4} microspheres as cathode in 3M LiCl aqueous solution, in two-electrode pouch cell configuration from 0 to 2.3V, at current density of 0.5A\textsuperscript{g}\textsuperscript{-1}}
\end{figure}

To construct a two-electrode pouch cell system, NVO rods is used as anode and LiMn\textsubscript{2}O\textsubscript{4} microspheres as cathode with a glass fiber separator soaked in an aqueous solution 3M lithium chloride as the electrolyte. Then, this pouch cell is subjected to a complete galvanostatic charge-discharge from 0 to 2.3V for hundred cycles. The Na\textsubscript{2.32}V\textsubscript{6}O\textsubscript{16} //LiMn\textsubscript{2}O\textsubscript{4} ARLB system gave an initial discharge capacity of 113mAh\textsuperscript{-1} and a charge capacity of 126mAh\textsuperscript{-1}(Figure 4.53.a). At the end of 100 cycles, the charge and discharge capacities fell to 48mAh\textsuperscript{-1} and 57mAh\textsuperscript{-1} respectively. Even though the capacity rapidly falls during the initial 20 cycles, it gets stabilized after 30 cycles and the coulombic efficiency also reaches \(\sim100\%\) at 30\textsuperscript{th} cycle (Figure 4.53.b)
To conclude, a full cell ARLB constructed using NVO rods as anode and LiMn$_2$O$_4$ microspheres as cathode provided a higher initial capacity of $>113$ mAh g$^{-1}$ at a current rate of 500 mA g$^{-1}$. Approximately 50\% of initial capacity was retained at the end of 100 cycles even after cycling at a high current density of 500 mA g$^{-1}$. Most importantly, the Na$_{2.32}$V$_6$O$_{16}$//LiMn$_2$O$_4$ ARLB shows a higher voltage of 2.3 V and a high rate discharge capability although there is a rapid drop in capacity from the 1$^{\text{st}}$ cycle to 20$^{\text{th}}$ cycle. Similar to LiV$_3$O$_8$, a three step lithium insertion process is expected to occur in NVO, after insertion of 4 Li$^+$ ions into the NVO lattice, phase change occurs from Na$_{2.32}$V$_6$O$_{16}$ to Na$_{2.32}$Li$_4$V$_6$O$_{16}$, these could have resulted in the phase change.\cite{162} Lithium insertion and deinsertion process involves two redox couples, V$^{5+}$/V$^{4+}$ and V$^{4+}$/V$^{3+}$, which results in the combination of the potential difference and the structural change makes the process of intercalation process uncontrollable which leads to amorphization on cycling and thereby capacity loss. Electrode-electrolyte reaction could also be one another reason for the electrode deterioration which is similar to as reported in LiV$_3$O$_8$.\cite{14}

The coulombic efficiency of the cell is as show in Figure 4.54. One can observe that the efficiency increases during the initial 20 cycles from 80\% to around 99\%. This is because, during the initial few cycles, there is a rapid fall in capacity which could be due to the vanadium dissolution in NVO. But after 20 cycles, the irreversible capacity loss achieves a saturation and gets stabilized which results in a stable insertion and extraction of lithium ion from the materials, which leads to better coulombic efficiency.
The capacity retention for the system is poor, which is around 50mAg\(^{-1}\) for the initial few cycles. But the energy density of the cell is around 57.5mWg\(^{-1}\) (calculated from area under the galvanic charge discharge curve). In most of the electronic and wireless sensor network applications that can be used for wearable applications including sports require much less power. From table 6.2, one can easily observe that most of the sensors require power in the range of few micro-watts to ~1milli-watts. Hence, these kind of aqueous rechargeable pouch batteries which has safe chemistries would be of great interest compared to the lithium ion batteries which are unsafe due to its potential fire hazard.

Further studies on NVO by alkali-metal ion replacement could target to improve the energy density and faster charging, while studies tailoring various porous and nano/micro architectures of LiMn\(_2\)O\(_4\) could improve the stability of the structure on long cycling thereby helping in capacity retention.\(^{[21]}\) Such studies would helpful in the development of an ARLB systems with high voltage and superior rate capabilities for many electronics applications.
4.5.2 CVO LMO Full cell

The current section studies the basic problems associated with energy storage and suggest novel methods for smart energy storage using high power aqueous rechargeable batteries made using optimized LiMn$_2$O$_4$ hollow spheres as cathode and CaV$_6$O$_{16}$.7H$_2$O hexagonal flakes as Anode for various electronic & large scale energy storage applications. CaV$_6$O$_{16}$.7H$_2$O flakes synthesized by one step sol-gel method using V$_2$O$_5$ and Ca(OH)$_2$, is used as an anode for the aqueous rechargeable lithium ion battery.

As CaV$_6$O$_{16}$.7H$_2$O is cycled between -1.2V to 0V vs SCE, it can be coupled with materials like LiMn$_2$O$_4$ with operating voltage window of 0 to 1.1V vs SCE, to operate between 0 to 2.3 V in the full cell configuration, thereby delivering an energy density of ~700Wh/kg at better rate capabilities with aqueous electrolyte which is higher compared to the energy densities offered by current lithium ion battery which uses flammable organic electrolytes.

The battery delivers a round trip efficiency of ~62.5% at the end of 100 cycles at a current density of 500mA g$^{-1}$. Further, the charge storage mechanism in CaV$_6$O$_{16}$.7H$_2$O are studied and methods to improve the cyclability are suggested so that it is used a potential commercial anode material in aqueous rechargeable lithium ion batteries.

Individual half-cell performance of CVO-TiO$_2$ and LMO-HS is shown in sections 4.3.1.1 and 4.4.2 respectively. CVO-TiO$_2$ is usually cycled between -1.2 to 0.0V making it suitable as an anode material while LMO-HS is cycled between 0.0 to 1.1V making it a potential cathode material. Combining LMO-HS with CVO-TiO$_2$ to fabricate a pouch results in the development of a ~2.2V battery.

When cycled between 0.0V to 2.2V, CVO-TiO$_2$/LMO-HS gives a capacity of 244Ah$^{-1}$ for the initial cycle and a capacity of 235mAh$^{-1}$ at the 25$^{th}$ cycle. (Figure 4.55).
Figure 4-55 Galvanic cycling of CVO-10%TiO₂ as anode and LMO-HS as cathode at 500mA g⁻¹ in a two electrode system pouch cell architecture from 0.0V to 2.2V vs. SCE in 3M LiCl aqueous solution.

This is the highest energy density reported so far for any aqueous rechargeable lithium ion battery making it competitive enough with the present lithium ion batteries. [71,107,163,164]

Figure 4-56 LMO as cathode and CVO-TiO₂ as anode in 3M LiCl aqueous solution, two-electrode pouch cell configuration from 0 to 2.2V, at current density of 0.5Ag⁻¹.
At the end of 100 cycles, the CVO-TiO$_2$/LMO-HS provides a capacity of 150 mAh g$^{-1}$, which is about 62.5% of its initial capacity but the columbic efficiency is $\sim$80% at the end of 100 cycles (Figure 4.56). This means that there is an irreversible capacity loss which is due to the inherent columbic inefficiency of anode material as discussed in section 4.3.1. Techniques to improve the columbic efficiency could also help in improving the cycling stability thereby making CVO-TiO$_2$/LMO-HS as a potential commercial anode//cathode combination for a full cell ARLB.

4.6 Summary

Structural, chemical, thermodynamic and electrochemical properties of the materials, LVO, NVO, KVO, CVO and SVO, synthesized by a facile low cost process (section 3.1) were studied using various characterization techniques discussed in section 3.2 and 3.3. Electrochemical experiments on the alkali and alkali earth metal ion hexavanadates show promises as superior bulk storage properties for LVO, NVO and CVO and surface storage properties for KVO and SVO. Among all the hexavanadates studied in section 4.2 and 4.3, CVO provides with a higher initial capacity (235 mAh g$^{-1}$) than others but with a rapid fall in capacity for its initial 30 cycles. Further, techniques to stabilize the electrochemical cycling of the materials were experimented and studies to understand the mechanism by which vanadium dissolution occurs were conducted. Further, the charge storage mechanism in CaV$_6$O$_{16}$.7H$_2$O are studied and methods to improve the cyclability (TiO$_2$ addition) are suggested so that it is used a potential commercial anode material in aqueous rechargeable lithium ion batteries. Further, section 4.4 studies various morphologies (Cubes, Hollow Microspheres and microspheres/nanocubes secondary hybrid structures) of LiMn$_2$O$_4$ for its application as cathode in ARLBs. Among all the LiMn$_2$O$_4$ morphologies, LiMn$_2$O$_4$ hollow microspheres provides with higher specific capacity ($\sim$139 mAh g$^{-1}$) and better rate performance under long cycling. Finally, two different architectures of full cell aqueous rechargeable battery were constructed using: a) LiMn$_2$O$_4$ microspheres/nanocubes secondary hybrid structure as cathode and NVO rods as anode; and b) LiMn$_2$O$_4$ hollow microspheres as cathode and CVO-TiO$_2$ as anode. Among both the full cells, CVO-TiO$_2$/ LMO-H$_2$S ARLB delivers a higher stable capacity of 150 mAh g$^{-1}$ at the end of 100 cycles and an initial capacity of 235 mAh g$^{-1}$ at 2.2V vs SCE compared to the NVO/LMO-SNM ARLB, which gives
an initial capacity of 113mAh$^{-1}$ at 2.3V vs SCE and 57mAh$^{-1}$ at 100$^{th}$ cycle. The inherent irreversible capacity loss which occurs during the cycling of CVO-TiO$_2$, could be reason for the loss of columbic efficiency in the anode material. Techniques to improve the columbic efficiency could also help in improving the cycling stability thereby making CVO-TiO$_2$/ LMO-H$_2$S as a potential commercial anode//cathode combination for a full cell ARLB. Further, chapter 5 of this thesis will discuss and study in detail various principles and methods, that could help in further improvements of the hexavanadates and lithium manganese oxide electrodes for ARLB performance. Finally, chapter 6 will show areas where the ARLB batteries developed in section 4.5 of this chapter might find suitable application.
Chapter 5 Discussion

This chapter inter-compares various hexavanadates like LVO, NVO, KVO, CVO and SVO studied in section 4.2 and 4.3 with respect to the effect on substitution of pillar ions from the $V_6O_{16}$ framework on morphology, crystal structure, interlayer water content, electrochemical performance and charge storage mechanism of hexavanadate bronzes (hewettites).

Further, different morphologies of LiMn$_2$O$_4$ are inter-compared for their effect on crystal structure and electrochemical performance. Effect of counter-ion ($SO_4^{2-}$, $NO_3^-$, $Cl^-$) in the lithium salt electrolyte on LiMn$_2$O$_4$ micro-structures' rate performance is discussed and an equation to select the best possible counter-ion for a certain electrode is developed. Finally, a short study on the effect of sintering temperature on the crystallinity, interlayer water content and electrochemical performance of barnesite (NVO) is performed along with the introduction of NVO as both cathode and anode in a symmetric cell architecture.
5.1 Effect of Alkali and alkali-earth metal ion substitution within Hexavanadates

Sections 4.2 and 4.3 has studied various hexavanadates like LVO, NVO, KVO, CVO and SVO. All the electrochemical studies were done in a similar setup and same conditions, while all the materials were synthesized from same precursor and conditions, the only variable here is pillar ion within the hexavanadates and hence understanding how they influence various physical, structural, thermodynamic and electrochemical property of a material will provide insights for improvements. Just with the variation in their pillar ions, these hewettites behave differently in an ARLB system and also their physical and structural properties vary. Pillar ions and the interlayer water present within the $V_6O_{16}^{2-}$ framework determines the third dimension($c$) and the angle($\beta$) of the unit cell for hewettites. Variations in the crystal size affects how it performs under an electrochemical experiment. Section 5.1 studies how the alkali and alkai-earth metal substitution in hexavanadates impacts the morphology, crystal structure, interlayer water content, charge-storage mechanism and the electrochemical performances of hewettites. Understanding the effect of pillar ion with respect to lithium intercalation and charge storage mechanism could help one to tune them for certain characteristics and performances.

5.1.1 On Morphology

When the size and oxidation state of the pillar ions within the $M_2^{x+}V_6O_{16}$ (where, $x=$ valency of alkali metal ion) is altered by selecting those interlayer ions from the group of alkali metals(Li, Na, K) and alkali-earth metals(Ca, Sr), keeping the $V_6O_{16}^{2-}$ framework intact, it is assumed that the interlayer distance would change and so is the third dimension and the angle($\beta$) of the unit cell. Hence, it would be interesting to note how different interlayer ion would impact the morphology of the overall compound, which plays a major role in the electrochemical performance of the material.
Section 3.11, 3.12, 4.2 and 4.3 discusses the synthesis, characterization and performance of $\text{Li}_3\text{V}_6\text{O}_{16}$, $\text{Na}_2\text{V}_6\text{O}_{16}$, $\text{K}_2\text{V}_6\text{O}_{16}$, $\text{CaV}_6\text{O}_{16}$ and $\text{SrV}_6\text{O}_{16}$ from the family of metal vanadium oxides ($\text{M}^{2+}_x\text{V}_6\text{O}_{16}$).

Below is a compilation of the morphologies, sizes and aspect ratio of all the vanadium hexavanadates discussed in this thesis.

**Table 5.1** Summary of the morphologies, sizes and aspect ratio of alkali and alkali-earth metal hexavanadates

<table>
<thead>
<tr>
<th>Material</th>
<th>Pillar ion: Size(pm)</th>
<th>Morphology</th>
<th>Length (appx. in µm)</th>
<th>Width (appx. in µm)</th>
<th>Aspect ratio (appx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVO</td>
<td>Li:90</td>
<td>1-D Rods</td>
<td>4</td>
<td>0.45</td>
<td>8.89</td>
</tr>
<tr>
<td>NVO</td>
<td>Na:116</td>
<td>Bundled rods</td>
<td>0.5-0.7</td>
<td>0.05-0.06</td>
<td>10-14</td>
</tr>
<tr>
<td>KVO</td>
<td>K:152</td>
<td>2D Belts</td>
<td>10</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>CVO</td>
<td>Ca:114</td>
<td>Bundled 2-D belts</td>
<td>3</td>
<td>0.15</td>
<td>20</td>
</tr>
<tr>
<td>SVO</td>
<td>Sr:132</td>
<td>3-D fiber network</td>
<td>35</td>
<td>0.14</td>
<td>250</td>
</tr>
</tbody>
</table>

From the Table 5.1, it can be clearly seen that LVO which has the lithium ion with the smallest size(90 pm) as its pillar ion preferably forms into a 1-D rod-type of morphology with a length and diameter of 4µm and 0.45µm respectively, while NVO, form a 2-D belt-type of morphology with a length and width of 0.6µm & 0.055µm respectively. Sodium and calcium has similar ionic radius, while KVO and CVO has similar aspect ratio. Hence, synthesis method plays a major role in the size(length and width) of hexavanadates’ morphology than the size of the pillar ion. Also, it can be observed that there is an increase in the dimension from 1-D to 3-D as the pillar ion selection moves down the alkali and alkali-earth metal group, but such a phenomena cannot be concluded only on the basis of the pillar ions and should take into consideration the methodology by which the crystal is grown.
5.1.2 On Crystal structure

By varying the pillar ion from the $V_6O_{16}^2-$ framework, one of the most important changes that one could expect to observe is the crystal structure and its associated lattice parameters and volume. Hewettite ($V_6O_{16}$)$_n$ sheets in a crystallographic unit are formed by alternatively joining tetravanadate chains and divanadate chains laterally by sharing corners. (Scheme 2.2 and Figure 2.5) The sheets are arranged to form a monoclinic structure with a space-group symmetry of $P2_1/m$ and characteristic dimensions within the layer of $a=12.0 \, \text{Å}$ and $b=3.6 \, \text{Å}$ (fiber axis). The third dimension and $\beta$ angle depends on the nature and amount of interlayer cations and water molecules.

Hence understanding the crystal structure and lattice parameters, one can estimate how much lithium ions could be accommodated within the interlayer and the ease with which the ions could diffuse into and out of them, during the charge/discharge process. All the hewettite bronzes have monoclinic structure with a space-group symmetry of $P1_{21}/m$.

Equation 5-1  
Volume of crystal for monoclinic structures = $a \times b \times c \times \sin \beta$

Figure 5-1  Hexavanadate crystal structures drawn from the lattice parameters as per table 5.2
Table 5.2 summarizes the lattice parameters and total crystal volume of alkali and alkali-earth metal hexavanadate bronzes belonging to the hewettite group. It can be clearly seen that CVO has higher cell volume and third dimension “c”, compared to LVO, NVO, KVO and SVO, which can be co-related to the capacity it presents during its electrochemical charge/discharge. Also, it can be observed that KVO and SVO represent similar crystal lattice parameters with lower dimension within the layer(‘a’) and slightly higher fiber axis(‘b’) length.

Table 5.2 Summary of the lattice parameters and total crystal volume of alkali and alkali-earth metal hexavanadate bronzes belonging to the hewettite group.

<table>
<thead>
<tr>
<th>Materials</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β(°)</th>
<th>Volume(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVO</td>
<td>12.160</td>
<td>3.607</td>
<td>7.306</td>
<td>107.735</td>
<td>305.22</td>
</tr>
<tr>
<td>KVO</td>
<td>8.373</td>
<td>4.973</td>
<td>7.625</td>
<td>96.884</td>
<td>315.286</td>
</tr>
<tr>
<td>CVO</td>
<td>12.168</td>
<td>3.505</td>
<td>11.241</td>
<td>96.418</td>
<td><strong>476.370</strong></td>
</tr>
<tr>
<td>SVO</td>
<td>8.377</td>
<td>4.902</td>
<td>7.649</td>
<td>96.864</td>
<td>311.926</td>
</tr>
</tbody>
</table>

So, this indicates that for charge storage to be predominantly bulk storage the ‘a’ dimension i.e. the within the layer dimension is crucial and further, higher ‘c’ dimension allows more lithium ions to be stored within the interlayer of this pseudo-layered structure.

Increased fiber axis length ‘b’ in KVO and SVO, could have presented with higher number of transport pathways for lithium ions to enter into and out of the crystal thereby co-relating with the superior stability during cycling even at high current density.

Hence, by co-relating the XRD analysis of the crystals with the electrochemical study of varying the pillar ions within the hewettite V₆O₁₆ framework, provided some value inference on how various electrochemical parameters like specific capacity, rate capabilities and cycling stability is influenced by the geometry and dimensions of the crystals. Such an understanding could provide cues on how to design an optimum crystal structure so as to obtain the desired electrochemical performance in an electrode material.

Hence, co-insertion of Calcium and Strontium ion into the V₆O₁₆ framework could provide with higher fiber axis(b) length along with the increment in interlayer(c) and
within-layer (a) dimension, thereby improving the cycling stability along with the attainment of higher specific capacity.

### 5.1.3 On Interlayer crystal water content

Figure 5.2 shows the TGA plots of hewettite compounds. Thermo-gravimetric analysis is very important to understand the amount of water present in hewettites as it plays a crucial role in the electrochemical performance of the hewettite materials.

![Thermo-gravimetric plots of LVO, NVO, KVO, CVO and SVO.](image)

**Figure 5-2** Thermo-gravimetric plots of LVO, NVO, KVO, CVO and SVO.

The Table 5.3 lists the amount of water lost during the TGA and the formula of hewettite calculated from the analysis. With increase in the pillar ion size in hexavanadates, amount of interlayer water increases, which in turn affects the structural and electrochemical property of the material.
Table 5.3  Amount of water lost during the TGA and the formula of hewettite calculated from the analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Water loss in (%)</th>
<th>Molecular weight of the materials (calculated) (g/mol)</th>
<th>Final Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVO</td>
<td>3.366</td>
<td>582.46</td>
<td>Li$_3$V$<em>6$O$</em>{16}$.1.129H$_2$O</td>
</tr>
<tr>
<td>NVO</td>
<td>5.92</td>
<td>614.977</td>
<td>Na$_{2.26}$V$<em>6$O$</em>{16}$.2.15H$_2$O</td>
</tr>
<tr>
<td>KVO</td>
<td>5.927</td>
<td>639.845</td>
<td>K$_2$V$<em>6$O$</em>{16}$.2.24H$_2$O</td>
</tr>
<tr>
<td>CVO</td>
<td>13.14</td>
<td>601.727</td>
<td>CaV$<em>6$O$</em>{16}$.5.05 H$_2$O</td>
</tr>
<tr>
<td>SVO</td>
<td>12.5</td>
<td>649.269</td>
<td>SrV$<em>6$O$</em>{16}$.5.15 H$_2$O</td>
</tr>
</tbody>
</table>

Water loss in CVO is the highest compared to other hexavanadates indicating more room for lithium ion to insert during the charging process, which agrees with higher specific capacity for CVO in comparison to other hexavanadates.

5.1.4 On Electrochemical performance

Comparitive study among Alkali-metal ion class of Vanadium oxide bronzes.

![Figure 5-3](image)

Figure 5-3  Cyclic voltammetric plots of LVO, NVO and KVO in 3M LiCl at a voltage sweep rate of 2mVs$^{-1}$. 

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From the cyclic voltammetric plots of LVO, NVO and KVO in Figure 5.3, it can be clearly seen that there is a shift in the redox potentials for all the three materials. All the materials underwent a cyclic voltammetric test under same three electrode set-up with 3M LiCl aqueous solution as the electrolyte with a voltage sweep rate of 2mVs⁻¹.

**Table 5.4** Redox potential peaks for LVO, NVO and KVO.

<table>
<thead>
<tr>
<th>Material</th>
<th>Oxidation Peak</th>
<th>Reduction peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dominant(reduced)(V)</td>
<td>Dominant(reduced)(V)</td>
</tr>
<tr>
<td>LVO</td>
<td>-0.15(-0.6)</td>
<td>-0.35(-0.45)</td>
</tr>
<tr>
<td>NVO</td>
<td>-0.47(-0.2)</td>
<td>-0.55(-0.3)</td>
</tr>
<tr>
<td>KVO</td>
<td>-0.2</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

From the above Table 5.4, it can be clearly seen that the NVO has its dominant redox peak at the higher voltage region compared to LVO and KVO, thereby making it a more suitable anode for a full cell ARLB that could result in a high voltage battery. Larger separation in the redox peaks indicate lower cumbic efficiency. More peaks indicate multi-level redox reactions happening during the voltage sweep across the potential, thereby more capacity can be extracted from the material. This could be reason for higher capacity in LVO and NVO compared to KVO.

**Figure 5-4** Inter-comparison of the (a) galvanostatic charge/discharge plots and (b) Galvanic cycling (charge & discharge) traces of LVO, NVO and KVO in 3M LiCl at 1C rate.
In terms of specific capacity, NVO outperforms both LVO and KVO. Even though NVO and LVO has only very less difference with respect to their initial capacities, but the energy density (Area under the curve) of NVO is higher than the LVO. From the Figure 5.4, it can clearly seen that the cycling stability of NVO is superior to that of LVO even at higher capacities.

KVO has slightly superior cycling stability in comparison to NVO and LVO, but at very low capacities, making it not suitable as a potential anode material in an ARLB system. Techniques to improve the capacity of KVO along with the maintenance of its cycling stability is essential for it to become a commercially potential anode material in ARLB system.

Hence from the inter-comparison of different alkali-metal ion based hexavanadates, NVO’s electrochemical performance is considered superior to LVO and KVO. Further improvements to its capacity and cycling stability during the long cycles, would make it an ideal anode material for ARLB systems.

**Inter-comparative study among the best performing Vanadium oxide bronzes of both Alkali-metal ion vanadium oxide bronze class and alkali-earth metal ion vanadium oxide bronze class**

**Table 5.5** Redox potential peaks for LVO, NVO, KVO, CVO and SVO

<table>
<thead>
<tr>
<th>Material</th>
<th>Oxidation Peak Dominant(reduced)(V)</th>
<th>Reduction peak Dominant(reduced)(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVO</td>
<td>-0.15(-0.6)</td>
<td>-0.35(-0.45)</td>
</tr>
<tr>
<td>NVO</td>
<td>-0.47(-0.2)</td>
<td>-0.55(-0.3)</td>
</tr>
<tr>
<td>KVO</td>
<td>-0.2</td>
<td>-0.3</td>
</tr>
<tr>
<td>CVO</td>
<td>-0.3</td>
<td>-0.4</td>
</tr>
<tr>
<td>SVO</td>
<td>-0.35</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

From the above table 5.5, NVO and SVO has a more negative redox potential peak compared to LVO, KVO and CVO. Hence, NVO and SVO kind of materials could prove to be helpful as a potential high voltage anode material. Hence, by careful
substitution of pillar ions, one could design anode materials which has its redox peaks falling in the higher negative voltage region. Hence, shift in the redox peaks is not only decided by the pH or the lithium ion concentration but also on the crystal structure and morphology of the electrode material.

Table 5.6 Initial and 100th cycle specific capacity values of hewettites (LVO, NVO, KVO, CVO and SVO)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Capacity mAh(^{-1}) (1(^{st}) cycle)</th>
<th>Capacity mAh(^{-1}) (100 cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVO</td>
<td>120</td>
<td>70</td>
</tr>
<tr>
<td>NVO</td>
<td>~160</td>
<td>~130</td>
</tr>
<tr>
<td>KVO</td>
<td>74</td>
<td>60</td>
</tr>
<tr>
<td>CVO</td>
<td>240</td>
<td>~102</td>
</tr>
<tr>
<td>CVO-TiO(_2)</td>
<td>225</td>
<td>~162</td>
</tr>
<tr>
<td>SVO</td>
<td>60</td>
<td>~60</td>
</tr>
</tbody>
</table>

As observed from the above table 5.6, CVO, gives a higher initial capacity of 240 mAh\(^{-1}\) but the capacity falls to ~102 at the end of 100 cycles, which makes it a non-stable electrode material for potential use as anode in ARLB systems, but addition of 10% anatase TiO\(_2\), improves its performance and reduces the capacity fading thereby maintaining 72% of its initial capacity (~162 mAh\(^{-1}\)) at the end of 100 cycles. It is noteworthy to note that NVO also performs decently better among the hewettite family even though the initial capacity is a bit lower in comparison with CVO. NVO’s capacity at 100\(^{th}\) cycle only degrades by 18%, which is 10% better than the CVO-TiO\(_2\) composite mixture.
Also, as seen from the table, there is no loss in capacity observed in the case of SVO even at the end of 100 cycles, making it an ideal anode material where cycling stability is of prime importance in comparison to the capacity and weight of the overall battery.

Figure 5.5 Inter-comparison of the galvanostatic charge/discharge plots of the initial cycle of LVO, NVO and CVO in 3M LiCl at 1C rate.

As seen from Figure 5.5, CVO presents with a much higher capacity approximately 2X in comparison to NVO and LVO. Such high capacity is due to the higher crystal cell volume of CVO in comparison to LVO and NVO (Table 5.2). Increase in the interlayer distance due to higher ion size of calcium helps in the insertion of more number of lithium ions during the charge/discharge process. But such increased accommodation of lithium ion create strain within the crystal which causes the flushing out of calcium, which eventually leads to structural collapse followed by vanadium dissolution and thereby the capacity falls during long cycling. Addition of additives like TiO₂ into CVO have shows some decent results in the stabilization of the crystal structure but complete stability preventing any capacity degradation has not been achieved and would be topic of further research.
5.1.5 On lithium-ion intercalation and charge storage mechanism

The mechanism by which charge is stored in a material determines the energy density it can hold, rate at which it can store and deliver current, number of cycles till which it can deliver the same energy it is designed for and the columbic efficiency of the system.

Charge storage mechanism can be classified into two main types:
1. Surface capacitance or Pseudo-capacity
2. Bulk insertion capacity

Surface capacitance occurs at the electrode/electrolyte interface. The Charge transfer occurs at that boundary. The charge is adsorbed at the surface alone with or without insertion into the crystal. If there is insertion into the bulk, then it will contribute to the bulk capacity.

So, if the surface area to the volume ratio is higher, which is the case of most nanostructured electrode and hence the ability of these electrodes to accept lots of charge at once is higher as it can adsorb those charge by spreading it across its enormous surface. Insertion into the bulk depends mostly on the crystal structure and orientation of the insertion planes. Insertion into the crystal varies with its lattice parameters and type like layered or spinel.

As it will determine the intercalation energy which stabilizes the charge or lithium once it is in the interstitial site. This stability of charge is what which helps to store the charge without any self-discharge. Hence, the bulk insertion helps to store more charge and helps to maintain them for a long time, hence such type of storage mechanism results in higher capacity, but such kind of insertion into the crystal structure is usually slower than the surface capacitance due to the inherent limitation of entry into the crystal lattices and interstitial sites. Hence, an open structure like layered and spinel presents better bulk insertion phenomena. Hence to obtain a better electrode material, that can store large amounts of charge in a stable manner in a short amount of time, will require designing of the materials which can incorporate both the charge storage phenomena. A nanostructured electrode could allow faster storage of charge by pseudo-capacitive charging, then this charge could seep into the crystal interstitial sites by having a crystal growth which has its preferred plane of insertion exposed to the lithium ion diffusion path and a layered structure with more room for lithium ion to be accommodated.
In this thesis, the above target was attempted through substitution of pillar ions in a pseudo-layered structure of $\text{V}_6\text{O}_{16}$ open framework to study the effect on the size of the pillar ions on the capacity that can be obtained or the amount of lithium ions that can be stored. Most optimum system for usage in wearable electronics would require about $\sim15\%$ pseudo-capacitive charge storage contribution and rest from the bulk storage, which enables larger energy density and decent rate capabilities.

![Figure 5-6](image)

**Figure 5-6** Charge storage contributions of different hexavanadates like LVO, NVO, KVO, CVO, SVO and CVO-TiO$_2$ mixture.

Charge storage mechanism in hexavanadates are studied using Randles-Sercik equation as mentioned in section 2.3. Figure 5.6. compares the charge storage contributions of LVO, NVO, KVO, CVO, SVO and CVO-TiO$_2$. KVO and SVO has most of its charge storage contribution from Surface capacitance approximately 88% and the rest from the bulk storage, while, LVO, NVO and CVO has a surface capacitance based charge storage contribution of 22%, 35% and 33% respectively. Improving the bulk storage is one of the important methodology to increase the specific capacity of the material and hence the energy density. Batteries typically have higher bulk storage compared to surface capacitance, while supercapacitors have higher surface capacitance and lower bulk storage. As reported in section 4.3.1.1, addition of TiO$_2$ into CVO was performed.
to study its role in the maintenance of CVO’s structural integrity during the charge/discharge process. Addition of 10% anatase TiO₂ proved provide the best results during the electrochemical cycling and hence a comparison of this mixture in comparison to the raw CVO, could explain if there is any changes in charge storage mechanism that would have occurred and assisted in the improvement of cycling performance. CVO-TiO₂ mixture has the highest bulk storage contribution of approximately 88% which is 24% more than that of the raw CVO. Hence, it can be clearly seen that an addition of the additive does impact the charge storage mechanism through the maintenance of the structural integrity by buffering the stress developed during the cycling process, which could have helped in faster stabilization of the lithium ions that would have intercalated within the bulk. Hence, one can design the required charge storage device not only by tailoring various nano-architectures but also by tuning the pillar ion size or by the addition of a particular additive like TiO₂. Further research could work to insert multiple pillar ions and additives to further explore its effect on the charge storage mechanism.

### 5.2 Inter-comparison of different Micro-architectures on electrochemical performance in LMO cathodes

Structure plays a very important role in the electrochemical property of a material. This is because it is through these structure that the lithium ion diffuse into the crystal lattices and intercalate into the vacant tetrahedral or octahedral sites thereby leads to charge storage and build-up of energy. Growth of crystals in a particular fashion is required to form certain kinds of morphologies and such a growth influences the way a structure would handle stress during the insertion and extraction of lithium. It is well proven that structural integrity is seen to be lost in materials which perform badly during the galvanic cycling. This section details and inter-compares various LiMn₂O₄ microarchitectures, their crystal structures and how these factors govern their electrochemical performance.

#### 5.2.1 With respect to Morphology

Three different morphologies of LiMn₂O₄ were prepared as per the synthesis procedure mentioned in section 3.1.3. FE-SEM image show in below Figure 5.7, shows the three
LiMn$_2$O$_4$ microarchitectures, which are: LiMn$_2$O$_4$ Cluster of microcubes (LMO-CµC), LiMn$_2$O$_4$ secondary hybrid structures of Nanocubes and microspheres (LMO-SNM) and LiMn$_2$O$_4$ hollow microspheres (LMO HµS). LMO-CµC shows cluster of microcubes of approximate side length of 1µm, and hence a volume of 1atto-m$^3$. LMO-SNM is formed of smaller nanocubes which cartel together to form secondary microspheres. Each micro-sphere is estimated to have approximately 4187 nanocubes and the total volume of the sphere is approximately 4.18 atto-m$^3$. LMO-HµS has a spherical geometry with a diameter between 3.5 to 5µm. It has holes in them, making it appear porous in nature. The approximate volume of these sphere neglecting any deformations in the structure is estimated to be 17.765atto-m$^3$.

![Figure 5-7](image)

**Figure 5-7** FE-SEM images of LiMn$_2$O$_4$ microarchitectures: a,d) LiMn$_2$O$_4$ Cluster of microcubes (LMO-CµC); b,e) LiMn$_2$O$_4$ secondary hybrid structures of Nanocubes and microspheres (LMO-SNM) and c,f) LiMn$_2$O$_4$ hollow microspheres (LMO HµS)

The volume of the LMO-HuS is greater than LMO-SNM which has higher volume in comparison. The ration of volume for LMO microstructures are HuS:SNM:CµC = 17.77:4.18:1. Volume increase factor at each morphological level is by 4X. But the volume of individual architectures are insignificant when taking into consideration the overall electrochemical performance of the material. But, it is seen that LMO-HuS performs better in terms of specific capacity and has sharp insertion of lithium ions than
LMO-SNM and LMO-CuC, which could be attributed to some extent to its volume and hollow structure.

5.2.2 With respect to Crystal structures

![Figure 5-8 XRD traces of LiMn_2O_4 microarchitectures: LiMn_2O_4 Cluster of microcubes(LMO-CuC), LiMn_2O_4 solid secondary hybrid structures of Nanocubes and microspheres(LMO-SNM) and LiMn_2O_4 hollow microspheres(LMO HµS)](image)

From the XRD plots comparison from the above Figure, it can be clearly seen that LiMn_2O_4 hollow microspheres has better crystallinity and sharp peaks compared to other two morphologies i.e. LiMn_2O_4 solid microspheres(LMO-SNM) and LiMn_2O_4 microcubes(LMO-CuC). Increase in crystallinity could help to improve the electrochemical performance of a material. Understanding the role of crystal structure and volume is crucial for designing novel morphologies that could help in the stable insertion and extraction of lithium as one of the issues with LiMn_2O_4 that is preventing it to become a viable commercial electrode material is the structural collapse that it undergoes during long cycling that causes rapid capacity fading in these materials.
5.2.3 With respect to electrochemical performance in ARLB

Figure 5-9 Cyclic voltammetric plots of LiMn$_2$O$_4$ microarchitectures: LiMn$_2$O$_4$ Cluster of microcubes (LMO-CµC), LiMn$_2$O$_4$ solid secondary hybrid structures of Nanocubes and microspheres (LMO-SNM) and LiMn$_2$O$_4$ hollow microspheres (LMO HµS) cycled in 3M LiNO$_3$ at 0.5mVs$^{-1}$.

From Figure 5.9, it can be seen that LMO-HuS has very sharp redox peaks compared to LMO-SNM and LMO-CuC. Sharper peaks indicates more current for the same redox reaction at the redox potential, which also means that more number of lithium ions could insert into the crystal structure along with the redox reactions and hence more specific capacity. Sharper redox reaction is also an indication of preferential bulk insertion based charge storage mechanism compared to the surface capacitance.
Table 5.7 The following table shows the redox peak’s potential values of LiMn$_2$O$_4$ microarchitectures: LiMn$_2$O$_4$ Cluster of microcubes(LMO-CµC), LiMn$_2$O$_4$ solid secondary hybrid structures of Nanocubes and microspheres(LMO-SNM) and LiMn$_2$O$_4$ hollow microspheres(LMO HµS)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Microcubes (LMO-CµC) Potential (V vs. SCE)</th>
<th>Solid Microspheres (LMO-SNM) Potential (V vs. SCE)</th>
<th>Hollow Microspheres (LMO-HµS) Potential (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction (appx.)</td>
<td>0.82</td>
<td>0.75</td>
<td>0.76</td>
</tr>
<tr>
<td>Oxidation (appx.)</td>
<td>0.9</td>
<td>0.82</td>
<td>0.82</td>
</tr>
</tbody>
</table>

From the above table 5.7, the redox potential of LMO-CµC is seen to be $\sim$0.1V more than LMO-HµS and LMO-SNM which would result in a higher voltage window for the material, which could also increase the overall energy density of a cell.

Galvanostatic charge/discharge of all the three LiMn$_2$O$_4$ morphologies were performed in 3M LiNO$_3$ at 1C rate to intercompare the capacities achievable by them. (Figure 5.10) The capacity obtained for LMO-HµS was $\sim$134mAh$^{-1}$ which is higher than that of LMO-SNM(115mAh$^{-1}$) and LMO-CµC(111mAh$^{-1}$).
Figure 5-10 Galvanostatic charge/discharge traces of LiMn2O4 microarchitectures: LiMn2O4 Cluster of microcubes(LMO-CµC), LiMn2O4 solid secondary hybrid structures of Nanocubes and microspheres(LMO-SNM) and LiMn2O4 hollow microspheres(LMO HµS) cycled in 3M LiNO₃ at 1C rate at the end of 100 cycles.

As expected from the comparison of XRD peaks, FE-SEM based volume calculation and cyclic voltammetric plots, LMO-HuS provided with higher capacity in comparison with other two morphologies. Hence, it is very clear that morphology of a material plays a very crucial role in the electrochemical performance of the material.

5.3 Effect of counter-ion (SO₄²⁻, NO₃⁻, Cl⁻) on LiMn₂O₄ micro-structures’ rate performance

One of the most important factor that determine the choice of the electrode is its rate capability or the current-density limits till which the material can insert charge in a stable manner without any irreversible capacity loss or structural breakdown. Along with the electrode, the electrolyte also determines its rate capabilities as the transport of ions into the electrode occurs through the electrolyte and through the electrode/electrolyte interface. The influence of counter-ion has been studied widely in lithium ion batteries but so far there are no reports of its study in ARLB systems.¹⁶⁵,¹⁶⁶

¹⁶⁵,¹⁶⁶
This section compares the rate performance of LiMn$_2$O$_4$ micro-architectures (Cubes, Hollow spheres, Nanocubes/Microsphere hybrid) in LiCl, LiNO$_3$, Li$_2$SO$_4$ electrolyte to study the effect of counter-ion with respect to morphology on the rate capabilities in ARLBs. Rate performance study of LMO-SNM, LMO-HuS and LMO-CµC in an electrolyte with lithium salt of three different counter-ion(Cl$^-$,NO$_3^-$, SO$_4^{2-}$) was performed at 0.1C, 0.2C, 0.4C, 0.8C and 1.6C.

![Graph showing specific capacity vs discharge cycles for different morphologies at various currents](image)

**Figure 5-11** Rate study of LiMn$_2$O$_4$ Hollow microspheres (HµS), LiMn$_2$O$_4$ Secondary hybrid structure of Nanocubes/Microspheres (LMO-SNM) and LiMn$_2$O$_4$ cluster of microcubes (LMO-CµC) in 3M LiCl at a rate of 0.1C, 0.2C, 0.4C, 0.8C and 1.6C.

From Figure 5.11, it is clear that LMO-HµC and LMO-SNM shows better rate capabilities than LMO-CµC in 3M LiCl. Cl$^-$ has a possibility to form Cl$_2$ at around 1V vs. SCE at higher currents, which could corrode the electrode surface thereby causing a degradation in capacity while cycling at those currents. LMO-HµC and LMO-CµC has similar architectures at secondary structural levels, as both of them have a spherical geometry which reduces the area of contact for the chloride ion to oxidize into chlorine in comparison with the LMO-CµC, with all its sides exposed for reaction, hence with highest relative mobility of $\sim$2X(relative to lithium ion), chloride ion counter-current could assist in faster development of negative surface charge at the counter-electrode, which might assist in increasing the conduction of lithium ions towards the working electrode, thereby increasing the rate capabilities.
Figure 5-12 Rate study of LiMn$_2$O$_4$ Hollow microspheres (HµS), LiMn$_2$O$_4$ Secondary hydrid structure of Nanocubes/Microspheres (LMO-SNM) and LiMn$_2$O$_4$ cluster of microcubes (LMO-CµC) in 3M LiNO$_3$ at a rate of 0.1C, 0.2C, 0.4C, 0.8C and 1.6C.

LiNO$_3$ and LiCl has similar mobility values of 0.972 and 1.03 relative to that of potassium, which is evident from the thermochemical radii of NO$_3^-$, (179pm) is smaller in comparison to SO$_4^{2-}$ (258pm) and bigger than Cl$^-$. Similar rate performance of LMO-SNM and LMO-HµS can be observed in the case of LiNO$_3$ aqueous electrolyte as per Figure 5.12, which is better in comparison to that of LMO-CµC. Due to the unique architecture of LMO-HµS, it presents with a very high initial capacity and faster insertion of lithium ions though its multiple channels and pores, which are absent in the case of LMO-SNM and LMO-CµC.
Figure 5-13 Rate study of LiMn$_2$O$_4$ Hollow microspheres (HµS), LiMn$_2$O$_4$ Secondary hyrid structure of Nanocubes/Microspheres (LMO-SNM) and LiMn$_2$O$_4$ cluster of microcubes (LMO-CµC) in 3M LiCl at a rate of 0.1C, 0.2C, 0.4C, 0.8C and 1.6C.

As seen in Figure 5.13, LMO-CµC in Li$_2$SO$_4$ performs better than LMO-SNM and LMO-HuS. It is well-known in lithium ion battery chemistries that ionic gel electrolytes with bulkier counter-ions has the best lithium ion transfer co-efficient and hence the conductivity. As the thermochemical radii of SO$_4^{2-}$ is higher, the counter-flow of these ions during the insertion and extraction of lithium restricts its transport, hence the rate performance of material, which favours lithium insertion without any assistance from the counter-ion motion, will perform better. Thus the rate performance of LMO-CµC is seen to outperform LMO-SNM and LMO-HµS in Li$_2$SO$_4$.

Size of an anion and its affinity to the electrode surface area could play a significant role in diffusion of Lithium ions which can affect the rate performance. The susceptibility of oxidation of a counter ion near the oxidation potential of the LMO could also play a role in causing side-reactions which might accelerate corrosion of the electrode which may leads to dissolution of manganese and hence decrease accelerate the capacity loses during high current operation. Hence, it is clear that one single factor could not explain the finding and a combination of factors are responsible for such a behaviour.
Based upon the understanding of the effect of counter-ion on the rate performance of LiMn$_2$O$_4$ microarchitectures and the various parameters that affect them, the overall rate kinetics behind the electrochemical reactions taking place can be summarized in the form of an expression as:

Equation 5-2  \( Rs \propto VOA \times AE \times MA \)

\( Rs = \) Rate kinetics  
\( VOA = \) oxidation limit of Anion  
\( AE = \) area of electrode  
\( MA = \) mobility of counter ion

Thus by knowing the oxidation limit of anion/counter-ion, the area of the electrode and the mobility of the counter-ion, one can calculate the rate kinetics of the reaction, which can give an indication of the rate performance of an electrode material of particular architecture/morphology in a definite aqueous lithium salt based electrolyte. This shows that the counter-ion plays a significant role in rate performance of electrode material. Hence, proper choice of electrolyte salt is also crucial along with the appropriate electrode to develop a high rate, high capacity and long-cycling stable ARLB system.

5.4 Effect of sintering temperature on the electrochemical performance of NVO

One of the approaches followed to improve the intercalation capacity in vanadium compounds is by increasing the distance between its individual layers. By tailoring the interlayer structure and interaction forces between them, the specific capacities can be improved. For example, V$_2$O$_5$.nH$_2$O with an interlayer distance of 11.52Å, provided with a 1.4times more intercalation capacity than the orthorhombic V$_2$O$_5$ with an interlayer distance of 4.56Å. When the water content from V$_2$O$_5$.nH$_2$O is removed by heat treatment, it gives an even higher capacity and better cycling efficiency. Various
studies have been reported on the influence of annealing in $\text{V}_2\text{O}_5\cdot\text{nH}_2\text{O}$ over the electrochemical performance in lithium ion batteries.

Figure 5-14 Bright-field transmission electron microscopy images of (a) NVO-200, (b) NVO-300, (c) NVO-400 and (d) high-resolution image with corresponding indexed selected-area diffraction pattern (SAED) (inset) of NVO-400. (Reproduced with permission from J. Electrochem. Soc., 61 (3) A256-A263 (2014). Copyright 2014, The Electrochemical Society.)

From the HR-TEM images as shown in Figure 5.14, it is clear that NVO-200, NVO-300 and NVO-400 has the same belt-type morphology, with NVO-200(Figure 5.14.a), NVO-300(Figure 5.14.b) and NVO-400(Figure 5.14.c) having a diameter of $\sim$50nm, $\sim$65nm and $\sim$100nm respectively. Annealing at higher temperatures would have resulted in belts with higher diameter. Further, XRD studies at the crystal level could give an explanation for the expansion in diameter with the annealing. (Figure 5.15)
Figure 5-15  a) Rietveld refinement of X-ray diffraction (XRD) pattern of NVO-400 and b) XRD patterns of NVO-200, NVO-300 and NVO-400 respectively. (Reproduced with permission from J. Electrochem. Soc., 61 (3) A256-A263 (2014). Copyright 2014, The Electrochemical Society.)

Table 5.8, presents the calculated lattice parameters from TOPAS refined XRD analysis of NVOs heated-treated at 200, 300 and 400 degree Celsius. A two-fold increase in annealing temperature resulted in a four-fold increase in average crystal size. Increase in the peak intensity and sharpness from NVO-200 to NVO-400, also indicates the increase in crystallinity. (Figure 5.15) Also it can been observed that with the increase in temperature, the cell volume also increases. Hence, it is apparent that, high temperature annealing could support the enhanced construction of a super-cell structure, resulting in Na$_{2.32}$V$_6$O$_{16}$. Also, the lattice parameters have similar values to those of Na$_2$V$_6$O$_{16}$,$x$H$_2$O as reported in the papers by Yu et.al$^{[42]}$ and Zhou et.al$^{[41]}$ the formation of Na$_{2.32}$V$_6$O$_{16}$,$x$H$_2$O can thus be confirmed.
Table 5.8 Calculated lattice parameters and volume of NVO heat treated at 200°C, 300°C and 400°C for 2h.

<table>
<thead>
<tr>
<th>NVO (annealing temperature in °C)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Crystal size(nm)</th>
<th>Volume(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>7.10(2)</td>
<td>3.45(5)</td>
<td>11.84(2)</td>
<td>~7(3)</td>
<td>277.9(10)</td>
</tr>
<tr>
<td>300</td>
<td>7.28(1)</td>
<td>3.591(4)</td>
<td>12.12(1)</td>
<td>9(4)</td>
<td>301.76(49)</td>
</tr>
<tr>
<td>400</td>
<td>7.306(2)</td>
<td>3.607(6)</td>
<td>12.160(2)</td>
<td>~28(5)</td>
<td>305.22(11)</td>
</tr>
</tbody>
</table>

Figure 5-16 TG curves of NVO-200, NVO-300 and NVO-400. (Reproduced with permission from J. Electrochem. Soc., 61(3),A256-A263,(2014).Copyright 2014, The Electrochemical Society.)
Annealing at 400°C is very effective in removing the water molecules from NVO completely while, NVO-200 and NVO-300 has 5.59wt% and 2.94wt% water content in them respectively(Figure 5.16). Absence of water molecule from the crystal after high temperature treatment increase the capacity along with the prevention of an irreversible capacity loss. Wang et.al has observed reduction in crystal volume and crystallinity with heat treatment due to the loss of water molecules from the Na$_2$V$_6$O$_{16}$·nH$_2$O crystal which he has confirmed using TGA and XRD.\cite{44} While in Na$_{4.16}$V$_3$O$_8$, we observe an increase in crystallinity along with higher loss of water molecule. Annealing in this case at higher temperatures has improved the crystallinity and the crystal size of a material Hence NVO-400 shows higher crystal volume compared to NVO-200 and NVO-300(Table 5.8).

So, in materials where there is loss of water of crystallization due to heat treatment, the overall crystal volume is dependent on the phenomena which dominates the most. Therefore, crystal structure of a material plays a very important role in the thermodynamic and crystalline nature of a material, which in-turn plays a key role in its electrochemical performance.

![Figure 5-17](image.png) Cyclic voltammograms (CV) of NVO-200, NVO-300 and NVO-400 as (a)Anode and (b)Cathode in three-electrode configuration (vs. SCE) from -1.0 to 0 V and 0 to 1.0V respectively, at scan rate of 5mVs$^{-1}$. (Reproduced with permission from J. Electrochem. Soc., 61 (3) A256-A263 (2014). Copyright 2014, The Electrochemical Society.)

Half-cell cyclic voltammetric plots of NVO-200, NVO-300 and NVO-400 as cathode is shown in Figure 5.17.b and anode is shown in Figure 5.17.a. The oxidation and
reduction peaks of NVO-200, NVO-300 and NVO-400 is tabulated for easily analysis in Table 5.9

Table 5.9  Oxidation and reduction potentials of NVO as seen from Figure 5.17 (a) and 5.17 (b).

<table>
<thead>
<tr>
<th>NVO all annealing temperatures</th>
<th>Oxidation peaks (V vs. SCE)</th>
<th>Reduction (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As anode</td>
<td>-0.49, -0.2</td>
<td>-0.58, -0.28V</td>
</tr>
<tr>
<td>As cathode</td>
<td>0.6</td>
<td>0.45</td>
</tr>
</tbody>
</table>

As per table 5.9, there is no major difference in the redox peak potential of NVO annealed at 200°C, 300°C and 400°C. Current density on subsequent cycling, falls in the case of NVO-200 more rapidly than NVO-300 and NVO-400, which could be an indication that heat-treatments at higher temperature could help to improve the cyclic stability of the NVO.

To further investigate the electrochemical performance of NVO as cathode, anode and symmetric full cell, cyclic voltammetric (CV) of NVO-400 was carried out in three-electrode configuration within the potential range of -1.0 to 0V, 0 to 1.0V and 0 to 2.0V vs. SCE respectively, at a scan rate of 5mVs\(^{-1}\) as shown in Figure 5.18.

Figure 5-18  Cyclic voltammograms (CV) of NVO-400 as Anode, full cell, Cathode in three-electrode configuration (vs. SCE) from -1.0 to 0V, 0 to 2.0V and 0 to 1.0 V respectively, at scan rate of 5 mV s\(^{-1}\). (Reproduced with permission from J. Electrochem. Soc., 61 (3) A256-A263 (2014). Copyright 2014, The Electrochemical Society.)
The redox peak at ~-0.5V might correspond to $V^{2+}/V^{3+}$ redox reaction.$^{[167]}$

$$V^{3+} + e^- + Li^+ \leftrightarrow V^{2+}^{(int)} \quad (1)$$

The redox peaks at ~0.5V & ~0.7V correspond to redox reaction 2 and 3.$^{[161]}$

$$VO_2^+ + e^- + Li^+ \leftrightarrow V^{3+}^{(int)} \quad (2)$$
$$VO_2^+ + e^- + Li^+ \leftrightarrow VO_2^{+}^{(int)} \quad (3)$$

The CV curve of NVO//NVO symmetric full ARLB fabricated using 4M LiCl in aqueous electrolyte studied between 0 to 2.0V vs. SCE showed 3 distinct redox couples with oxidation peaks at 0.52V, 0.8V, 1.6V and corresponding reduction peaks at 0.14V, 0.5V, 1.32V vs. SCE respectively.

Complete full cell reaction can be written as follows:

$$VO_2^+ + 3e^- + 3Li^+ \leftrightarrow V^{2+}^{(int)} \quad (4)$$

Figure 5.19  Galvanostatic charge-discharge profiles of NVO-200, NVO-300 and NVO-400 respectively, as (a) Anode in three-electrode configuration (vs SCE) from -1 to 0V and (b) Cathode in three-electrode configuration(vs SCE) from 0 to 1V, in 4M aqueous solution of LiCl, at current density of 5A g$^{-1}$. (Reproduced with permission from J. Electrochem. Soc., 61 (3) A256-A263 (2014). Copyright 2014, The Electrochemical Society.)

As shown in Figure 5.19, half cell electrochemical performance of NVO as cathode and anode was further studied using galvanostatic charge/discharge cycles, in three
electrode configuration, at a current density of $5\text{Ag}^{-1}$ and tabulated as below for easy comparison.

**Table 5.10** Charge and Discharge capacities of NVO-200, NVO-300 and NVO-400.

<table>
<thead>
<tr>
<th>NVO-temperature($^\circ$C)</th>
<th>As Anode</th>
<th>As Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charge Capacity in mAh$^{-1}$ (approximately)</td>
<td>Discharge Capacity in mAh$^{-1}$ (approximately)</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>300</td>
<td>125</td>
<td>120</td>
</tr>
<tr>
<td>400</td>
<td>130</td>
<td>121</td>
</tr>
</tbody>
</table>

Multi-lithium ion intercalation/de-intercalation process could explain the reason behind the absence of a real discharge plateau.$^{[41]}$ Figure 5.20, shows the galvanostatic charge/discharge traces of NVO electrode as both cathode and anode in a full cell configuration (ratio of anode and cathode used is 1:1.5), in a three electrode configuration, at a high current density of $5\text{Ag}^{-1}$ between 0 and 1.9V vs. SCE respectively.

The initial charge and discharge capacities for all NVO’s are ~156.18mAh$^{-1}$ and ~152.42mAh$^{-1}$ respectively. Vanadium in NVO undergoes redox reaction from $V^{5+}$ to $V^{2+}$ during the charge/discharge cycle thereby inserting 3 moles of lithium. (Reactions 1-4) Therefore, one redox change is accompanied by insertion of 3 moles of lithium per formula unit of $\text{Na}_{1.16}V_3\text{O}_8$, which is in accordance with the structural similarity and lithium insertion observed in $\text{LiV}_3\text{O}_8$. $^{[39,40,168]}$
The overall voltage of the symmetric cell is around 1.8(±0.5)V, according to the redox potentials of individual cathode and anodes with an energy density of ~120Whkg⁻¹. Side reaction reads to rapid capacity loss on cycling and charging above 1.9V leads to that by causing oxidation of water and hence the symmetric cell voltage has been restricted to 1.9V. Figure 5.21 shows the cyclic stability of NVO up to 100 cycles, at a current density of 5Ag⁻¹. NVO-200 gave a discharge capacity of 70.33mAh g⁻¹, equivalent to ~50 % of its initial capacity, while NVO-300 and NVO-400 retained >60 % and ~80 % of the initial capacity respectively.
Figure 5-21 Specific capacity vs. cycle no. and Coulombic efficiency of NVO-200/NVO-200, NVO-300/NVO-300 and NVO-400/NVO-400 respectively, in three-electrode configuration from 0 to 1.9V, at current density of 5Ag⁻¹. (Reproduced with permission from J. Electrochem. Soc., 61 (3) A256-A263 (2014). Copyright 2014, The Electrochemical Society.)

Capacity fading observed in NVO-200 and NVO-300 can be attributed to their poorer crystallinity. The superior cycling stability of NVO-400, compared to NVO-200 and NVO-300 can be attributed to larger crystal size as observed from the TEM (Figure 5.14) and confirmed by XRD (Figure 5.15). NVO symmetric cell shows a greater capacity retention (~80 %) at the end of 100 cycles compared to the 55% capacity retention shown by LiMn₂O₄ symmetric cell reported by Park et al. at the end of 30 cycles.[169]

Increase in the diameter and aspect ratio with temperature, leads to higher electroactive surface and hence reduced diffusion path for lithium ions to travel into the interstitial sites within the crystal, facilitating the insertion of large number of lithium ions into the vacant tetrahedral sites. Structure, particle size reduction, porosity of the electrode and material composition are the factors that influence the rate capability in material.[170] Therefore, for high rate capabilities, proper electronic and ionic wirings of the active mass to allow faster pathways for ions and electrons to conduct is essential. The layered crystal structure of Na₁₁₆V₃O₈ facilitates the lithium insertion / de-insertion into and from the layers via the diffusion, while presence of sodium ions (Na⁺) residing in the octahedral sites[44,171,172] prevent structural collapse by supporting the V₃O₈⁻
Chapter 5

Discussions

puckered layers, during the electrochemical lithiation / de-lithiation processes, resulting in excellent electrochemical performance in terms of stable cycling at various rate capabilities.\[51,104\] The superior electrochemical performance of NVO-400, compared to NVO-200 and NVO-300, can be attributed to the increased cell size and volume. The expansion of the $a$, $b$ and $c$ lattice parameters indicate that the tetrahedral voids are larger than those in NVO-200 and NVO-300, thereby facilitating the entry of lithium ions into the crystal structure. 98-100 % columbic efficiency at a high current density of 5A g$^{-1}$ was achieved over the cycles. Further studies on NVO could aim to do partial substitution of alkali, alkali-earth or even transitional metal ions to advance its volumetric energy density by augmenting the diffusion controlled lithium transport along with surface-capacitive charging.

5.5 Summary

From section 5.1, we can summarize various effects that we observe in hexavanadate material with alkali and alkali-earth metal ion substitution. From the electrochemical studies (section 4.2 and 4.3), it is clear that CVO provides with higher initial specific capacity while SVO provides with higher stability compared to other hexavanadates studied in this thesis(Section 5.1.5). NVO provides with a slightly higher capacity as compared to LVO but lower than CVO. Capacity of KVO and SVO are the lowest compared to LVO, NVO and CVO. LVO and NVO has higher within layer crystal size ‘a’, which increases the exposed area for preferred lithium insertion plane, thereby improving the bulk storage and hence better capacity. An ideal anode material should have the electrochemical characteristics of both CVO and SVO i.e. high capacity and better cycling efficiency. Higher capacity of CVO could be attributed to its higher crystal volume and higher interlayer distance(‘c’), which is due the bigger Ca$^+$ ion size and the amount of water present between the layer(‘c’ axis). KVO and SVO which shows predominantly surface charge storage property has slightly higher fiber axis length(‘b’), which provides with more surface area for the charge to accumulate on, while their within the crystal layer length(‘a’) is lower, thereby reducing the number of sites available for lithium ions to insert into the bulk of the crystal. Hence, both the interlayer distance and the size of the insertion plane, plays a vital role in the achieving higher specific capacity, while the fiber axis length, plays a major role in increasing the surface charge storage phenomena. Hence, co-insertion of Calcium and Strontium ion
into the $\text{V}_6\text{O}_{16}$ framework could provide with higher fiber axis (‘b’) length along with the increment in interlayer (‘c’) and within-layer (‘a’) dimension, thereby improving the cycling stability along with the attainment of higher specific capacity.

For the development of a superior ARLB battery with higher capacity and rate capabilities, optimization of all the components of an ARLB system (Cathode, anode and electrolyte) is required. Section 5.1 discusses various factors and technical outputs that will help in the development of better anodes, similarly section 5.2 discusses, how morphology can influence the performance of a well-studied and prominent cathode material in the ARLB system – $\text{LiMn}_2\text{O}_4$. Hollow microspheres morphology provides with multiple pathways for $\text{Li}^+$ insertion/de-insertion, hence provides with better rate capabilities and higher capacity. Hollow microspheres is more crystalline and has sharp redox peaks indicating higher bulk intercalation phenomena for it in comparison to $\text{LiMn}_2\text{O}_4$ SNMs and cubes. Further, electrolyte optimization studies were performed by studying the effect of counter ion on rate performance of various $\text{LiMn}_2\text{O}_4$ morphologies. Section 5.4 studies the effect of sintering temperature on the electrochemical performance of the material. When the materials with interlayer water are heat treated at high temperatures, there is loss of water molecules and also expansion of the crystal lattices, hence with the Materials where there is loss of water of crystallization due to heat treatment, the overall crystal volume is dependent on the phenomena which dominates the most. From our studies discussed in section 5.4, NVO heat treated at higher temperature of 400°C has better cycling stability and capacity in comparison to NVO heat treated at 200°C and 300°C. This co-relates very well the increase in crystal volume for NVO-400 compared to NVO-200 and NVO-300. Further, an attempt to study NVO as cathode was also performed along with its anodic part of study and a symmetric cell was constructed using NVO as both cathode and anode and its electrochemical performance was studied. The symmetric full cell provides with an initial capacity of $\sim155\text{mAhg}^{-1}$, and a greater capacity retention ($\sim80\%$) at the end of 100 cycles compared to the 55% capacity retention shown by $\text{LiMn}_2\text{O}_4$ symmetric cell reported by Park et al. at the end of 30 cycles. Various techniques like adjusting the pH of electrolyte, modification of electrode surface by nano-designing or by making porous aerogels and by addition of additives like $\text{Al}_2\text{O}_3$ or $\text{TiO}_2$ could enhance the capacity retention over long cycling, which will be the object of future research.
Chapter 6 Applications

Chapter 6 begins an introduction to the need of having an energy harvesting and storage module that continues into section 6.1 to 6.3 which provides an introduction to various energy harvesting modules, storage options and consumption pattern of various components that play a major role in the development of IOTs and Wireless sensor networks (WSNs) that find many applications in sports, energy monitoring, location tracking and health science. In section 6.4, a comprehensive study of energy harvesting using the kinetic or vibration energy is performed and augmented using a RMS simulation for vibration energy harvesting for its potential use in WSN based application. Further, in section 6.5, an “Intelligent Power Sourcing, Storage and Consumption” (IPSSC) model is proposed that would aid a user in tailoring the individual energy storage component accordingly to the consumption needs with an optional add-on of energy harvesting component that harvests energy from its ambient environment. To make this selection easier, an ontology for the IPSSC model is developed and its usage is shown in two real-time case scenario. Finally, this chapter end with Section 6.6, which provides with a brief conclusion on how IPSSC model could help in maintenance of the health & life-time of batteries by power management and preventing abrupt power consumption practices.
6.1 Introduction: Need for an Intelligent Energy harvesting, Storage and Consumption system

Interconnectivity and inter-operability among devices has helped to build a tertiary level of knowledge sharing and formation of “Internet of Things” (IOT), which helps manufacturers not only to build better devices but also allow them to monitor and regulate remotely thereby adding a knowledge-based service on top of these systems. Such services not only help in efficient operation of devices but also help to manage resource through end of life-cycle analysis and power management. Recent progresses in technology and manufacturing will lead to an increasing demand on energy consumption and storage. New types of devices are deployed in highly sophisticated applications that will require power efficiency. Very little research has been focused onto using the knowledge of energy signatures obtained from various devices and their components to build efficient energy storage and harvesting module.\cite{173} By the fact that we are able to harvest energy using generators (which includes piezoelectric, electromagnetic and photovoltaic) and store it locally, the expertise needed for anyone to build such an application is getting higher. Information obtained from the operation & real time feedback of a device in a particular application can be utilized to acquire proper understanding of the energy usage of these devices at a particular instant and also look for options that might aid in harvesting energy from its ambient environment. Hence, utilizing this information with proper knowledge about various energy storage and harvesting options available, one can not only incorporate better power option but also increase the overall energy efficiency of the device making it functional even for energy hungry applications.

The following work investigates the energy-harvesting domain by using a semantic modeling approach. User defined applications can be driven by an ontology that gathers all of the domain knowledge and specifications. The targeted domain is a highly encouraging domain that is of great interest during the recent years due to the large number of applications that make use of it. Applications such as the ‘Internet of Things’, Wearable technologies, Location Tracking and Energy Monitoring demand sources of power that may be non-conventional or relative complex compared to traditional applications.

By adding semantics to this domain the user should be abler to find better solutions that will fit his needs. Ontologies can help towards this direction more precisely and
automatically as they provide reasoning and adaptation to changes. Such ontology will have inter-operability with other real-time application specific ontologies, which will help in an efficient integration within the cyber physical space.

Further, using the knowledge obtained with the help of the IPSSC ontology, two real-time case studies are performed:

a) Sports related application: Fitness tracking

b) Energy monitoring in manufacturing industry.

Future work involves an approach derived from the IPSSC model that would result in development, optimum combination and usage of energy storage devices along with the continuous monitoring of their health for superior performance and cost-saving refurbishment.

6.2 Role of Energy harvesting in Wireless Sensor Networks (WSNs)

Wireless sensor networks are used in various applications and it forms the main skeleton on which the IOT is being built on. Recently, the U.S. Department of transportation decided to establish in light weight vehicles the “Vehicle-to-Vehicle communication technology” to avoid accidents and for various other benefits.\(^\text{174}\) Some of the features that will be co-implemented with this project will be continuous monitoring and firmware upgrades for vehicles and asset tracking of goods on the move, automatic traffic management. Wireless sensor networks are used in areas like machine-to-machine/infrastructure communication, telehealth: remote or real-time pervasive monitoring of patients, diagnosis and drug delivery is implemented in areas where heathcare services are not adequately available.\(^\text{175,176}\)

Applications such as the Internet of Things, Wearables, Location Tracking and Energy Monitoring, demand sources of power that may be non-conventional or relatively complex compared to traditional applications. WSNs also has a lot of role in remote security and control, environmental monitoring and control, home and industrial building automation and “Smart” applications, including cities, water, agriculture,
buildings, grid, meters, broadband, cars, appliances, tags, animal farming and the environment, to name a few.\textsuperscript{175} Most of these systems require energy to operate efficiently and cannot completely depend on batteries for their continuous operation.

The total power requirements of a WSN has reduced below 1mW due to the progress made in integrated circuits’ manufacturing, networking techniques and low power circuit designs. A dense ad-hoc network of such WSNs would help transmit data over longer distances say between 1 to 10 meters. When the communication distances are loner than 10 meters, the energy required for such data transmission takes an upper hand.

Multi-hop operation of such WSNs could help in the construction of a low cost, low power sensor nodes for transmission over large distances.

It is extremely difficult to power such dense networks of nodes due to very high cost involved in wiring them and also for batteries that power them which might need occasional replacement. Inorder to be conveniently place, the size of the device has to be small, which puts serious limitations on the power of the battery and hence on the lifetime of the device. In most of the present-day devices, the battery dominates most of its volume and most batteries, even the best of lithium ion batteries are inefficient with the energy density that it can provide for such systems Even at an average power consumption of 0.1mW, the device would run out of power after a year. Hence it is crucial to look out for alternative method of power for wireless sensor and actuator nodes.\textsuperscript{177}

**Different methods to power a wireless sensor networks:**

a. By improving the energy & power density of energy storage devices.

b. Novel methods of better power distribution to nodes.

c. Energy harvesting at the node.

Improving the energy density of batteries is a research which is still not achieved greater results due to the inherent limitation of materials which store energy. Miniature heat engines including fuel cell are sort out to be the next generation power storage devices but it is difficult to predict their availability as a fully functional product in the near future.
Most common wireless method of power transmission is through RF (radio frequency) is to power small RFID tags and sensors. Flooding the entire room with RF radiations to provide power to the nodes is not a practical methods considering a dense ad-hoc network of WSNs. Such high amount of radiations would probably present a health and safety risk and would exceed Ofcom regulations. Assuming no interference, the mount of power transmitted to a node is given by

\[ P_t = \frac{P_o \lambda^2}{(4\pi R^2)} \]

Where, Po is the transmitted power, \( \lambda \) is the wavelength of the signal and R is the distance between transmitter and receiver. To power a node that is consuming 0.1mW of power, the power transmitter needs to emit more than 14W of RF energy, which is much above the exposure stated by the regulations (i.e. 0.6 mW/cm²)\(^{[177]}\)

The third method is that each nodes produces its own energy from the ambient environment by leveraging on the different energy harvesting options available to power themselves. As each environment is different and hence different forms of ambient energy would be present in them, hence there is no single solution that will suit all or even majority of applications and hence it is one of the difficult methods to leverage on. Also, most of these systems will require batteries to store the energy and hence, the inherent problem of replacing these batteries still exist.

Designing any energy harvesting based application requires thorough analysis of energy requirement, consumption modules, energy storage options and detailed understanding of the availability of ambient energy and its fluctuations.
6.3 Energy Harvesting, Storage and Consumption: An Introduction

Zero Power Wireless Sensors using Energy processing

![Diagram of zero power wireless sensor using energy processing and harvesting]

**Scheme 6.1** Schematic block diagram of zero power wireless sensor using energy processing and harvesting

Zero power wireless sensor networks can be designed with Energy harvesters and processors efficiently by using multiple energy sources at the same time and having better power distribution and management circuitry along with smart energy storage units. (Scheme 6.1)

### 6.3.1 Energy Harvesting

Energy harvesting or scavenging is a process of converting energy from different sources like light, vibration, wind, kinetic, heat, salt/pH gradient and radio frequency into electricity and storing them for the purpose of powering wireless sensor networks or wearable devices which require less power.

With the advent of low energy electronics, energy harvesting from ambient sources is getting attractive. Other means of energy production like fuel to energy (oil, coal and nuclear) is costly and is harmful and not environmentally sustainable, while energy
harvesting from ambient & freely available sources like light, vibration and radio waves.

Typical Power densities of these Energy sources are:
- Solar cells – 15mW/cm$^3$
- Piezoelectric - 330µW/cm$^3$
- Vibration - 116µW/cm$^3$
- Thermoelectric - 40µW/cm$^3$

Other large scale energy sources are tidal energy, wind, geo-thermal and hydro-electric but energy harvesting from these sources require huge transducers for large scale energy generation but could be interesting for environmental monitoring applications.

Many off-the-shelf energy harvesters or modules can be used for testing purposed and each of them has its own advantages and disadvantages. The following table below enlists different energy harvesting modules and features of each device including the types of energy resource it supports and its energy monitoring capabilities.

**Table 6.1 Prominent multi-source energy harvesting system reported in literature or commercial products**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No. Harvesters/Stores</td>
<td>3/3</td>
<td>6 (shared)</td>
<td>3/2</td>
<td>3/1</td>
<td>2/1</td>
<td>4/2</td>
<td>3/1</td>
</tr>
<tr>
<td>Swappable Sensor Node</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Swappable Storage</td>
<td>No</td>
<td>Yes, &lt;6</td>
<td>Yes, battery</td>
<td>No</td>
<td>Yes, battery</td>
<td>No</td>
<td>Yes, battery</td>
</tr>
<tr>
<td>Swappable Harvesters</td>
<td>No</td>
<td>Yes, &lt;6</td>
<td>Yes, 3</td>
<td>Yes</td>
<td>Yes, 1 of 2</td>
<td>Yes, 4</td>
<td>Yes, 3</td>
</tr>
<tr>
<td>Energy Monitoring</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Limited</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Digital Interface</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Quiescent Current Draw</td>
<td>5µA</td>
<td>7µA</td>
<td>&lt; 5µA</td>
<td>75µA</td>
<td>&lt; 1µA</td>
<td>20µA</td>
<td>&lt; 2µA</td>
</tr>
<tr>
<td>Storage</td>
<td>Fuel cell, Li-ion, NiMH, Supercap,</td>
<td>Supercap, Li-ion/poly, 2xAA recch. batt., Li non-rech. batt.</td>
<td>Supercaps, Li-ion/poly, 2xAA recch. batt.</td>
<td>AA recch. batt.</td>
<td>Thin-film battery</td>
<td>Thin-film batt., optional Li batt.</td>
<td>Thin-film</td>
</tr>
<tr>
<td>Commercial Product</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 6.1 enlists the prominent systems reported in literature or commercial products. Swappable storage or Energy harvesting hardware indicate that the devices are not soldered onto the board and may be connected to the terminals. The input power conditioning circuitry of both the original and alternative EH device should match. Each
energy harvester/storage device has an interface circuit that brings its characteristics into line with those required by the power unit for system B. The most commonly used harvester types are photovoltaic (PV) cells, wind turbines, and vibration energy harvesters.

6.3.2 Energy Storage

Energy storage are the devices that store energy in the form of chemical energy (batteries, fuel cell), electrical energy (capacitors) and mechanical energy (compressed air, flywheel). Various energy storage options are discussed in detail in chapter 1 of this thesis. Based on the energy density, life time, power density and rate capabilities each system finds its usage in certain applications. Appropriate usage of each application requires proper understanding of the device’s energy usage and output capabilities related to energy. For example, applications that require very small bursts of energy separated over a range of time intervals, could use capacitors or super-capacitors as it can charge itself during the intervals, while in applications that continuously consume energy would require something that is capable of supplying it like batteries, fuel cells, and for applications that fall in between these usage patterns could use a combinations of different energy storage systems. The same usage pattern could be applied to the powering pattern also to charge these energy storage devices. Hence for an application which needs to capture large amount of energy in a short amount of time to store it in systems that maintains the energy longer without self-discharge, would require to combine capacitors with batteries or use advanced super-capacitors or hybrid electrochemical capacitors. Hence depending on the size, geometry, application, user requirements, energy and power densities, one can design the best possible energy storage device by careful selection across a wide range of possible options.

Most of the power generated by energy sources like vibration, temperature difference, sound and ambient RF are stored in capacitors and in some cases in supercapacitors. Energy densities of these devices are very low and hence the energy generated needs to be consumed immediately before self-discharge happens in these systems.

Another method to improve the energy storage is combining capacitors and super-capacitors with batteries. The energy produced by the harvesters are stored in the capacitor till it reaches a particular voltage say above 1V and when it reached 1V, the capacitor is discharged to power the battery and this happens till the capacitor voltage
falls down to a certain voltage say ~0.7V. In this way, the battery is continuously charged for future energy consumption. This method of energy storage improves the overall efficiency of the system by 30-40%. Most of the energy storage options can be utilized according to the user or application requirement to engineer an appropriate energy harvesting and storage system.\textsuperscript{[75]}

### 6.3.3 Energy Consumption

Energy is stored inefficiently within batteries. Most of the energy is lost in the form of heat and in processes by which the current is supplied for various application. This wastage increases radically when a battery is asked to supply a level of current it isn’t designed for. Significant amounts of energy are lost in the peaks and troughs of a device’s usage as the batteries are only optimized for an average load.\textsuperscript{[179]}

### 6.3.4 Energy Requirement

It is very important to understand the energy requirements of different types of devices and sensors so that optimum energy harvesting and power storage & management systems can be designed.

#### Table 6.2  Different power requirements of different devices & sensors\textsuperscript{[180]}

<table>
<thead>
<tr>
<th>Type of System</th>
<th>Name</th>
<th>Power requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensors</td>
<td>PPG sensor</td>
<td>1.471mW</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>27μW</td>
</tr>
<tr>
<td></td>
<td>Humidity</td>
<td>1mW</td>
</tr>
<tr>
<td></td>
<td>Accelerometer (3D)</td>
<td>0.324mW</td>
</tr>
<tr>
<td></td>
<td>Pressure</td>
<td>0.5mW</td>
</tr>
<tr>
<td></td>
<td>Motion</td>
<td>14.4mW</td>
</tr>
<tr>
<td>Communication system</td>
<td>Bluetooth</td>
<td>10mW</td>
</tr>
<tr>
<td></td>
<td>Miniature FM</td>
<td>1mW</td>
</tr>
<tr>
<td></td>
<td>RF transmission</td>
<td>Sub mW</td>
</tr>
<tr>
<td></td>
<td>RF receiver chip</td>
<td>24mW</td>
</tr>
</tbody>
</table>
From table 6.2, one can easily observe that most of the sensors require power in the range of few micro-watts to ~1milli-watts.

### 6.3.5 Energy Harvesting sources

To find out the capabilities of energy harvesting, it is essential that we know the limitation of those systems with respect to the possible energy that can be scavenged from them.

Table 6.3 enlists the most viable ambient energy sources, their challenges, electrical impedance, typical voltage and estimated power outputs from them. Out of all these energy sources, light and vibration has the capability to provide better power outputs (~100s micro-watts to sub milli watts). Also, the availability of light and vibration in the ambient environment is much higher compared to other energy sources.

Hence, further study would try to focus on these energy sources for energy harvesting.
Table 6.3 Below are tabulated different transducers for various energy sources, their key issues, typical electrical impedance, voltages and estimated power output.[181]

<table>
<thead>
<tr>
<th>Energy-Transducers</th>
<th>Challenges</th>
<th>Typical Electrical Impedance</th>
<th>Typical Voltage</th>
<th>Estimate Power Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light-Photo voltaic cells</td>
<td>Conform to small surface area &amp; wide input voltage range</td>
<td>Varies with light Input Low kΩ to 10s of kΩ</td>
<td>DC:0.5V to 5V [Depends on no of cells in array]</td>
<td>10µW-0.72W (Outdoor s:0.15m W-15mW) (Indoors&lt;10µW)</td>
</tr>
<tr>
<td>Vibration-Piezoelectric</td>
<td>Variability of vibration</td>
<td>Constant impedance 10s of kΩ to 100kΩ</td>
<td>AC : 10s of volts</td>
<td>1µW-200µW (electrostatic:50µW-100µW) Electromagnetic: &lt;1µW</td>
</tr>
<tr>
<td>Thermal-Peltier</td>
<td>Small thermal gradients</td>
<td>Constant impedance 1Ω to 100s of Ω</td>
<td>DC: 10s of mV to 10V</td>
<td>15µW₀ (10°C gradient)</td>
</tr>
<tr>
<td>Motion/pressure-Piezoelectric</td>
<td>RF Coupling &amp; rectification</td>
<td>Constant impedance</td>
<td>AC: Varies with</td>
<td>Various µW</td>
</tr>
</tbody>
</table>
6.4 Vibration based Energy Harvesting

Various sources of vibrations available in our environment can be broadly classified as seen in Figure 6.1

![Classification of potential sources for vibration based energy harvesting](image)

**Figure 6-1** Classification of potential sources for vibration based energy harvesting

Such a classification of vibration energy sources will help identify potential case scenarios where a certain application or device needs to be operated. Further, in this
section, the vibration acceleration and frequency values from this sources are tabulated and calculated for its energy output that would help in a WSN application to send data packets at a fixed range of communication.

6.4.1 RMS simulation for vibration energy harvesting

Scheme 6.2 Energy Harvesting Systems: A Block Diagram

This is a typical vibration based energy harvesting diagram (Scheme 6.2) in which the current flow and control signals are shown. An (Response surface modelling) RSM design explorer simulation as shown in Scheme 6.2 is used to calculate the number of packets that can be transmitted.

RSM design explorer is obtained from “www.holistic.ecs.soton.ac.uk/resources.php”
Energy consumption is pre-fixed as 100μJ per transmission at the Super-capacitor threshold voltage of 3.0V. The resonant frequency is set to 50Hz. The power processing is done using the diode bridge circuit. An electromagnetic micro-generator is used as a transducer. Cantilever length is 10mm and width is 2mm.

From the simulation experiment, we can clearly observe that more close the applied frequency is to the resonant frequency, the higher the power produced and hence more number of transmissions. This tuning can be done to generate more power by design a proper cantilever and tuning the coil turns and setting the appropriate proof mass of the micro-generator.
Table 6.4 Summary of various sources of Vibrations present in our environment along with their peak acceleration, frequency and estimated number of transmission calculated from RMS simulation as per scheme 6.4

<table>
<thead>
<tr>
<th>No.</th>
<th>Vibration Source</th>
<th>Peak Acc. (ms(^2))</th>
<th>Peak Freq (Hz)</th>
<th>Estimated Number of Transmissions (calculated using RMS Simulation)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Household (Kitchen blender, Dryer, Microwave oven, Breadmaker, Fridge, Door frame, Washing Machine)</td>
<td>2-6</td>
<td>~121</td>
<td>30-50</td>
<td>183</td>
</tr>
<tr>
<td>2</td>
<td>Human Motion (Head, Wrist, Hip) Lower leg</td>
<td>5-19(10(^{-5})) 252(10(^{-5}))</td>
<td>~20-28 21.3</td>
<td>TBD</td>
<td>184</td>
</tr>
<tr>
<td>3</td>
<td>Large Scale (Rail, Manhole) Bridge</td>
<td>~100(10(^{-5})) 5-250(10(^{-5}))</td>
<td>278-300 15(30-40)</td>
<td>40-60 ~60</td>
<td>184</td>
</tr>
<tr>
<td>4</td>
<td>Car</td>
<td>0.5-1</td>
<td>12-30</td>
<td>TBD</td>
<td>185</td>
</tr>
<tr>
<td>5</td>
<td>Aircraft</td>
<td>~</td>
<td>1850-2350</td>
<td>TBD</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Ferry</td>
<td>100-1450(10(^{-5}))</td>
<td>47-50</td>
<td>60-1124</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6.4, summarizes the maximum number of data packets that can be transmitted after harvesting energy from a set of vibration sources as shown in Figure 6.1. The peak acceleration and frequency was obtained from the “EH Network Data Repository (http://eh-network.org/data)”. To calculate the estimated maximum number of transmission the RMS simulation software as detailed above is used.

To harvest maximum energy from a given vibration source, optimizing the transducer to the peak amplitude and the resonant peak frequency is very important. Proper understanding of the kinetic energy or vibration energy transducer along with the appropriate design approach to tune the transducers with the energy source will result in maximum energy output.

6.4.2 Piezoelectric convertor design, modeling and optimization for desired source\textsuperscript{[177]}

Piezoelectric generators are materials which convert mechanical vibrations into electrical energy. Analogy between electrical and mechanical parameters in Piezoelectric system is:

\begin{align*}
\text{Force} \ [N] & \quad - \quad \text{Voltage} \ [V] \\
\text{Velocity} \ [m/s] & \quad - \quad \text{Current} \ [A] \\
\text{Mass} \ [kg] & \quad - \quad \text{Inductance} \ [H] \\
\text{Compliance} \ [m/N] & \quad - \quad \text{Capacitance} \ [F] \\
\text{Damping} \ [Ns/m] & \quad - \quad \text{Resistance} \ [\Omega]
\end{align*}

Piezoelectric(Pz) effect:

Direct Pz effect:

- Mechanical Strain
- Electrical Charge
Converse Pz effect:

![Diagram](image)

Piezo materials are basically ferroelectric materials. Ferroelectric materials have randomly oriented dipoles which when cooled after heating under electric field re-orient themselves in the electric field. This process is called poling. This process when completed, the material becomes piezoelectric.

Direct Piezoelectric effect:

**Equation 6-1** \[ \{D\} = [e]^T\{S\} = [a^s]\{E\} \]

\(\{D\}\) : Electric displacement vector, \(\{T\}\) is the stress vector, \([e]\) is the dielectric permittivity matrix, \([C^E]\) is the matric of elastic coefficients at constant electric field strength, \(\{S\}\) is the strain vector, \([a^s]\) is the dielectric matrix at constant mechanical strain, & \(\{E\}\) is the electric field vector.

There are two configurations in which Piezoelectric materials operate:

Stack configuration: -33 mode
Bender configuration: -13 mode

‘3’ is the poling direction,

In the -33 mode, the electric field is applied in the ‘3’ direction & the material is strained in the poling or “3” direction, in the -31 mode, the electric field is applied in the “3” direction and the material is strained in the”1” direction or perpendicular to the poling direction.

When, Resonance frequency of source = convertor

**Equation 6-2** Power \(\propto\) (vibration frequency)\(^3\)

Low damping factor is required to maximize the power generation and hence the design must allow for larger deflection of mass. For e.g.: 1µW of power is produced at an excitation frequency of 70Hz and 0.1mW at 330Hz (assuming deflection of 50µm). For a given amplitude;
**Equation 6-3**  \( \text{Power} \propto 1/\text{frequency} \)

**Equation 6-4**  \( \text{Power} \propto \text{Proof mass of convertor} \)

Hence, by appropriate design of the piezo-electric transducer and study of the possible energy that can be harvested from any vibration based environment, one would design an optimum data transmission that would function continuously without any break in its activity.

### 6.5 IPSSC ontology

#### 6.5.1 Introduction to Intelligent Power Sourcing storage and Consumption (IPSSC) architecture

As each environment is different and hence different forms of ambient energy would be present in them, hence there is no single solution that will suit all or even majority of applications and hence it is one of the difficult methods to leverage on. Also, most of these systems will require energy storage systems to store the energy as energy that can be harvested and consumed fluctuates throughout the operation of the device and would require consistent power during its task.

![Scheme 6.4 Schematic block diagram representation of IPSSC model](image)

- EPS: External Power Source (AC/DC)
- EH: Energy Harvester
- EP: Energy processors
- PH: Power house
- ARLB: Aqueous rechargeable battery
- SS LIB: Solid state Lithium Ion battery

Red: Discharge
Green: Charge
Blue: Information
The use of IPSSC architecture (Scheme 6.4) is proposed for better power management. As seen in Scheme 6.4, two different energy storage devices are used but multiple devices with different capabilities can be used according to the need. One of them is a Lithium ion battery which is used for low current rate operations while the ARLBs are used for applications which require high current rate capabilities. A multi-source energy harvester can be used to power them smartly. The sensor array containing multiple sensors for light, vibration, temperature, RF are used for sensing and also detecting the available ambient energy sources. Once the sensor detects an available ambient energy, it communicates this to the processor within the Energy harvester module, which then triggers the generator for operation thereby harvesting the energy. Depending the quanta of energy obtained, it charges the lithium ion battery (LIB) or the ARLB accordingly. Hence the charging of the batteries also takes place according to the current densities, thereby preventing over-charging or under-charging of the batteries.

Similarly, the discharging of the batteries also happens in a smart way, in which the application which requires high current drains it from the ARLB while those in quiescent state drains it from the LIB. The EP-PH is used to judge the power requirements of the application and it switches the power sources accordingly.

Such, smart power storage and consumption reduces the strain on the batteries and helps in improving the cycle life and overall efficiency of the systems.

These IPSSC systems can be used in mobile phones, laptops, electric vehicles and WSNs which requires variable current during their different modes of operation.

Designing any energy harvesting based application requires detailed analysis of energy requirement, consumption modules, energy storage options and methodology along with the knowledge of energy harvesting components that would suit a particular application depending on the application and the availability of the energy source. Hence, we have developed an ontology to intelligently provide the best possible combinations of Energy harvesting component and batteries that could be used to power a device catered towards a certain application taking into consideration, the most available ambient energy in that environment.
6.5.2 Introduction to Ontology and Semantics

Domain knowledge can be captured in a structural form by the use of ontologies. Ontologies provide a formal representation of objects, entities or even concepts and are widely used in software engineering and information technology. The main benefits of ontologies are that they facilitate interoperability and machine reasoning. This means that entities can react autonomously to contextual information according to system’s rules. Moreover, ontologies can act as relational databases for storing data as well as querying those data. Of great importance is the fact that ontologies can be interconnected such that different domain knowledge can be captured in a higher level of abstraction. By this, one can build lightweight ontologies that can easily be monitored but at the same time satisfy completeness by capturing information from linked ontologies. We used Protégé for building the ontology used for this paper as it provides a friendly user interface, which allows the non-expert user to work in it. All of the domain entities can be stored in classes and characterized by object and data properties. Hence, we have developed an ontology to intelligently provide the best possible combinations of Energy harvesting component and batteries that could be used to power a device catered towards a certain application taking into consideration, the most available ambient energy in that environment. Figure 6.2, gives a brief overview of a short version of the complete ontology.
Figure 6-2 Ontology overview of an IPSSC system
6.5.3 Brief Description of the architecture

6.5.3.1 Objectives

The main idea of this ontology is to specify the most important properties of energy harvesting applications and their requirements. This includes, among other things, classifying the domain into different variants and supporting the representation of particular applications as individuals. Additionally the ontology also captures several of the terms and concepts that are used in the energy-harvesting domain. Most of the information on energy harvesting domain has been described in section 6.3 above.

6.5.3.2 Focus

The developed ontology aims for the representation of energy harvesting domain. It can be used for decision support on the selection of components in different energy harvesting applications. Reasoning is not supported yet, but it is a future task that we will implement.

6.5.3.3 Overview

The ontology interacts with several other ontologies built for similar domains. The links can be provided even by classes or subclasses that own the share the same name, or by properties and individuals.

6.5.3.4 Needs

Semantic compatibility. The increasing use of sensors and sensor data increases the heterogeneity of measurement procedures. Means for enhancing interoperability are provided by ontologies. These semantic technologies can assist in managing, reasoning and combining observation data and applications related to them.

6.5.3.5 Development of the ontology

It was not possible to review existing ontologies because there are not deployed yet. Our use cases are focused in the following categories:
The device infrastructure use case for example requires the ontology to represent infrastructure types, architectures, ambient environment and common metrological definitions like power usage, accuracy and details of the expected output. Such definitions would enable a developer to search a database for components matching required parameters of operation and even run a simulator to analyze performance of such an application.

The energy sources use case focused on gathering and linking possible sources of energy that could be used for that kind of applications given qualitative or spatial context.

The applications use case requires sufficient information to understand the deployment in terms of, say, time, cost, effort, or difficulty.

6.5.3.6 Development Environment

The following tools have been used for developing the ontologies:
- Protege 5.0 Beta – OWL Plugin 1.3 for Protege
- http://owlged.lumii.lv/online_visualization/caro and OWLViz plug-in is used for creating the Figures

6.5.3.7 Device Infrastructure

Understanding the device infrastructure is important to not only build the most energy efficient device but also to optimize the various components to provide the best possible desired user output based on the user’s budget, frequency of usage and environment.

The device infrastructure covers the following areas:
1. Peripheral devices
2. Communication medium
3. Sensors
4. Processing unit
5. Energy storage devices
6. Transducers

Knowledge about the energy usage of each component and the energy that can be harvested from its ambient environment will help optimize the system so as to make them self-sufficient or prolong the need to replace the batteries. Hence, it is very important to understand the energy requirements of different types of devices and sensors so that optimum energy harvesting and power storage & management systems can be designed. Table 6.2, provides the power requirements of different components detailed in the device infrastructures mentioned in the ontology overview.(Figure 6.2). Hence, when the user selects a certain set of device infrastructural components and specifies the details of the application(type of application or type of usage, usage environment and frequency of usage) and the expected outcome, the ontology will be able to suggest the best possible energy harvesting and storage option. To find out the capabilities of energy harvesting, it is essential that we know the limitation of those systems with respect to the possible energy that can be scavenged from them. From Table 6.3, we know the possibilities and limitation of an energy harvesting transducer and source.

6.5.3.8 Information inputs

Following are the inputs required to assist the user to build a device for the user.

i. Operating time
ii. Operating location/environment
iii. Frequency of usage
iv. Budget
v. Type of usage
vi. desired output
We plan to help the user build the device with the best possible energy efficiency through our ontology by suggesting various options for selecting the device components of the energy storage systems around with the most suitable ambient energy harvester.

6.3.4 Ontology based case studies

METHODOLOGY

For a list of application, the information that would help in deciding the best possible energy storage and harvesting component are ‘where’, ‘when’ and ‘for what’ is the user is using it. Figure 6.3, provides a process over-flow of the IPSSC ontology functionality which helps to answer the following queries and from the queries intelligently provides the best possible energy harvesting and storage solution according to the user’s budget. ‘Where’ is defined by location and placement of the device such as: over stationary/moving/vibrating objects.

‘When’ is defined by time and duration.

‘For which’ could be defined by area of usage.

‘For what’ is defined by the intended purpose.

![Figure 6-3](image.png) Process over-flow of the functionality behind the IPSSC ontology
6.3.4.1 Case study-1: Fitness tracking during running

Here in, the application is running. The kind of application is defined by the question ‘for which’. We can answer the ‘where’ question easily be the ‘isLocated’ property. It has two outputs: indoors/outdoors. The ‘when’ question can be answered by specifying the time duration and frequency of usage. ‘For what’ is answered by verbs like monitoring, sensing, tracking, measuring and counting. Multiple for ‘what/which/when/where’ questions can also be selected along with the user’s budget. From these questions we will be able to provide the best possible selection the components associated to the applications, which will satisfy performance conditions bringing value to the user. This is the knowledge provided by the ontology. Now, the data properties that are assigned to the components will give us the most optimum power required for the complete device. This could be part of our ontology or even taken from different ontologies.

From the device infrastructure we derived power requirements. Based upon these requirements calculated by our ontology we will be able to map the best possible energy storage device and harvesting system to the user’s energy consumption and budget. The best possible price profile for the suggested device with or without the energy-harvesting component will be provided.

6.3.4.2 Case Study-2: Energy monitoring in a manufacturing industry

Questions:
Where ➔ industry (indoors), CNC machine
For what ➔ energy monitoring
For which ➔ manufacturing processes
How long/when ➔ operating time

The active power usage time is calculated by the frequency of an operating device and the total time of operation. Assuming that the ontology has the knowledge required of the machine under study. Based upon all these the ontology will list all the device components. The questions ‘For Which’ and ‘For What’ will give us the best possible device infrastructure and power requirements. This will suggest the best possible
energy storage devices. Energy harvesting will require this information along with the information obtained from the question ‘where’. In this case it is on the CNC machine.

### 6.6 Role of Energy Harvesting for performance improvement in batteries

Lot of progress can be made in this topic because devices nowadays don’t use batteries judiciously. Microsoft is working on a software based research prototype known as “E-Loupe, which allows a mobile operating system to identify and police apps that consume a lot of power even when a person is not actively using them. It can pause or slow the activity of a background process—for example, an app downloading a large file—to maximize battery life."[179]

Most of the current lithium ion batteries are designed for certain current loads/rates. Operating at variable current rates causes stress in the electrode material during its operation. This stress causes irreversible capacity loss and also degrades the cycle life of the battery.

In general, most of the operation of any electronic devices say mobile phones, laptops, electric vehicles and sensor nodes can be categorized into two main modes:

1. High rate mode
2. Idle or low rate mode

In high rate mode, the devices are drawing a lot of current from the battery for example during acceleration in electric vehicles or during quick charge, while calling or playing a game in mobiles and in sensor nodes while it is continuously transmitting data. In low rate mode, the devices are usually in idle state or low power state, like silent nodes, or electric vehicles in constant speed or in stay mode.

The above issue can be tackled by having devices that could use two (or more) smaller lithium-ion batteries instead of one large one.[179] One of those batteries would be augmented to provide higher current based on the usage like for example: during attending a call or playing a game or video, while the other battery would be optimized to work under idle conditions which trickles only small amount of currents.

Also, the selection of these batteries can be different based on their energy storage capabilities. As aqueous rechargeable lithium ion batteries (ARLB) have higher power but lower energy densities compared to lithium polymer batteries. ARLBs have much better rate capabilities (10-5000mA·g⁻¹) compared to lithium ion batteries(0.1-10mA·g⁻¹).
Hence, a combination of lithium ion batteries and aqueous rechargeable batteries will be best possible option for such systems.

Information obtained from the operation & real time feedback of a device in a particular application can be utilized to acquire proper understanding of the energy usage of these devices at a particular instant and also look for options that might aid in harvesting energy from its ambient environment. Hence, utilizing these information with proper knowledge about various energy storage and harvesting options available, one can not only incorporate better power option but also increase the overall energy efficiency of the device making it functional even for energy hungry applications.

Thus the current work has investigated the application of energy-harvesting and storage domain by using a semantic modeling approach and a user defined application driven by an ontology that gathers all of the domain knowledge and specifications. Thereby a targeted domain like this is a highly promising domain of great interest for a large number of applications.
Chapter 7 Conclusion

Numerous technological and scientific contributions have been made in this thesis, some of the most important ones are discussed as below in section 7.1 and 7.2
7.1 Scientific Contribution

1) Synthesis of $M^\text{x+}^2_2\text{V}_6\text{O}_{16}$ (M : Li, Na, K, Ca, Sr and x : 1,2) pseudo-layered bronzes by M-site substitution, using simple one step hydrothermal and sol-gel synthesis by varying precursor hydroxide with different alkali and alkali earth metals.

2) Fundamental studies of sub-micro-structured fibers, rods and belts with varying aspect ratios and its influence on the electrochemical properties and lithium transportation in aqueous rechargeable lithium ion batteries.

3) XPS studies on CVO (material with very high specific capacity amongst other hexavanadates), to understand the rapid fading of capacity till the 1st 30 cycles revealed the process by which the inherent issue of vanadium dissolution occurs in vanadium oxide compounds during the electrochemical cycling. Loss of pillar ion i.e. calcium in the case of CVO, initiates the structural collapse, which leads to vanadium dissolution and eventually capacity fading.

4) Addition of TiO$_2$ rutile and anatase into CVO, holds the calcium ion within the interlayer intact thereby preventing the structural collapse and vanadium dissolution. XPS studies even after 50cycles in CVO-TiO$_2$ displayed the presence of calcium ions within the compound while in the standalone CVO, calcium ion is completely absent by 30cycles.

5) Effect of the alkali and alkali-earth metal substitution in $M^\text{x+}^2_2\text{V}_6\text{O}_{16}$ on the charge storage mechanism was elucidated with splitting the total charge storage contributions into bulk storage and surface capacitance. Knowledge of which could be used to design devices with better power and energy density capabilities.

6) Synthesis of LiMn$_2$O$_4$ hollow spheres, hybrid secondary structures of nanocubes/microspheres and microcubes by using different concentrations of the oxidizing agents. Hollow spheres presented with more number of channels for lithium transport thereby helping in improving rate capability, cycling stability and higher specific capacity.

7) Investigations on the effect of electrolyte’s counter-anion towards the rate performance capabilities of LiMn$_2$O$_4$ micro-architectures in ARLB system inspired in the development of the equation “$R_s \propto VOA \times AE \times MA$” which can be used to select the appropriate lithium salt for ARLBs.
7.2 Technological Significance

1) Demonstrated a scalable synthesis method for all hexavanadate bronzes.
2) Reported the use of CVO as a high capacity anode materials amongst other hexavanadates for ARLBs and improved its capacity retention over cycling by the addition and optimization with TiO₂.
3) Improved the specific capacity and cycling performance of LiMn₂O₄ by morphology related studies. LiMn₂O₄ hollow spheres provide near-theoretical capacities (≈142mAhg⁻¹) with decent cycling stability over 1200 cycle at a current density of 500mA. ⅁̅.g⁻¹.
4) Optimized the perfect lithium salt electrolyte through studies on the effect of counter anion in the rate performance of LiMn₂O₄ microstructures. LiNO₃ proves to be the best lithium salt compared to Li₂SO₄ and LiCl, allowing faster and stable insertion of lithium ion over repeated charge/discharge process.
5) Flexible pouch cells of aqueous rechargeable lithium ion batteries were constructed using NVO, CVO as anode and LiMn₂O₄ hybrid secondary structures of nanocubes/microspheres and hollow microspheres as cathodes respectively. Also demonstrated the use of NVO as cathode and anode to develop a symmetric full cell.
6) Proposed a novel IPSC method for conserving the health of the battery and also combined it with energy harvesting components to develop a complete energy sourcing and storage device.
7) Developed an ontology to intelligently provide the best possible combinations of Energy harvesting component and batteries that could be used to power a device catered towards a certain application taking into consideration, the most available ambient energy in that environment.
Chapter 8  Future Works

This thesis has presented various studies and strategies for the development of ARLB electrodes as a potential safe, better energy density with high rate capabilities. ARLB systems was developed by using hewettite group bronzes as a potential anode material and LiMn$_2$O$_4$ spinel microstructures as a potential high capacity cathode, but one of the inherent issue that requires attention to make aqueous rechargeable batteries as a feasible alternative to lithium ion batteries and other energy storage devices is the overall energy density of the device which is limited due to the redox potential of water electrolyte. So, the alternative approach is to develop novel systems that can remain stable even beyond the redox potential of water or to develop electrode that present with higher and stable capacity when compared to traditional electrode materials in LIBs.
8.1 Fundamental studies on SVO to improve its specific capacity.

Although among all the hexavanadates studied for this thesis, CVO has presented with very high specific capacity, the cycling performance of the material was not good and hence studies involving adding TiO$_2$ to stabilize the capacity was performed. Among all the hewettite group bronzes, SVO present with a very stable capacity retention i.e. 99\% for over 100 cycles, but the capacity offered by SVO is very low and this makes it a potential anode material for the study.

Partial substitution of strontium with calcium could provide the required capacity along with the cycling stability. Fundamental understanding about the lithium insertion into SVO could provide cues to how its crystal structure could be tuned to accommodate more charge or increase its bulk storage based charge storage component in comparison to its pseudocapacitance based energy storage.

8.2 Testing in other electrolyte & salts system (Organic & Na, Ca, Mg)

With the increasing energy requirement around the world and with the recent progress in the digital electronics and electric vehicle sectors, there is an increased demand for better energy storage device and amongst all the lithium ion batteries tops the list. But the current lithium reserves across the world won’t last even a decade and hence there has been a mad-rush to recover lithium from used batteries and also from sea-floors. Also, the research field also has taken a turn towards alternative forms of charge storage i.e. sodium-ion batteries, magnesium and aluminium ion batteries. Eventhough aqueous rechargeable batteries doesn’t use expensive and toxic electrolyte salts like LiPF6 or lithium ion based ionic gels, still salts like LiCl, LiNO$_3$, Li$_2$SO$_4$ will also face soon extinction. Hence, development of an aqueous rechargeable battery with alternative salt systems will become mandatory. Preliminary studies on NVO used for sodium ion batteries shows a promise and avenue for further research in this domain which will make aqueous rechargeable batteries as a low cost potential energy storage device for large scale and wearable electronic applications.
8.3 In-situ studies of ARLB (XRD, XPS)

As evident from the XPS studies during the cycling in CVO, the vanadium dissolution is followed by structural collapse. Release of the calcium ion which acts as a pillaring ion cause the layers to collapse. It is well-known that the stress caused by lithium insertion/extraction during the charge/discharge causes volumetric changes within the crystal. The exact mechanism by which lithium insertion/extraction causes the knocking out of calcium ion will help design new crystal structures by co-insertion of other ions from the alkali-metal or transition metal group or by growing crystals with preferred plane orientation that helps in lithium insertion with reduced stress, could help to buffer the stress preventing the flushing of the interlayer pillar ion and thereby preventing a structural collapse. In-situ XRD studies will help understand the crystal structural changes during the lithium insertion/extraction. Stress acting on the crystal and volumetric changes during lithium insertion and extraction at various current density will help in understanding how lithium inserts into the interstitial sites between the pseudo-layers and also give a cue about the irreversible structural changes that could have caused an irreversible capacity loss.

In-site XPS, could help in understanding the redox reaction happening at the electrode surface during the charge/discharge process. It could give an indication of the oxidation state of the vanadium at different redox potentials along with the relative ratio of lithium to vanadium. The shift in the binding energy of V-O could also indicate any defects related to oxygen induced vacancies in the compound that could provide explanation for the redox activities in hewettite compounds.

Co-relating the insitu-XPS studies with insitu-XRD will help to un-earth the various steps of lithium insertion and extraction into the crystal, preferred crystal plane of lithium transport into the material, sites within the crystal where the lithium has preferable intercalation, redox reactions which aid in lithium insertion into the material, volume changes occurring within the system and how to buffer them with the use of various techniques. It could also provide the mechanism for modelling an energy storage device that could enable faster charging tuning the pseudo-capacitive property of the electrode surface, which can then in-turn facilitate the traditional slower bulk
insertion into the electrode, thereby achieving both high energy and power densities in these materials.

8.4 Energy Harvesting to power ARLBs for Sensing, IOT & Energy monitoring.

Even though a short introduction has been made in thesis about the advantages of using energy harvesting and ontology to power ARLB, not much applications using this system has been demonstrated. Further works could demonstrate the usage of ARLBs with other energy storage devices like solid state lithium ion batteries, supercapacitors, hybrid electrochemical capacitors, ultra-capacitors and energy harvesting systems in an intelligent way that will not only enhance the power efficiency but also the long-term health of such integrated Energy harvesting & storage systems for a wide variety of applications. Such systems are in high demand due to the inherent limitation of energy storage system and even aspiring needs of applications that voraciously consume power. Such IPSSC systems could prove a solution to applications that need energy storage systems that charge within few seconds preferably from ambient sources of energy and could last longer during its usage and requires very less replacement over long time.
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Appendix A

A1: List of Publications


4. Vivek Sahadevan Nair, Sivaramapanicker Sreejith, Hrishikesh Joshi, Yanli Zhao, Andrew West, Srinivasan Madhav; The fabrication of LiMn$_2$O$_4$ and Na$_{1.16}$V$_3$O$_8$ based full cell aqueous rechargeable battery to power portable wearable electronics devices, Materials and Designs, 93, 291-296, 2016.

A2 : List of Patents

1. Patent application No. : 61/760,347 (US Provisional)
   Inventors: 1) Vivek S. NAIR; 2) Madhavi SRINIVASAN; 3) CHEAH Yan Ling
   Title: Novel Symmetric Aqueous Rechargeable Batteries With High-Power And Energy
   Densities As Well As Superior Cycling Stability Using Nanostructures Of Ammonium, Alkali-
   Metal, Alkali-Earth Metal Vanadium Oxide Bronze Compounds As Both Cathode And Anode
   Electrodes.
   A PCT International Patent Application No. PCT/SG2014/000044 was filed on 04 February 2014
   for the invention titled “Method Of Preparing A Vanadium Oxide Compound And Use Thereof In
   Electrochemical Cells”.

   Inventors : 1) Wong Chui Ling; 2) Vivek Nair; 3) Madhavi Srinivasan;
   Title : Novel Non Combustible Methodology And Device For Converting Waste Polymers/Plastics
   Into Carbon Nano Tube.
   Title: Method Of Forming Carbonaceous And Mineral Nanostructured Materials From Plastics.
   Complete patent details: Singapore Patent Application No. 11201600768X

   Inventors: 1) Steffen Uwe HARTUNG; 2) Nicholas Joachim BUCHER; 3) Vivek S. NAIR; 4)
   Madhavi SRINIVASAN; 5) Harry Ernst HOSTER
   Title: Rechargeable Battery [sodium ion battery using hewettites]

4. US Patent application No. : 61/772,780 [Filing date : 5 March 2013]
   Inventors: 1) KANHERE Pushkar Dilip; 2) CHEN Zhong; 3) NAIR Vivek; 4) SRINIVASAN
   Madhavi
   Title: Multifunctional nanocomposites coatings and their applications thereof
A3 : Oral Presentations and Awards

1. Vivek Sahadevan Nair, Andrew West, Srinivasan Madhavi, "LiMn$_2$O$_4$ and Na$_{2.32}$V$_6$O$_{16}$ nanostructures for aqueous rechargeable batteries: A full cell configuration and study for sports application", ICSST conference, Singapore, 2014.

2. Vivek Sahadevan Nair, Andrew West, Srinivasan Madhavi, “LiMn$_2$O$_4$ and CaV$_6$O$_{16}.7$H$_2$O Nanostructures for aqueous rechargeable batteries: A Full cell configuration and study for large scale energy storage application”, Energy & Material Research conference » (EMR) 2015, Madrid, Spain


5. Vivek Sahadevan Nair, Iordanis Kerasiotis, Navjot Kaur, Asia Ramzan, Srinivasan Madhavi, Andrew West, “Intelligent Power Sourcing, Storage and Consumption Ontology for wireless sensor network based applications in an ambient energy environment”, IMCR 2016, UK (Submitted)
Appendix A

Oral Presentations & Awards

Awards

“IES Most Prestigious Engineering Achievement award” for “Aqueous rechargeable batteries for wearable electronics.”

Awarding body: Institute of Engineers, Singapore

Date: 13 September 2013
Appendix B: Auxiliary details

B1 Raman study

Figure A1  Raman study to find the effect of cation Substitution in Hexavanadates bronzes (hewettites)
Figure A2  EIS Study: Effect of Cation substitution in Hewettites on Impedance and Diffusion Kinetics.
B3 Effect of sintering temperature on the electrochemical performance of hewettites : HT-XRD study on Hexavanadates

To study the effect of high temperature annealing on different hewettites, a standard laboratory X-ray diffractometer (Siemens D5005) equipped with parallel beam optics and a high temperature XRD-chamber (Paar HTK-1200) which can be used for temperatures up to 1200°C. In combination to the HT-appliance, a high vacuum (up to 5 E-6 mbar) and gas supply station for reaction- and inert gases has been installed to provide the flexibility of different well defined gas atmospheres in the chamber in order to prevent uncontrolled reactions such as oxidation and/or reduction.

| Powder diffractometer | Siemend D505
8 / 8 goniometer, Scintillation Counter with attached high temperature Chamber (Paar HTK-1200) |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray tube /settings</td>
<td>fine focus Cu anode; 40kV 40mA</td>
</tr>
<tr>
<td>Primary parallel beam optic</td>
<td>Goebel mirror 2nd generation, 2° Soller slit</td>
</tr>
<tr>
<td>Secondary parallel beam optics</td>
<td>Soller slit 0.4 mm</td>
</tr>
<tr>
<td>Primary slits</td>
<td>1; 0.6 mm</td>
</tr>
<tr>
<td>Secondary slit</td>
<td>2 mm</td>
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B3.1 NVO

Figure A3 HT-XRD analysis at various temperatures on NVO

B3.2 KVO

Figure A4 HT-XRD analysis at various temperatures on KVO
B3.3 CVO

![CVO HT-XRD analysis at various temperatures](image1)

**Figure A5** HT-XRD analysis at various temperatures on CVO

B3.4 SVO

![SVO HT-XRD analysis at various temperatures](image2)

**Figure A6** HT-XRD analysis at various temperatures on SVO