

**Transmission Electron Microscopy Investigation of Ion Intercalation in Vanadium  
Pentoxide Polymorphs**

BY

Arijita Mukherjee

Bachelor of Science (B.Sc.) (Physics) , University of Calcutta (2010)  
Master of Science (M.Sc.) (Physics), Indian Institute of Technology, Madras, (2012)

THESIS

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Defense Committee:

Robert F. Klie, Chair and Advisor

George Crabtree

Anjum Ansari

Jordi Cabana, Chemistry

Alan W. Nicholls, Research Resources Center

Sarbajit Banerjee, Texas A&M University

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## **LIST OF ABBREVIATIONS**

|       |                                           |
|-------|-------------------------------------------|
| TEM   | Transmission Electron microscope          |
| STEM  | Scanning transmission Electron microscope |
| HAADF | High-angle annular dark field             |
| LAADF | Low-angle annular dark field              |
| ABF   | Annular Bright Field                      |
| EELS  | Electron Energy Loss spectroscopy         |
| EDX   | Energy Dispersive X-ray spectroscopy      |
| XAS   | X-ray absorption spectroscopy             |
| XANES | X-ray absorption near edge structure      |
| NMR   | Nuclear Magnetic Resonance                |
| GLC   | Graphene Liquid cell                      |
| BNLC  | Boron nitride liquid cell                 |

## SUMMARY

This thesis constitutes the experimental results, analysis and relevant discussions pertaining to my studies on ionic intercalation into Vanadium pentoxide ( $V_2O_5$ ) polymorphs. More specifically, I have investigated both monovalent lithium (Li) and divalent Magnesium (Mg) ion intercalation into the orthorhombic  $\alpha$ - $V_2O_5$  polymorph and the metastable, tunnel structured  $\zeta$ - $V_2O_5$  polymorph. I have done these experiments using state-of-the-art Transmission electron microscopy (TEM) techniques, including Aberration-corrected Scanning Transmission electron microscopy (STEM) imaging which allows direct visualization of the atomic columns of a material, thereby aiding structural characterization at the atomic scale; electron energy loss spectroscopy (EELS) which allows identification of the chemical species in the specimen as well as determination of the valence state of an element which changes upon ion intercalation; electron diffraction which allows for phase identification and energy dispersive X-ray spectroscopy (EDX) which allows elemental mapping of the specimen, clearly indicating phase inhomogeneity, if present and also allows quantitative analysis for the elements constituting the specimen, thus quantifying amounts of intercalation. I have also collaborated with both first principles theorists as well as electrochemists to complement my own experiments and adopt a comprehensive, multimodal study of ionic intercalation into  $V_2O_5$  polymorphs. This approach has led to direct correlation between the electrochemical performances with structural modifications at the atomic scale as well as verification of metastable structures predicted by density functional theory (DFT) calculations with atomic-resolution imaging.

Chapter 1 gives a broad overview of battery technologies, covering both the advantages and challenges of conventional Li-ion batteries and the prospect of multivalent batteries.

## SUMMARY (continued)

I also review DFT predictions on ion intercalation trends into oxide cathodes.

Chapter 2 covers the principles of the experimental techniques : STEM, EELS and EDX. This chapter also reviews some of the challenges in studying battery materials in the TEM, particularly beam sensitivity and the need to handle samples under an inert atmosphere. It also presents the methods I developed/employed to deal with such challenges and introduces the graphene liquid cell (GLC) method as a novel way to work with beam-sensitive samples, such as proteins.

Chapter 3 presents my results from *in situ* TEM experiments investigating lithiation of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires. This combines both high-resolution imaging as well as electron diffraction and EELS to dynamically study the phase evolution in the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowire as a consequence of *in situ* lithiation. This chapter also presents results from lithiation experiments on the metastable  $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode.

Chapter 4 presents the results from Mg intercalation experiments into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> particles by combining atomic-resolution Annular bright field (ABF) imaging directly revealing the intercalation sites, electron diffraction, EELS and EDX. These experiments proved that the chemically synthesized sample represents the stoichiometric  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> phase while the electrochemically cycled sample exhibited a local formation of the theoretically predicted metastable  $\epsilon$ -Mg<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub> phase. It also includes results from Mg intercalation studies into metastable  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires.

## SUMMARY (continued)

Along with these, I also explore the effects of temperature on Mg intercalation by studying high temperature electrochemical Mg cycling into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires as well as particle size effects by comparing the Mg cycling performance of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires with that of particles in the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> phase

Chapter 5 presents results from a different system exhibiting a conversion based reaction instead of intercalation, chemical cycling of Calcium (Ca<sup>2+</sup>) ion into Manganese dioxide ( $\alpha$ -MnO<sub>2</sub>) cathode.

Chapter 6 reviews the state-of-the-art techniques for performing *in situ* liquid stage experiments inside the TEM, with both the liquid stage holder as well as monolayer window encapsulated liquid cells. It also presents results from the novel Boron nitride liquid cells using cutting-edge monochromated EELS to do vibrational spectroscopy and resolving isotopic differences in regular water *versus* heavy water. It also discusses possible applications of these methods in studying battery materials.

Chapter 7 is the concluding chapter, summarizing the work presented in the thesis, identifying the major challenges and possible directions going forward and the significance of multimodality as an overarching approach for studying complicated battery systems.

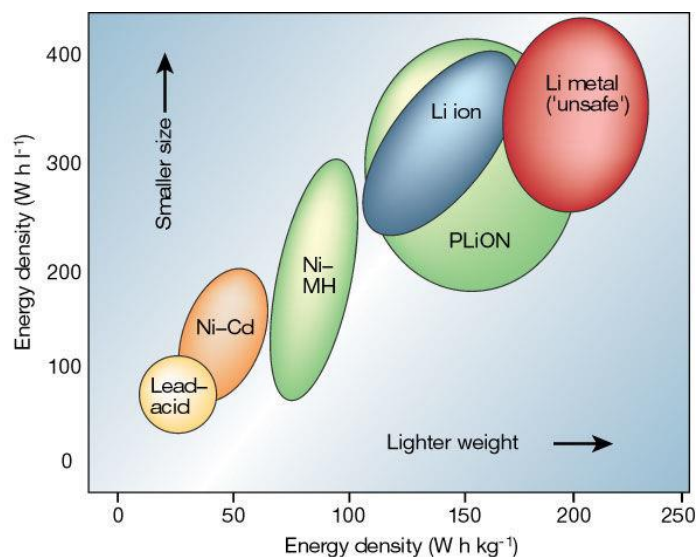
## CHAPTER 1

### Introduction

#### 1.1 Overview of different battery technologies

Ever-growing demands for energy necessitated by the modern industrial civilization has put significant strain on the Earth's limited reserve of conventional energy source: fossil fuels. This has motivated scientists and engineers to harness alternatives such as solar, wind, hydro-electric and thermal energy which can provide novel sources of renewable energy as well as be a more environment-friendly and sustainable option. However, the successful implementation of such alternative energy sources require a more efficient and inexpensive energy-storage option that can compensate for their seasonal and intermittent nature. The ideal energy-storage system would allow consumers to draw the electricity when it is readily available, and store it for future use, that implies designing a powerful and flexible electricity grid. These requirements call for development of next-generation batteries that can successfully power the technological revolution. However, compared with Moore's law that predicts a doubling of memory capacity every two years, the improvements in battery capacities have been much slower. Figure 1.1 presents a comparison of the different battery technologies based on their specific energy (also known as gravimetric energy density) which is defined by weight ( $\text{Whkg}^{-1}$ ) and that by volume, the volumetric energy density ( $\text{WhL}^{-1}$ ). As is clear from Fig. 1.1, Lithium ion batteries outperform the other technologies due to their high energy density and are therefore widely used both in portable electronics such as laptops and cell-phones as well as large volume applications such as electric cars. This is also why most of the ongoing research efforts focus on further

development of the widely successful lithium ion battery technology. Section 1.2 gives a broad overview of lithium ion batteries.

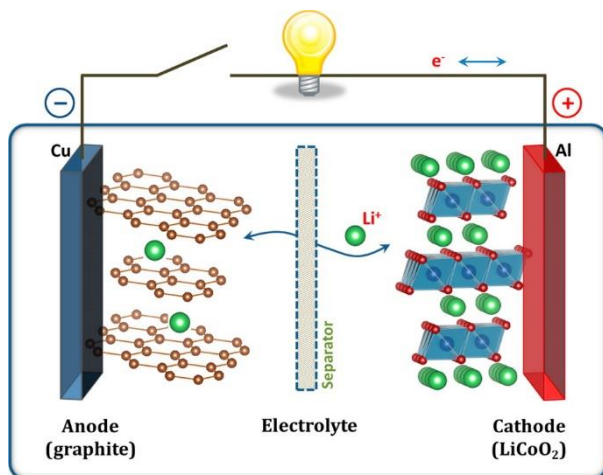


**Figure 1.1** Different battery technologies in terms of their respective energy densities. Adapted with permission from Tarascon, J. M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, 414 (6861), 359-367.

As an example, in the United States, personal electronics account for 2% of energy use and constitute the majority of the lithium ion battery market, amounting between US \$15 billion and \$20 billion. Transportation and grid account for 70% of electricity use, thus if even half of this usage were to be met with stored energy, that would create a market roughly 15 times the current size. However, to meet the goals of developing affordable electric cars with a range of hundreds of kilometers as well as replacing unsustainable fossil fuels with alternative solar, wind or hydro-electric energy, about five-fold improvement in battery performance and cost are required. These five-fold improvements in batteries demand fundamental innovations in the underlying science and one promising area is development of multivalent batteries, where the working ion is replaced from monovalent Li with divalent or trivalent elements.<sup>1</sup> Section 1.4 discuss about the opportunities for multivalent batteries.

## 1.2 Lithium ion batteries

The lithium (Li) ion rechargeable battery has revolutionized personal portable electronics market, even extending their use to electric vehicles, since their first commercial launch by Sony in 1991. Fig. 1.2 shows the schematic of an electrochemical cell inside a commercial lithium ion battery. It consists of three main components: the two electrodes (anode and cathode) which are electronic conductors, separated by an electrolyte that may be either liquid/solid. The electrolyte is so chosen to be a poor electronic conductor, however a good ionic conductor, so that the working ion, Li in this case, is forced to move through the electrolyte driving the associated electron through the external circuit, doing work. Even if the active material for the electrode does not have good electronic conductivity, while making electrodes, carbon black is added to increase the electronic conductivity.



**Figure 1.2 :** Schematic of a commercial lithium ion battery. Adapted with permission from Goodenough, J. B.; Park, K.-S., The Li-Ion Rechargeable Battery: A Perspective. *Journal of the American Chemical Society* **2013**, 135 (4), 1167-1176. Copyright (2013) American Chemical Society.

So, essentially in a rechargeable Li ion battery, reversible chemical reactions, namely the charge and discharge cycles, occur at both electrodes. During charging, an external voltage is applied to drive a chemical reaction, while during discharge, the opposite chemical reaction: movement of

the Li ion into the cathode delivers energy. As shown in Fig. 1.2, a common design for the Li ion battery employs graphite as the anode and lithium cobalt oxide (LiCoO<sub>2</sub>) as the cathode, reaction scheme in this case during the discharge cycle is as follows



To understand the electrochemical performance of such a system, certain parameters need to be defined. <sup>2</sup> The *discharge and charging voltages* ( $V_{\text{dis}}$  and  $V_{\text{ch}}$ ) can be related to the *open-circuit voltage* by the following scheme:

$$V_{\text{dis}} = V_{\text{oc}} - \eta (q, I_{\text{dis}}) \quad [1.3]$$

$$V_{\text{ch}} = V_{\text{oc}} + \eta (q, I_{\text{dis}}) \quad [1.4]$$

$$\text{where, } \eta = I_{\text{dis}} R_b = I_{\text{ch}} R_b \quad [1.5]$$

So the polarization factor  $\eta$  that depends on the internal battery resistance ( $R_b$ ) and the ionic current ( $I_{\text{dis}}/I_{\text{ch}}$ ) reduces the output voltage from the open-circuit voltage and also increases the voltage required to charge the cell, this is known as the *overpotential*. The total charge can be defined as:

$$Q = \int_0^{\Delta t} I dt = \int_0^Q dq \quad [1.6]$$

$Q(I)$  is referred to as the *cell capacity* at a given current,  $I$  and the *percent Columbic efficiency* for a single cycle is,

$$100 * Q_{\text{dis}}/Q_{\text{ch}} \quad [1.7]$$

The cycle life of the battery is defined by the number of cycles it takes for the capacity to fall to 80% of its initial reversible value.

Other parameters that are commonly used for determining the performance metrics are *output power*  $[P(q)]$  , specific energy, defined by weight (gravimetric, usually expressed in  $\text{Whkg}^{-1}$ ) and energy density, defined by volume (volumetric, usually expressed in  $\text{WhL}^{-1}$ ). The *volumetric energy density* is an important operating parameter for portable devices such as laptops/cell phones. We have,

$$P(q) = V(q) I_{\text{dis}} \quad [1.8]$$

$$\text{Energy} = \int_0^{\Delta t} I V(t) dt = \int_0^Q V(q) dq \quad [1.9]$$

As illustrated in Fig. 1.2, the Li ion is inserted/extracted reversibly from both the anode and cathode materials. In the ideal case, such an ion insertion process leads to minimal structural rearrangement of the electrodes, this mechanism is known as *intercalation*. The concept of *electrochemical intercalation* was recognized in the early 1970's as a possible energy storage mechanism with potential application in the Li-ion battery field.<sup>3</sup> It was found that this intercalation behavior was exhibited by primarily two classes of materials: i) layered compounds such as Lithium titanium disulfide ( $\text{LiTiS}_2$ ) or lithium cobalt oxide ( $\text{LiCoO}_2$ ) and ii) those with an open structure such as Vanadium oxides ( $\text{VO}_2/\text{V}_2\text{O}_5$ ), tunnel compounds such as Manganese dioxide ( $\text{MnO}_2$ ) and also lithium iron phosphate ( $\text{LiFePO}_4$ ).<sup>4</sup>

The following two paragraphs are partially reproduced from [A. Mukherjee, H. A. Ardakani , T. Yi , J. Cabana , R.S. Yassar , R. F. Klie, Direct characterization of the Li intercalation mechanism into  $\alpha\text{-V}_2\text{O}_5$  nanowires using *in-situ* Transmission Electron Microscopy, *Appl. Phys.*

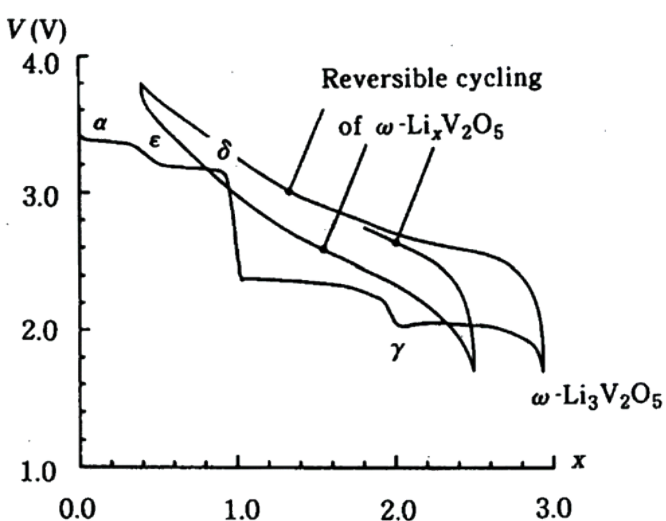
*Lett.* **2017**, 110, 213903 with permission from the American Institute of Physics (AIP Publishing LLC).]

To be an ideal cathode candidate for Li ion batteries, a material needs to incorporate several key features such as, possess a cation that can be easily oxidized/reduced (such as a transition metal), provide high voltage and high capacity that would lead to high energy density, be a good electronic conductor and as discussed above, undergo an intercalation type reaction with Li ion involving minimal structural changes that would yield good cyclability.<sup>4</sup>

Vanadium Pentoxide ( $V_2O_5$ ) is a well-known cathode candidate for Li ion intercalation and has been studied since the 1970's.<sup>5,6,7</sup> The  $\alpha$ - $V_2O_5$  polymorph has a layered structure consisting of two dimensional sheets of distorted square pyramids of  $VO_5$  sharing corners and edges, and held together by weak Van der Waal's interactions.<sup>4,8</sup> Due to the weak interlayer bonding,  $\alpha$ - $V_2O_5$  can accommodate ions along the interlayer direction to form intercalated compounds. It crystallizes in an orthorhombic structure with the space group *Pmmn*. Vanadium exhibits +5 valence state in  $V_2O_5$ , so it can be reduced easily to lower valence states with subsequent ionic intercalation.<sup>9</sup> Also,  $\alpha$ - $V_2O_5$  exhibits a high redox potential vs Lithium (3.5 V)<sup>10,11</sup> and high theoretical capacity (440 mAh/g) upon intercalation of 3 Li ions/ $V_2O_5$  unit.<sup>12</sup>

It has been well-established that Li insertion into bulk crystalline  $\alpha$ - $V_2O_5$  proceeds through several intermediate phase transitions. Initially, about 1% Li is inserted, forming the  $\alpha$ - $Li_xV_2O_5$  phase, followed by the formation of the  $\epsilon$ -phase in the range  $0.35 < x_{Li} < 0.7$ . While some puckering of the layers can be seen at this stage, no significant structural distortion is observed, and in fact, the lithiation reaction is commonly found to be completely reversible till the  $\delta$ - $LiV_2O_5$  composition [ $x_{Li} = 1$ ]. At this point, the specific capacity corresponds to  $\sim 147$  mAh/g. Upon intercalation of

more than one Li ion/  $\text{V}_2\text{O}_5$  unit, the layered structure shows significant strain, and the formation of the  $\gamma\text{-Li}_2\text{V}_2\text{O}_5$  phase sees severe puckering of the layers. Upon further lithiation, the  $\omega\text{-Li}_3\text{V}_2\text{O}_5$  phase forms which has a tetragonal structure, Delmas *et. al.*<sup>11</sup> reported that after one electrochemical cycle, the tetragonal superstructure vanishes, instead a disordered rock-salt type structure appears with lattice constant of 4.1 Å. It was also reported that direct chemical lithiation of  $\text{V}_2\text{O}_5$  in n-butyllithium also led to the formation of tetragonal  $\omega\text{-Li}_3\text{V}_2\text{O}_5$ .<sup>11</sup> This phase evolution of  $\alpha\text{-V}_2\text{O}_5$  upon subsequent Li intercalation can be seen in Fig. 1.3. Upon formation of  $\gamma\text{-Li}_2\text{V}_2\text{O}_5$  and  $\omega\text{-Li}_3\text{V}_2\text{O}_5$  phases, subsequent charging does not lead back to the pristine material with the last Li coming out at  $> 4$  V, showing the structural differences between these phases and the pristine  $\alpha\text{-V}_2\text{O}_5$  phase (starting material) which has an open-circuit voltage of 3.5 V. In Chapter 3 of this thesis, I contrast the electrochemical lithiation in  $\alpha\text{-V}_2\text{O}_5$  with that of the metastable  $\zeta\text{-V}_2\text{O}_5$  polymorph, and present results showing more reversible behavior in the  $\zeta\text{-V}_2\text{O}_5$  phase upon intercalation of  $1.5 < x_{\text{Li}} < 2$  Li ions / formula unit.



**Figure 1.3** Electrochemical cycling and subsequent phase transitions for Li into  $\alpha\text{-V}_2\text{O}_5$ . Adapted with permission from Whittingham, M. S., Lithium Batteries and Cathode Materials. *Chemical Reviews* **2004**, 104 (10), 4271-4302. Copyright (2004) American Chemical Society.

It was also found that the increase in Li content, starting from the empty  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure, led to reduction in the diffusivity, possibly due to kinetic limitations imposed by deep discharge conditions, ( $x_{Li} > 1$ ) which induced strain on the lattice. Impedance spectroscopy measurements revealed that the diffusion coefficient  $D_{Li}$  for low lithium content ( $0.4 \leq x_{Li} \leq 0.7$ ) was  $\sim 3.3 \times 10^{-9} \text{ cm}^2\text{s}^{-1}$  which reduced to  $\sim 10^{-10} \text{ cm}^2\text{s}^{-1}$  for  $x_{Li} = 2$ , and further reduced to  $\sim 10^{-12} \text{ cm}^2\text{s}^{-1}$  for  $x_{Li} = 3$ .<sup>8</sup>

While electrochemical lithiation and associated phase transitions into bulk  $\alpha$ -V<sub>2</sub>O<sub>5</sub> is quite well studied, the lithiation mechanism of nanoscale  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, in particular phase evolution in nanoscale  $\alpha$ -V<sub>2</sub>O<sub>5</sub> upon Li intercalation, is relatively unexplored. In Chapter 3 of this thesis, I will present detailed results exploring *in situ* Li intercalation into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires, directly demonstrating evolution of the nanowire phase upon increasing amounts of Li intercalation. Interestingly, in my *in situ* lithiation experiments, it was found that the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowire mostly transforms into the  $\gamma$ -Li<sub>2</sub>V<sub>2</sub>O<sub>5</sub> phase, with some unlithiated domains, however no evidence of the formation of the  $\omega$ -Li<sub>3</sub>V<sub>2</sub>O<sub>5</sub> phase was found.

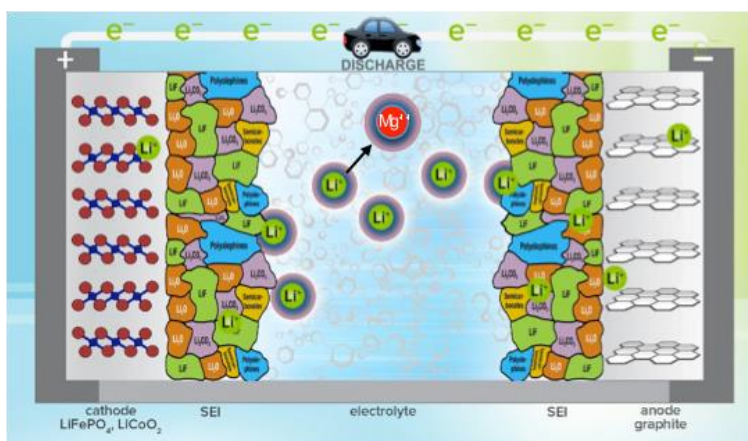
### 1.3 Challenges for Li ion batteries

While rechargeable Li-ion batteries have been very successful, ever-growing demands for batteries with higher energy densities for developing next generation mobile electronics and electric vehicles, coupled with requirements on cost reduction and safety have motivated researchers to explore alternative options. One of the critical parameters for several applications is gain in volumetric energy density. Since the number of available intercalation sites inside the cathode would be constant, one way to achieve higher volumetric energy densities would be to store more charge per ion in the cathode, which implies switching to a multivalent ion chemistry.

Such multivalent batteries could also prove to be a safer and more cost-effective option compared to conventional Li-ion batteries, as explained in Section 1.4.

## 1.4 Multivalent Batteries

Multivalent batteries follow the same basic principles of the lithium ion battery, with the important distinction of exploiting multi-electron transfer on the cathode side coupled with a multivalent metal anode. Zinc ( $\text{Zn}^{2+}$ ), Calcium ( $\text{Ca}^{2+}$ ), Magnesium ( $\text{Mg}^{2+}$ ) and Aluminum ( $\text{Al}^{3+}$ ) are some of the multivalent ions that are currently being studied in the field as potential candidates to go beyond existing Li ion battery technology. Among the potential candidates for multivalent metal anodes, Mg is regarded as the most promising candidate. Being divalent, the specific volumetric capacity for Mg metal anode is very high ( $3,833 \text{ mAh/cm}^3$ ), greater than that of the commonly used graphite anode ( $\sim 800 \text{ mAh/cm}^3$ ) and even the Li metal anode ( $2,046 \text{ mAh/cm}^3$ ). Batteries based on Mg could be relatively inexpensive considering the relative abundance of Mg metal compared to Li. Additionally, the Mg metal anode has a non-dendritic morphology, which provides significant safety benefits over Li metal and can lead to longer lifetimes as well.<sup>13,14</sup> Fig. 1.4 elucidates the working principle of a Mg-ion based battery.



**Figure 1.4 :** Schematic of a multivalent Mg-ion battery

However, one of the crucial aspects for such Mg ion based multivalent batteries is identification of cathodes that can reversibly intercalate Mg, and provide stable electrochemical performance yielding high voltage and high capacity. This calls for a systematic multimodal approach combining (i) first principles calculations that can theoretically estimate mobility of multivalent ions within the cathode framework, determining reaction kinetics, thermodynamic stability of intercalated structures and predict the expected voltages and capacities for the intercalation reactions (ii) electrochemical experiments testing the various parameters for battery operations followed by (iii) systematic characterization, probing different aspects of the intercalation phenomenon such as structural changes both at the bulk and atomic scales, phase evolution upon Mg intercalation, direct investigation of the intercalation sites and study of the valence changes (for example via EELS/XAS) as well as elemental distributions (for example, via EDX) to rule out any Mg-rich surface layer and confirm true intercalation based reaction.

In fact, nature of multivalent reactions with oxide cathodes can be quite complex, and does not always follow the intercalation pathway. To understand such diverse kinds of multivalent electrochemistry, I studied the cycling of  $\text{Ca}^{2+}$  ion with  $\alpha\text{-MnO}_2$  cathode host, which exhibits a conversion based reaction instead of intercalation, results from these experiments are presented in Chapter 5.

### **1.5 Density Functional Theory (DFT) predictions on ion intercalation trends in oxide cathodes**

First principles modeling and simulations pave the way for discovery and implementation of novel cathode materials. Especially, in the relatively new field of multivalent batteries, such computational tools are indispensable as they open up the phase space with promising cathode

candidates as well as multivalent ion intercalants, that can then be employed as experimental test vehicles.

One of the critical parameters that need to be considered while evaluating electrochemical performance of such systems is the ionic mobility of the multivalent intercalant within the cathode host. From a computational perspective, the ionic mobility is estimated by looking at the migration energy barrier ( $E_m$ ) along the intercalation path, which can be defined as the maximum energy difference encountered by the intercalant ion along the diffusion path inside the cathode, as it moves from one stable intercalation site to the next. This migration barrier can also be directly correlated to the ionic diffusivity, ( $D$ )

$$D \approx \nu \times a^2 \times \exp (-E_m/kT) \quad [1.10]$$

In eqn. 1.10,  $\nu$  represents the atomic jump frequency ( $\sim 10^{12} \text{ s}^{-1}$ ) and  $a$  is the atomic jump distance ( $\sim 3 \text{ \AA}$ ). It is clear from Eqn. 1.10 that in order to increase the ionic diffusivity, (also called diffusion coefficient,  $D$ ), one strategy would be to lower the migration energy barrier ( $E_m$ ) and another could be to increase temperature ( $T$ ). At room temperature  $E_m \sim 525 \text{ meV}$  yields a diffusivity of  $\sim 10^{-12} \text{ cm}^2\text{s}^{-1}$ , and a 60 meV change in  $E_m$  was found to change the ionic diffusivity accordingly.

Another useful parameter is the (dis)charge time ( $t$ ) that can also be related to the diffusion coefficient, ( $D$ ) and diffusion length ( $L$ ),

$$L \sim \sqrt{Dt} \quad [1.11]$$

The time  $t$  determines the  $C$  rate, so 1C means  $t = 1$  hour. The particle size can be taken as the diffusion length (for example, radius for a spherical particle), and this determines the diffusion coefficient, for a given particle size and  $t$ . Then Eqn. 1.10 determines the upper bound of  $E_m$  that

can be tolerated for those particles. As an example for 1  $\mu\text{m}$  active particles, upper bound of  $E_m \sim 525$  meV while for 100 nm particles, it was estimated that  $E_m \sim 650$  meV could be acceptable.

Migration barriers also very depending on the intercalant valence, stronger electrostatic interactions between a divalent ion such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and the surrounding anion environment of the cathode implies higher  $E_m$  for such systems compared to monovalent  $\text{Li}^+$ . Of course,  $E_m$  for a trivalent system such as  $\text{Al}^{3+}$  would be even higher than the divalent ions.<sup>15</sup>

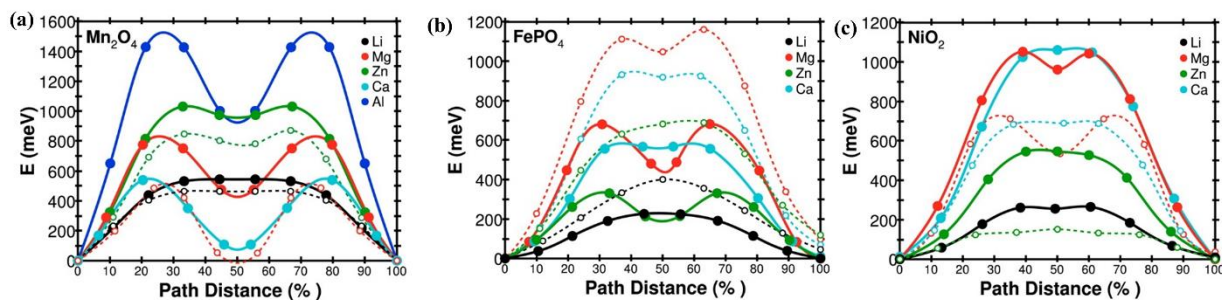
Fig. 1.5 (a), (b) and (c) present migration barrier plots for different intercalant ions for three oxides that are well-known as Li-ion cathodes; spinel  $\text{Mn}_2\text{O}_4$ , olivine  $\text{FePO}_4$  and layered  $\text{NiO}_2$ . It was concluded from DFT calculations that both the changing anion coordination environment of the cathode host along the intercalation path and the specific coordination environment preference of the intercalant ion play a crucial role in determining the migration energy barriers. Thus a direct migration from octahedral (*oct*) - octahedral (*oct*) or tetrahedral (*tet*) - tetrahedral (*tet*) sites (migration between equivalent sites) is not energetically favorable, rather the ion hops through *tet* – *oct* – *tet* [Fig. 1.6 (a)] or *oct* – *tet* - *oct* [Fig. 1.6 (b)] pathways, depending on which insertion site is more stable. For example, in the spinel cathodes, the tetrahedral site is lower in energy (hence, more stable) than the octahedral site. Therefore, as shown in Fig. 1.6 (a), the intercalant ion initially resides in the stable tetrahedral site, hops through the adjacent intermediate octahedral site and follows a symmetric path to the next equivalent tetrahedral site. Similarly, for the olivine and layered materials, the principle for ion diffusion is the same, except in this case, the octahedral sites are more stable, hence diffusion proceeds between equivalent octahedral sites via intermediate tetrahedral site, as illustrated in Fig. 1.6 (b).

Another important criterion is the site preference of the intercalant ion. It has been seen from the study of anion coordination topologies that  $\text{Li}^+$  and  $\text{Zn}^{2+}$  prefer four,  $\text{Mg}^{2+}$  prefers six while  $\text{Ca}^{2+}$

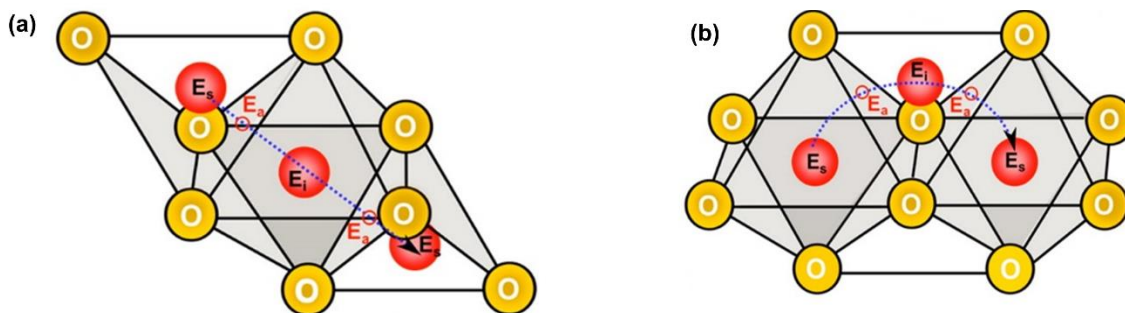
prefers eight coordinated environments.<sup>16,17</sup> Studies also found that the tetrahedral site preference reduces in the order of Li, Zn, Mg and Ca.<sup>18,19</sup> Thus, the tetrahedral site coordination is particularly unfavorable for  $\text{Ca}^{2+}$  (higher energy), as it prefers to be eight-coordinated. So when  $\text{Ca}^{2+}$  ion diffuses through systems such as layered  $\text{NiO}_2$  or olivine  $\text{FePO}_4$ , which provide lower coordination in the intermediate site, it encounters higher migration barriers.

If the coordination of the stable insertion site in the cathode material aligns with the preferred coordination of the intercalant ion, it will be reluctant to diffuse, resulting in higher migration barrier. This is why  $\text{Zn}^{2+}$  has a higher  $E_m$  in the spinel structure, since the stable insertion site of the spinel (tetrahedral) aligns with the favorable coordination of  $\text{Zn}^{2+}$  ion. On the other hand, if the intermediate site offers the preferred coordination, the ion would be encouraged to diffuse, resulting in lower  $E_m$ , as is the case of  $\text{Zn}^{2+}$  in olivine and layered materials. The same principle applies to  $\text{Mg}^{2+}$  in olivine and layered materials where the stable insertion site is six-coordinated (as preferred by  $\text{Mg}^{2+}$  ion), resulting in higher  $E_m$ . However, the spinel with the tetrahedral insertion site offers lower  $E_m$  for  $\text{Mg}^{2+}$  diffusion.<sup>20</sup>

Another important consideration is the thermodynamic stability of the charged (deintercalated) and discharged (intercalated) states. These would directly influence the cycle life of the battery as well as determine whether synthesizing the materials under ambient experimental conditions would be feasible. This thermodynamic stability is usually measured by the driving force for the compound to separate into its most stable constituent compounds. From DFT calculations, the thermodynamic stability can be estimated by comparing the energy of the compound with the convex energy hull ( $E_{\text{hull}}$ ) of all the available ground states in the phase diagram ; such that a smaller value of  $E_{\text{hull}}$  implies greater thermodynamic stability of the material under ambient experimental conditions.<sup>15</sup>



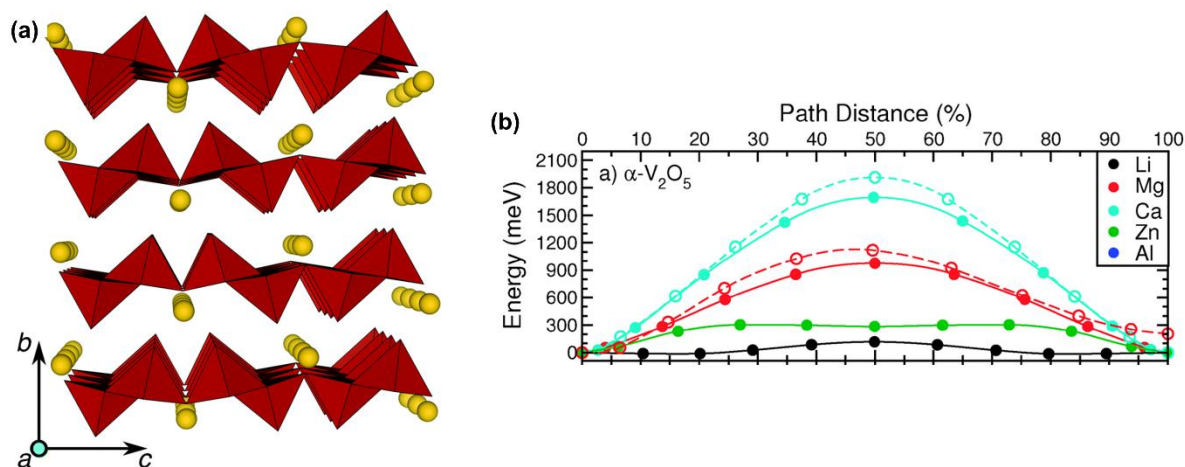
**Figure 1.5:** Migration energy barrier for ionic intercalation into oxide cathodes (a) Spinel Mn<sub>2</sub>O<sub>4</sub>; (b) olivine FePO<sub>4</sub>; (c) Layered NiO<sub>2</sub>. Adapted with permission from Rong, Z.; Malik, R.; Canepa, P.; Sai Gautam, G.; Liu, M.; Jain, A.; Persson, K.; Ceder, G., Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures. *Chemistry of Materials* **2015**, 27 (17), 6016-6021. Copyright (2015) American Chemical Society.



**Figure 1.6** Low energy ion intercalation paths in oxide cathodes (i) tet – oct – tet and (ii) oct – tet – oct topologies. Adapted with permission from Rong, Z.; Malik, R.; Canepa, P.; Sai Gautam, G.; Liu, M.; Jain, A.; Persson, K.; Ceder, G., Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures. *Chemistry of Materials* **2015**, 27 (17), 6016-6021. Copyright (2015) American Chemical Society.

As previously pointed out, out of all the multivalent intercalants,  $\text{Mg}^{2+}$  is considered as the most promising candidate, and so far, very few oxide cathodes demonstrated reversible  $\text{Mg}^{2+}$  intercalation. The notable ones are Chevrel  $\text{Mo}_6\text{S}_8$ , layered  $\text{MoO}_3$  and orthorhombic  $\alpha\text{-V}_2\text{O}_5$ . Out of these,  $\alpha\text{-V}_2\text{O}_5$ , which as already described in Section 1.2 is a well-known cathode for Li ion batteries, is usually considered to be a promising material, since it can theoretically provide higher voltage for  $\text{Mg}^{2+}$  intercalation compared to the other two candidates. In fact,  $\alpha\text{-V}_2\text{O}_5$  shows potential as a versatile cathode, having demonstrated intercalation type behavior with other multivalent cations such as  $\text{Ca}^{2+}$  and  $\text{Y}^{3+}$ , along with  $\text{Mg}^{2+}$ .<sup>21</sup>

Fig. 1.7 (a) and (b) present the conventional orthorhombic  $\alpha\text{-V}_2\text{O}_5$  crystal structure and migration barrier plots for different ionic intercalants into the  $\alpha\text{-V}_2\text{O}_5$  lattice. As presented in Fig. 1.7 (a),  $\alpha\text{-V}_2\text{O}_5$  structure has an open layered framework consisting of alternating corner and edge sharing  $\text{VO}_5$  pyramids. The intercalation sites [illustrated in Fig. 1.7 (a) as yellow spheres] are located between the layers. It can be seen from the plots in Fig. 1.7 (b) that the migration barriers systematically go up with increase in intercalant valence, as also noted before in case of the other oxide cathodes. [Fig. 1.5]. In addition, the change in the migration barriers for divalent ions, [ $\text{Ca}^{2+}$  ion has higher  $E_m$  compared to  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ ] is explained on the basis of ‘preferred’ anion coordination geometry. If the coordination of the stable insertion site for the cathode aligns with the preferred coordination of the multivalent intercalant, it would be stable and sluggish to diffuse through the lattice, resulting in poor mobility and higher  $E_m$ . For  $\alpha\text{-V}_2\text{O}_5$ , the stable insertion site is eight-coordinated. Thus  $\text{Ca}^{2+}$  is in its ‘preferred’ 8-fold coordinated site in  $\alpha\text{-V}_2\text{O}_5$  and has higher  $E_m$ , unlike  $\text{Mg}^{2+}$  or  $\text{Zn}^{2+}$  which prefer 6-fold and 4-fold coordinated sites respectively.<sup>21</sup>



**Figure 1.7** Orthorhombic  $\alpha$ - $\text{V}_2\text{O}_5$  lattice (i) Structure of  $\alpha$ - $\text{V}_2\text{O}_5$  along the  $b$ - $c$  crystallographic plane (ii) Migration energy barrier for ionic intercalation into  $\alpha$ - $\text{V}_2\text{O}_5$  cathode. Modified with permission from Gautam, G. S.; Canepa, P.; Malik, R.; Liu, M.; Persson, K.; Ceder, G., First-principles evaluation of multi-valent cation insertion into orthorhombic  $\text{V}_2\text{O}_5$ . *Chemical Communications* **2015**, 51 (71), 13619-13622. Published by The Royal Society of Chemistry.

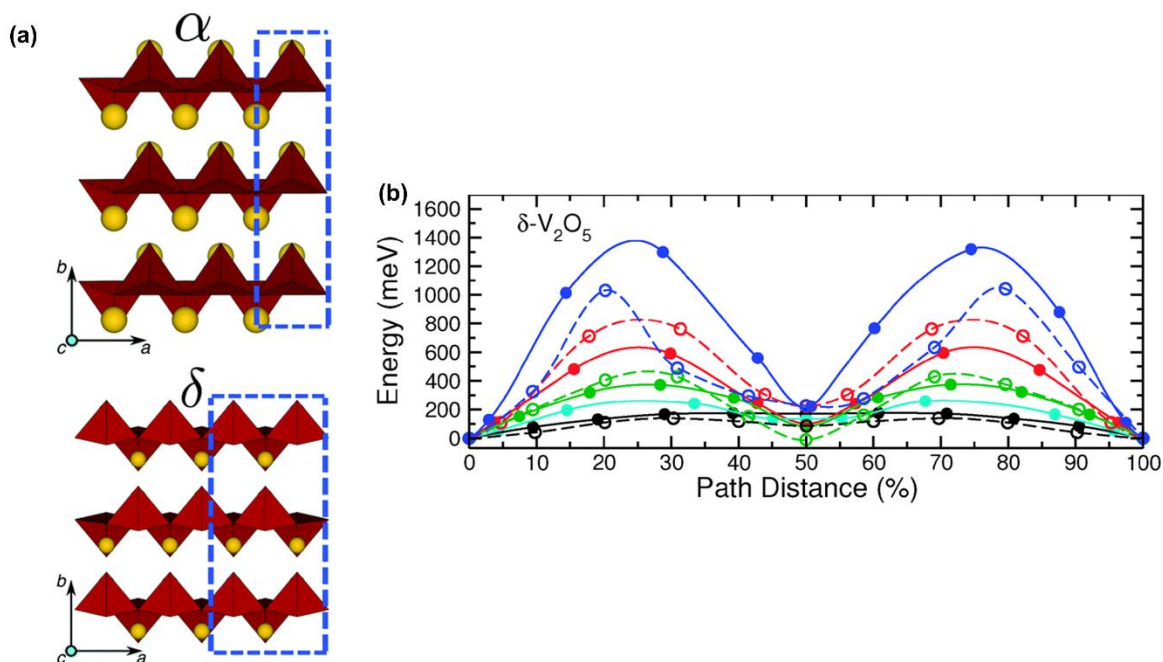
## 1.6 Role of anion coordination environment in determining migration barriers for ionic intercalation in $\text{V}_2\text{O}_5$ polymorphs

As previously mentioned, the change in anion coordination environment along the intercalation path plays a major role in determining the migration barrier ( $E_m$ ). This effect is demonstrated in a rather dramatic manner among the several different  $\text{V}_2\text{O}_5$  polymorphs. Fig. 1.7 presents the crystal structure and migration barrier plots for the conventional, orthorhombic  $\alpha$ - $\text{V}_2\text{O}_5$  polymorph. One of the reasons of the higher  $E_m$  for multivalent ion intercalation in this polymorph is the somewhat unfavorable anion coordination environment change along the intercalation path, the intercalating species encounters a  $8 - 3 - 8$  evolution in the oxygen

coordination along the intercalation path. In contrast, in the  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorph, the change in anion coordination environment along the intercalation path is much less severe: “4+2” – 3 – 5 – 3 – “4+2”.

Thus, the resulting migration barrier for ionic intercalation is predicted to be lower in this case according to DFT calculations.

Fig. 1.8 (a) presents the crystal structure of  $\delta$ -V<sub>2</sub>O<sub>5</sub>, contrasting it with the conventional  $\alpha$ -V<sub>2</sub>O<sub>5</sub> case. Fig. 1.8 (b) presents the migration barrier plots for different ionic intercalants into the  $\delta$ -V<sub>2</sub>O<sub>5</sub> lattice. The different shape of the migration barrier plots for the two V<sub>2</sub>O<sub>5</sub> polymorphs:  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\delta$ -V<sub>2</sub>O<sub>5</sub> can be explained on the basis of the difference in the change of the anion coordination environment along the intercalation path for these two polymorphs. In the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph, the ion moves from one stable insertion site (eight-coordinated) to the next via an intermediate site (three-coordinated), and this is reflected in the shape of the migration barrier plot. [Fig. 1.7 (b)]. On the other hand, in the  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorph, the stable insertion site adopts a “4+2” coordination and during diffusion through the lattice, the intercalant ion moves through a 3-coordinated face shared with an intermediate 5-coordinated (pyramidal) site, lastly hopping over to the next stable site. The local minima in the migration barrier plot [Fig. 1.8 (b)] corresponds to occupation of the intermediate pyramidal site. The maximum energy difference encountered along the diffusion path defines the migration barrier ( $E_m$ ) which is obviously lower in the  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorph since the overall change in the anion coordination environment along the intercalation path is much less drastic in this case compared to the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph.



**Figure 1.8** Crystal structure and migration barriers into  $\delta$ - $\text{V}_2\text{O}_5$  (i) Comparison of crystal structures for  $\alpha$ - $\text{V}_2\text{O}_5$  and  $\delta$ - $\text{V}_2\text{O}_5$  along the  $a$ - $b$  crystallographic plane (ii) Migration energy barrier for ionic intercalation into  $\delta$ - $\text{V}_2\text{O}_5$  lattice. Modified with permission from Gautam, G. S.; Canepa, P.; Malik, R.; Liu, M.; Persson, K.; Ceder, G., First-principles evaluation of multi-valent cation insertion into orthorhombic  $\text{V}_2\text{O}_5$ . *Chemical Communications* **2015**, 51 (71), 13619-13622. Published by The Royal Society of Chemistry.

In this thesis, I present detailed results comparing phase formation upon electrochemical Mg intercalation into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> versus chemical magnesiation which leads to the  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> phase (Chapter 4). Unfortunately, experimental efforts to directly synthesize  $\delta$ -MgV<sub>2</sub>O<sub>5</sub>, remove Mg ions from the material and use the subsequent  $\delta$ -V<sub>2</sub>O<sub>5</sub> as the cathode material failed, possibly due to thermodynamic instability of the empty  $\delta$ -V<sub>2</sub>O<sub>5</sub> structure.

However, it was recently predicted that some metastable polymorphs of V<sub>2</sub>O<sub>5</sub>, such as  $\zeta$ -V<sub>2</sub>O<sub>5</sub> and  $\varepsilon$ -V<sub>2</sub>O<sub>5</sub> could also provide lower migration barriers for ion intercalation.<sup>22</sup>

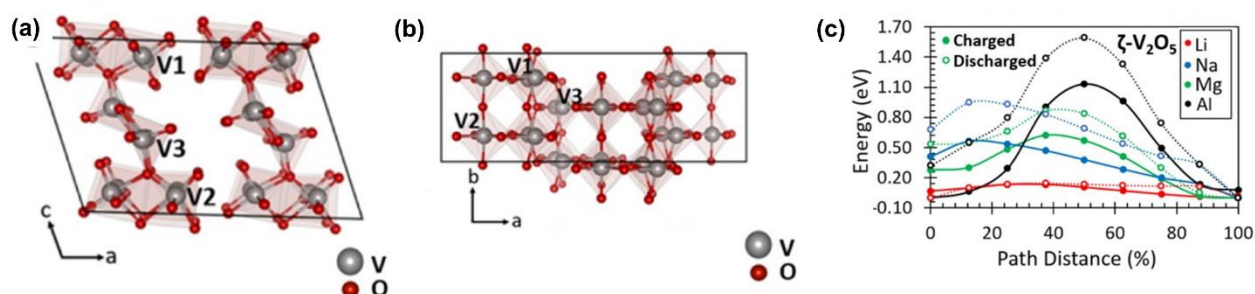
The  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph is experimentally derived from the leaching of Ag ions from the  $\beta$ -Ag<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> phase, the resulting structure was found to retain the unique 1-D tunnel framework, recent work also showed that both Li and Mg ions could be chemically inserted into this material, thus indicating its potential as a versatile cathode host.<sup>23</sup>

Fig. 1.9 (a) and (b) present the crystal structure of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> along the  $a$ - $c$  plane and the  $a$ - $b$  plane respectively.  $\zeta$ -V<sub>2</sub>O<sub>5</sub> has the space group  $C2/m$  and as shown in Fig. 1.9 (b), its structure consists of linked chains of vanadium centered polyhedra that enclose 1-D tunnels along the ‘b’ axis.

Fig. 1.9 (c) shows the migration barrier plot for ionic intercalation into  $\zeta$ -V<sub>2</sub>O<sub>5</sub>, as can be seen these barriers are systematically lower than those calculated in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>. This lowering of migration barrier results from the somewhat favorable anion coordination topology seen in this polymorph, the change in anion coordination environment along the intercalation path is 4 – 3 – 5 – 3 – 4, much less dramatic than that encountered in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>.

Further details on the synthesis and characterization of the pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> material, confirming its unique tunnel framework that clearly distinguishes it from the layered  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, along with

results exploring Li and Mg intercalation into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> adopting a multimodal approach, will be presented in Chapters 3 and 4 respectively.

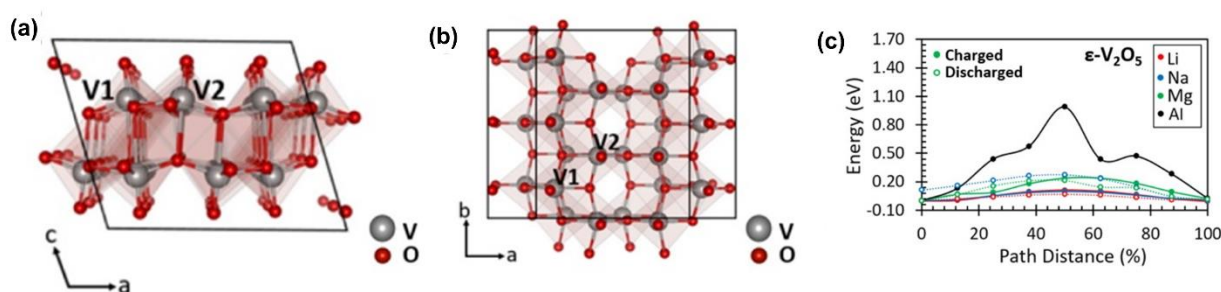


**Figure 1.9** Crystal structure and migration barriers into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> (a) Structure of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> along the *a*-*c* crystallographic plane (b) Structure of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> along the *a*-*b* crystallographic plane (c) Migration energy barrier for ionic intercalation into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> lattice. Modified with permission from Parija, A.; Liang, Y.; Andrews, J. L.; De Jesus, L. R.; Prendergast, D.; Banerjee, S., Topochemically De-Intercalated Phases of V<sub>2</sub>O<sub>5</sub> as Cathode Materials for Multivalent Intercalation Batteries: A First-Principles Evaluation. *Chemistry of Materials* **2016**, 28 (16), 5611-5620. Copyright (2016) American Chemical Society.

The  $\epsilon$ -V<sub>2</sub>O<sub>5</sub> was predicted to be experimentally derivable from Cu<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase. This polymorph also has the space group *C2/m* and consists of a double-layered structure held together by Van Dar Waal's bonding, with interlayer sites larger than either  $\alpha$ -V<sub>2</sub>O<sub>5</sub> or  $\zeta$ -V<sub>2</sub>O<sub>5</sub>. Fig. 1.10 (a) and (b) present the crystal structure of  $\epsilon$ -V<sub>2</sub>O<sub>5</sub> along the *a*-*c* and *a*-*b* crystallographic planes

respectively, while Fig. 1.10 (c) show the migration barrier plot for ionic intercalation into  $\epsilon$ - $\text{V}_2\text{O}_5$  lattice. As can be seen, the barriers in this case are lower than both  $\alpha$ - $\text{V}_2\text{O}_5$  and  $\zeta$ - $\text{V}_2\text{O}_5$ .

Unfortunately, experimental synthesis of this material was not very successful, due to the hygroscopic nature of the samples, and rapid auto-hydration under atmospheric conditions. If the synthesis methodology could be standardized for this material, it has the potential to be a promising cathode for multivalent batteries.



**Figure 1.10** Crystal structure and migration barriers into  $\epsilon$ - $\text{V}_2\text{O}_5$  (a) Structure of  $\epsilon$ - $\text{V}_2\text{O}_5$  along the  $a$ - $c$  crystallographic plane (b) Structure of  $\epsilon$ - $\text{V}_2\text{O}_5$  along the  $a$ - $b$  crystallographic plane (c) Migration energy barrier for ionic intercalation into  $\epsilon$ - $\text{V}_2\text{O}_5$  lattice. Modified with permission from Parija, A.; Liang, Y.; Andrews, J. L.; De Jesus, L. R.; Prendergast, D.; Banerjee, S., Topochemically De-Intercalated Phases of  $\text{V}_2\text{O}_5$  as Cathode Materials for Multivalent Intercalation Batteries: A First-Principles Evaluation. *Chemistry of Materials* **2016**, 28 (16), 5611-5620. Copyright (2016) American Chemical Society.

## 1.7 Concluding remarks on V<sub>2</sub>O<sub>5</sub> polymorphs

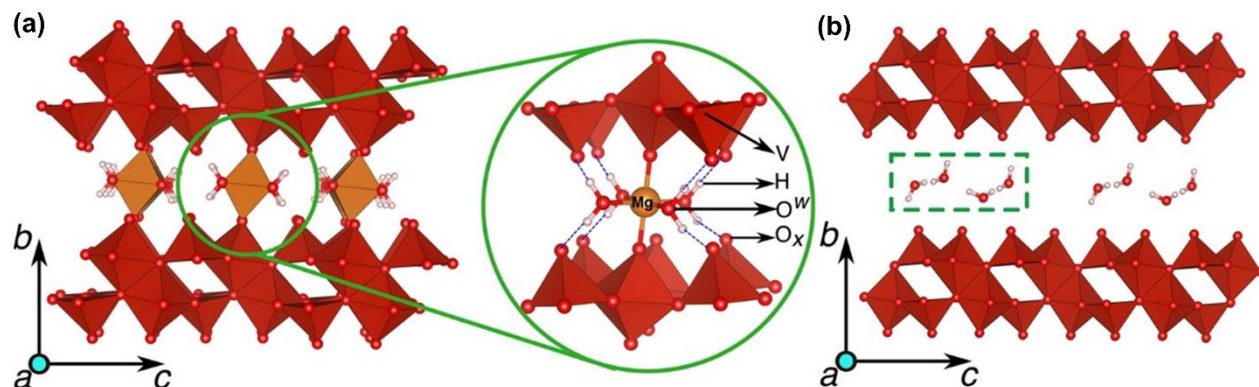
It would be worthwhile at this point to compare the four V<sub>2</sub>O<sub>5</sub> polymorphs that have been discussed so far: the orthorhombic  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, tunnel structured  $\zeta$ -V<sub>2</sub>O<sub>5</sub>,  $\delta$ -V<sub>2</sub>O<sub>5</sub> and  $\epsilon$ -V<sub>2</sub>O<sub>5</sub> regarding their potential as Mg-ion battery cathodes. In terms of mobility of the intercalant ion through the lattice, the calculated migration energy barrier ( $E_m$ ) is lowest for the  $\epsilon$ -V<sub>2</sub>O<sub>5</sub> and  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorphs, which would mean these should offer faster kinetics and mitigate the sluggish diffusion of Mg<sup>2+</sup> ion. Unfortunately, due to the reasons outlined before, these two polymorphs could not be synthesized successfully, however if future experimental efforts can solve the synthesis challenges, these would prove to be of great interest as Mg-ion cathodes. The low  $E_m$  for the  $\epsilon$ -V<sub>2</sub>O<sub>5</sub> and  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorphs can be explained on the basis of the favorable anion coordination topology for Mg ion. The predicted voltages for the polymorphs are  $\sim 2.21$  V ( $\alpha$ -V<sub>2</sub>O<sub>5</sub>) ;  $\sim 2.56$  V ( $\delta$ -V<sub>2</sub>O<sub>5</sub>)<sup>21</sup> ;  $\sim 3.28$  V ( $\zeta$ -V<sub>2</sub>O<sub>5</sub>) and  $\sim 2.92$  V ( $\epsilon$ -V<sub>2</sub>O<sub>5</sub>).<sup>22</sup> It was also predicted that Mg insertion into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> would attain the most stable configuration at  $x_{Mg}=0.5$ , forming the  $\epsilon$ -Mg<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub> phase.<sup>24</sup> For the  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorph, metastable Mg insertion was predicted to result in a phase separation between  $\delta$ -Mg<sub>0</sub>V<sub>2</sub>O<sub>5</sub> and fully intercalated  $\delta$ -Mg<sub>1</sub>V<sub>2</sub>O<sub>5</sub>.<sup>24</sup> For the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> and  $\epsilon$ -V<sub>2</sub>O<sub>5</sub> polymorphs, the intercalation limits were predicted to be  $x_{Mg} = 0.33$  and  $x_{Mg} = 1$  respectively.<sup>22</sup>

## 1.8 V<sub>2</sub>O<sub>5</sub> gels as multivalent cathodes

Another reason behind the sluggish kinetics of Mg<sup>2+</sup> diffusion through the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> lattice is due to the higher positive charge on the divalent cation that results in strong electrostatic interactions with the surrounding anion (oxygen) environment, causing higher  $E_m$ . The strategy that was discussed in Section 1.6 involved modifying the available anion coordination topology along the intercalation path by exploring other V<sub>2</sub>O<sub>5</sub> polymorphs such as  $\delta$ -V<sub>2</sub>O<sub>5</sub>,  $\zeta$ -V<sub>2</sub>O<sub>5</sub> and  $\epsilon$ -V<sub>2</sub>O<sub>5</sub>. Another strategy that has also been often employed in the field is the incorporation of solvent molecules in the cathode structure that can partially shield the charge on the multivalent intercalant and somewhat reduce the electrostatic interactions with the anion environment, thereby reducing  $E_m$ . This phenomenon is referred to as “solvent co-intercalation”. This polymorph of V<sub>2</sub>O<sub>5</sub>, referred to as xerogel-V<sub>2</sub>O<sub>5</sub>, is usually represented chemically as V<sub>2</sub>O<sub>5</sub>.nH<sub>2</sub>O and comprises of a “bilayered” arrangement of V<sub>2</sub>O<sub>5</sub> layers,<sup>25,26</sup> as shown in Fig. 1.11. This is also a metastable structure and upon heating to ~350 °C, it loses the structural water and irreversibly transforms to  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase.<sup>27</sup> A single “bilayer” in the xerogel structure consists of two individual V<sub>2</sub>O<sub>5</sub> monolayers with the spacing between bilayers set by both the intercalated H<sub>2</sub>O<sup>27</sup> as well as the type and quantity of intercalant cations.<sup>28</sup> Due to its structural motif, some researchers also refer to it as “Bilayered-V<sub>2</sub>O<sub>5</sub>”. This material has been explored as a cathode for Li-ion<sup>29</sup>, Mg-ion<sup>28,30</sup> and Zn-ion<sup>31</sup> batteries. Another gel like polymorph, termed V<sub>2</sub>O<sub>5</sub> aerogel has also been looked at, primarily for Li-ion batteries.<sup>32</sup> This material has a slightly different synthesis methodology compared to the xerogel, but is believed to have a similar double-layered structure.<sup>8</sup>

The exact structure of the xerogel material and the sites for H and the cation intercalation has not been clearly resolved, with the nano-crystalline nature of this material making high-resolution X-

ray/TEM characterization difficult. Recently, Gautam *et. al.* <sup>26</sup> investigated Mg intercalation into this xerogel system using first principles calculations and reported three distinct phases. The first case is for the “wet” electrolyte ( $a_{H_2O} \approx 1$ ) where each  $Mg^{2+}$  ion intercalates with two  $H_2O$  molecules and a decrease in Mg content corresponds with a decrease in intercalated water ; experimentally this represents cases where aqueous electrolytes are used, there is a thermodynamic driving force for the water content to change with the  $Mg^{2+}$  content. The second case is where Mg intercalation occurs with a “dry” electrolyte ( $10^{-2} < a_{H_2O} < 10^{-6}$ ), and here  $H_2O$  co-intercalates with Mg for  $x_{Mg} < 0.25$  and the water content remains unchanged as more Mg is inserted. Thirdly, for the superdry electrolyte ( $a_{H_2O} < 10^{-7}$ ), it was found that the stable phase shows a clear separation between fully magnesiated ( $x_{Mg} = 0.5$ ) and fully demagnesiated ( $x_{Mg} = 0$ ) domains. Very interestingly, as presented in Chapter 4 of this thesis, my experimental results investigating electrochemical Mg intercalation into  $\alpha$ - $V_2O_5$  with a 15 ppm electrolyte shows this two-phase behavior, with the atomic-resolution ABF image [Fig. 4.9 (c)] showing clear phase separation between Mg-rich and Mg-poor domains. Thus, this study established that the activity of water in the electrolyte not only controls the level of co-intercalation but also the nature of Mg intercalation. Without water, Mg intercalation occurs as a two-phase reaction between  $x_{Mg} = 0$  and  $x_{Mg} = 0.5$ , whereas presence of water in the electrolyte stabilizes intermediate Mg states.



**Figure 1.11** Structure of the (a) fully magnesiated and (b) fully demagnesiated xerogel with one  $\text{H}_2\text{O}/\text{V}_2\text{O}_5$  formula unit. Adapted with permission from Sai Gautam, G.; Canepa, P.; Richards, W. D.; Malik, R.; Ceder, G., Role of Structural  $\text{H}_2\text{O}$  in Intercalation Electrodes: The Case of Mg in Nanocrystalline Xerogel- $\text{V}_2\text{O}_5$ . *Nano Letters* **2016**, 16 (4), 2426-2431. Copyright (2016) American Chemical Society.

## CHAPTER 2

### Experimental Methods

#### 2.1 Scanning transmission electron microscopy (STEM)

The STEM images, EELS and EDX data presented in this thesis were acquired with the JEOL JEM ARM 200CF (later referred to as ARM) analytical transmission electron microscope at University of Illinois-Chicago. The primary energy was chosen to be 200 keV for the work on cathode materials, including  $\alpha$ -V<sub>2</sub>O<sub>5</sub>,  $\zeta$ -V<sub>2</sub>O<sub>5</sub> and  $\alpha$ -MnO<sub>2</sub>. For the graphene liquid cell experiments, the primary energy was lowered to 80 keV. This microscope is equipped with a cold-field emission gun as the electron source, probe-side aberration corrector leading to a spatial resolution of 0.78 Å at 200 keV, HAADF, LAADF and ABF detectors allowing simultaneous imaging of heavy and light atomic columns of the specimen at atomic-resolution. It is also equipped with post-column Gatan Enfina EELS spectrometer (Model 766 Enfina 1000), recently replaced with the Gatan Quantum Dual EELS system and Oxford-XMAX100 TLE silicon drift detector (SDD) for EDX for obtaining chemical information about the specimen.

The discussion in this chapter pertains to the basic principles of STEM imaging, EELS and EDX. Parallels are drawn, where relevant, between the general discussion and the specific instrument used for these experiments.

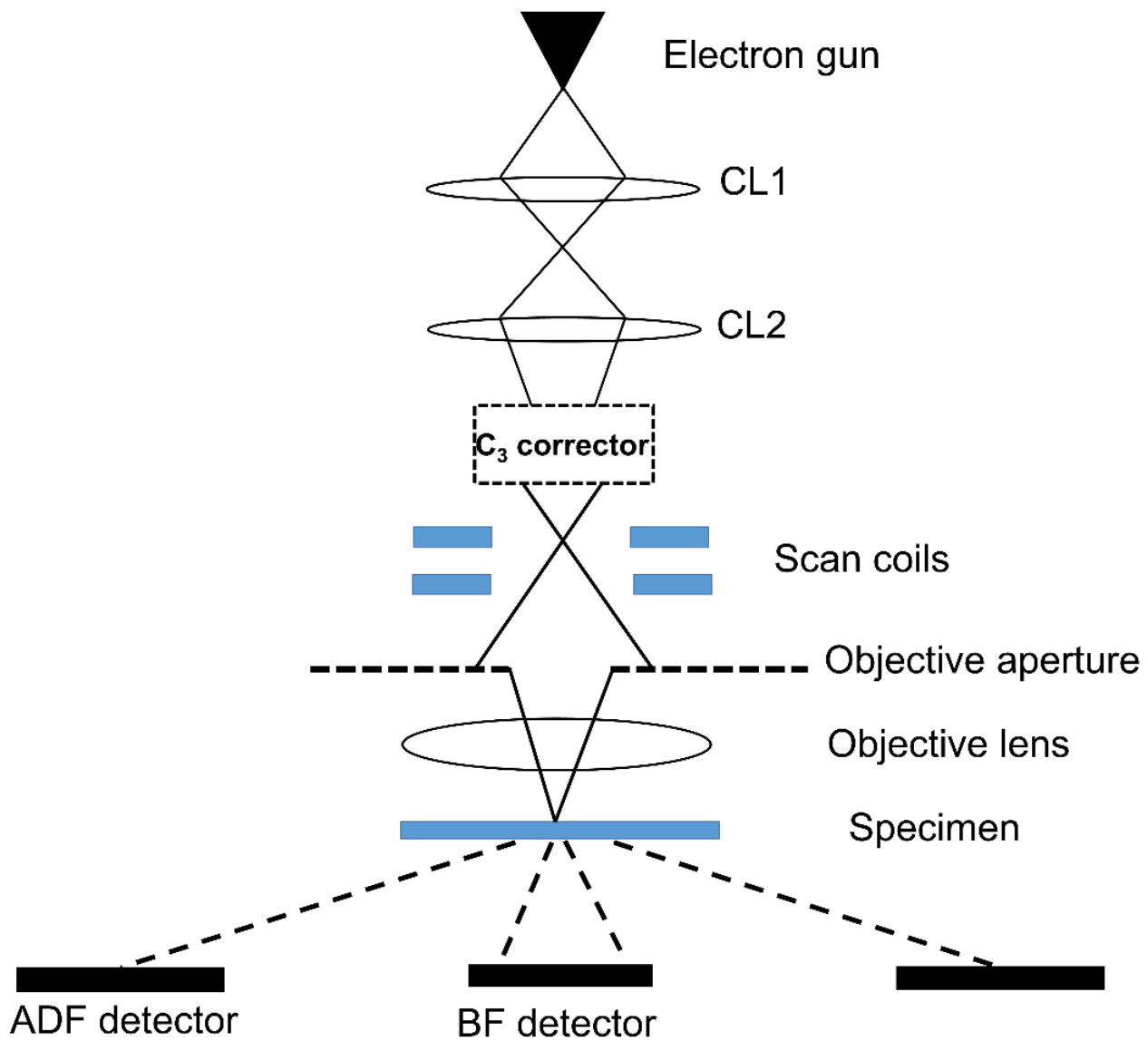
Historically, the first STEM was developed in 1937-38 by Manfred Von Ardenne, the major limitation in the early STEM was noise, owing to limited brightness of the electron source and lens aberrations. Scherzer showed in 1949 that correcting higher order geometric aberrations require employing non-rotationally symmetric lenses and laid the foundation for the development of the multipole corrector lenses that are in use today.<sup>33</sup> He showed that these non-round lenses could achieve negative spherical aberration coefficients that could compensate for

the inherent positive aberrations of the probe-forming lenses, particularly the objective lens. In recent years, successfully correcting lens aberrations has required coupling these multipole corrector lens systems with advanced, fast electronics precisely tuning and controlling them as well as implementation of high brightness field emission electron source, pushing the achievable spatial resolution below 1Å and sub-Å atomic-resolution STEM imaging is now routinely done in the various electron microscopes around the world, including the ARM at UIC.

Fig. 2.1 illustrates the schematic of the experimental setup employed for STEM imaging. The electron gun acts as the source producing a highly collimated beam of electrons. The cold field-emission gun, (cold-FEG), such as the one used in ARM produces a monochromatic electron beam, can operate at room temperature and achieve a brightness (current/unit area/solid angle) at the source of  $\sim 10^{13}$  A/m<sup>2</sup>sr.<sup>34</sup>

A collection of lenses, termed collectively as the condenser lens is used to create a demagnified image of the electron source, the final lens system used in the demagnification step is termed as the objective lens. This is primarily done to reduce the effects of partial coherence at the electron source. The strongly focused spot created by such demagnification is termed as the electron probe, which is ideally at the atomic-scale. As shown in Fig. 2.1, the probe convergence angle formed at the cross-over point on the specimen can be controlled by the size of the objective aperture. For a non aberration-corrected system, a smaller objective aperture is used to limit the amount of spherical aberration arising from higher angle rays. This, in turn, leads to a small probe convergence angle and reduces the amount of probe current. Hence a higher brightness source, such as a cold FEG, is required to produce enough probe current even for the small probe convergence angle to provide enough signal to noise ( $s/n$ ) for high resolution images and spectra. In fact, this is also the main reason that aberration correctors, such as the one in ARM, helps to

improve spatial resolution, since it becomes possible to further open up the objective aperture and allow more probe current, provided the specimen is stable under the electron beam.



**Figure 2.1 :** (a) Schematic representation of a scanning transmission electron microscope (STEM) instrument. Redrawn from [35].

The electron probe is scanned across the thin, electron-transparent sample in a raster by the set of scan-coils. In an aberration-corrected electron microscope, such as the ARM, the corrector is another set of lenses that remove third order spherical aberration. The transmitted electrons are intercepted by a set of detectors intended to collect different and complementary signals to gather sufficient structural and chemical information about the sample being studied.

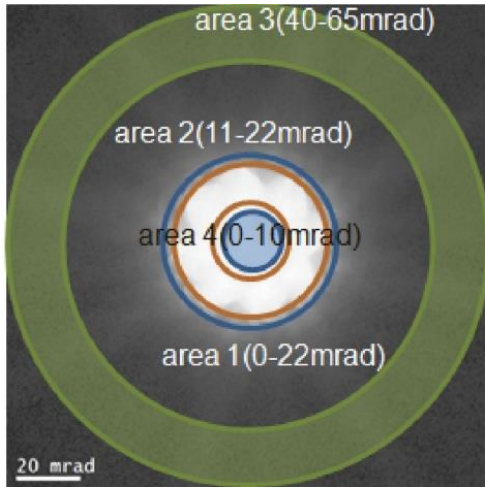
A wide range of structural and chemical information about the specimen can be obtained by studying a number of signals. The incident electrons would undergo both *elastic* and *inelastic* scattering events with the specimen. The *elastically scattered* incident electrons that interact with the atomic nuclei of the specimen would lose minimal energy, and are intercepted by complementary detectors placed at high and low angles with respect to the optic axis:

i) The electrons that are *elastically* scattered close to the optic axis are collected in the angular range represented as Area 1 in Fig. 2.2 below. This is referred to as Bright field (BF) mode. The signal in this region can be further subdivided by masking the direct beam in order to image light elements, leading to the development of Annular bright field (ABF) imaging mode as discussed later. In the representative schematic of Fig. 2.2, this has been shown as Area 1 being further split into Area 2 and Area 4.

ii) The transmitted electrons that are *elastically* scattered at high angles with respect to the optic axis have been represented by the angular range designated as Area 3 in Fig. 2.2. This mode is referred to as Annular dark field (ADF) imaging.

The *inelastically scattered* incident electrons that lose a part of their kinetic energy due to interaction with the specimen electrons can be intercepted by a magnetic prism and used to form a spectra according to the energy lost, this is referred to as electron energy loss spectroscopy

(EELS). The sample electrons that gain energy and are excited to higher energy levels as a consequence of these inelastic scattering events would subsequently undergo deexcitation, emitting X ray photons, which can also be intercepted in the mode referred to as Energy dispersive X ray spectroscopy (EDX).<sup>35</sup>



**Figure 2.2 :** View of the diffraction plane highlighting the angular range of the various signals employed in STEM.

Adapted with permission from Okunishi *et. al.*[47].

## 2.2 Spatial Resolution in the TEM/STEM: Effect of Aberrations and aberration correction

In an ideal world, if the lens systems employed in an electron microscope were perfect, the spatial resolution would be determined by Rayleigh criterion which determines the theoretical resolution limit for an incoherent point source, in the absence of any lens aberrations

$$r_{th} = 1.22 \lambda / \beta \quad [2.1]$$

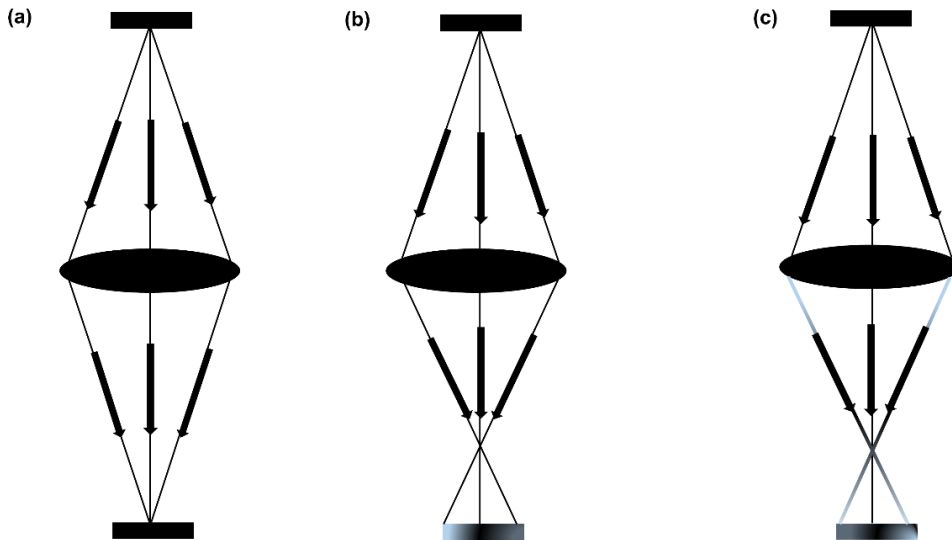
The most important consequence of this Rayleigh criterion is that even in a perfect lens, the image of a point source would suffer diffraction broadening at the lens forming an “Airy disk”. Extent of this diffraction broadening is determined by the outermost collection angle of the lens (limiting aperture,  $\beta$ ). As a first approximation, we can get better resolution by lowering  $\lambda$  or increasing  $\beta$ . However, in reality, aberrations are always present. So using a bigger lens aperture,

ideally an infinitely large one, would introduce more aberrations into the system. So, the effects of diffraction broadening at the lens and inherent lens aberrations are opposite to each other, and the optimum resolution can be achieved with an aperture size that balances these two.

There are primarily two types of aberrations in any optical system, such as an electron microscope (i) geometric aberrations, caused primarily due to differences in the path lengths of the rays travelling near and away from the optic axis, resulting in the off axis rays being focused at a different point and (ii) chromatic aberration, caused primarily due to the inherent energy spread of the electron beam at the source. These are illustrated in Fig. 2.3 below.<sup>36</sup>

The dominant and most well-known type of geometric aberration is spherical aberration. Ignoring rotationally non symmetric aberrations, the aberration function can be expressed as a power series in  $\theta$  as:

$$\chi(\theta) = \frac{1}{2} \Delta f \theta^2 + \frac{1}{4} C_s \theta^4 + C_5 \theta^6 + C_7 \theta^8 + \dots \quad [2.2]$$



**Figure 2.3:** (a) Action of an ideal lens (b) Effect of spherical aberration that scatters rays far away from optic axis by a greater amount and focuses at a different point (c) Effect of chromatic aberration that blurs ray paths due to energy spread of the beam. Redrawn from [36].

In equation 2.1 above,  $\Delta f$  is the defocus,  $C_s$  is the coefficient of third order spherical aberration which is usually the most dominant geometric aberration while  $C_5$  and  $C_7$  represent coefficients of higher order spherical aberrations. The effect of geometric aberrations, as also illustrated in Fig. 2.3(b) is to bring the off axis rays to a different focus, thereby those are laterally displaced from the true Gaussian focus by an amount  $\delta(\theta)$  (which can be expressed as the gradient of the aberration function

$$\delta(\theta) = \Delta f \theta + C_s \theta^3 + C_5 \theta^5 + C_7 \theta^7 + \dots \quad [2.3]$$

So the most dominant factor is  $C_3$  (third order spherical aberration). In the presence of spherical aberration, the resolution limit is determined by the Scherzer condition,

$$r_{\min} \sim 0.91 (C_s \lambda^3)^{1/4} \quad [2.4]$$

In a STEM, the objective lens is the most important probe-forming lens, so the aberration corrector is aimed at primarily correcting the aberrations of this lens. The ARM employs a hexapole aberration corrector, the basic idea as mentioned before, is exploiting the Scherzer criterion, corrector lenses employ a negative spherical aberration to compensate for the positive aberrations of the microscope.

### 2.3 Annular Dark field (ADF) imaging

The ADF mode of imaging is usually realized in a STEM by using an off-axis annular detector with a large acceptance angle, (usually  $>40$  mrad) commonly referred to as High-angle annular dark field (HAADF) imaging. Thus this image integrates the diffraction pattern and is sensitive to the total scattered intensities that reach the detector for each point on the specimen. Therefore, it is devoid of the effects of phase contrast and is instead an *incoherent image*. The contrast seen in the image is directly proportional to the high-angle Rutherford scattering cross-section of the

atoms, ( $\sim Z^2$ ) and is thus also called Z-contrast image. The acceptance angle of the HAADF detector is selected so as to exclude the effects of coherent Bragg scattering, to preserve the incoherent nature of the image.

The image intensity for an incoherent image can be expressed as a convolution between the object function and the probe intensity profile

$$I(\mathbf{R}) = O(\mathbf{R}) * P^2(\mathbf{R}) \quad [2.5]$$

This Z-contrast imaging technique found important applications in studying semiconductor materials.<sup>37,38,39</sup> It also enabled direct visualization of grain-boundary dislocations inside perovskite oxides such as Strontium titanate ( $\text{SrTiO}_3$ )<sup>40,41,42</sup> as well as in the catalysis field imaging clusters of single atoms on supports.<sup>43</sup>

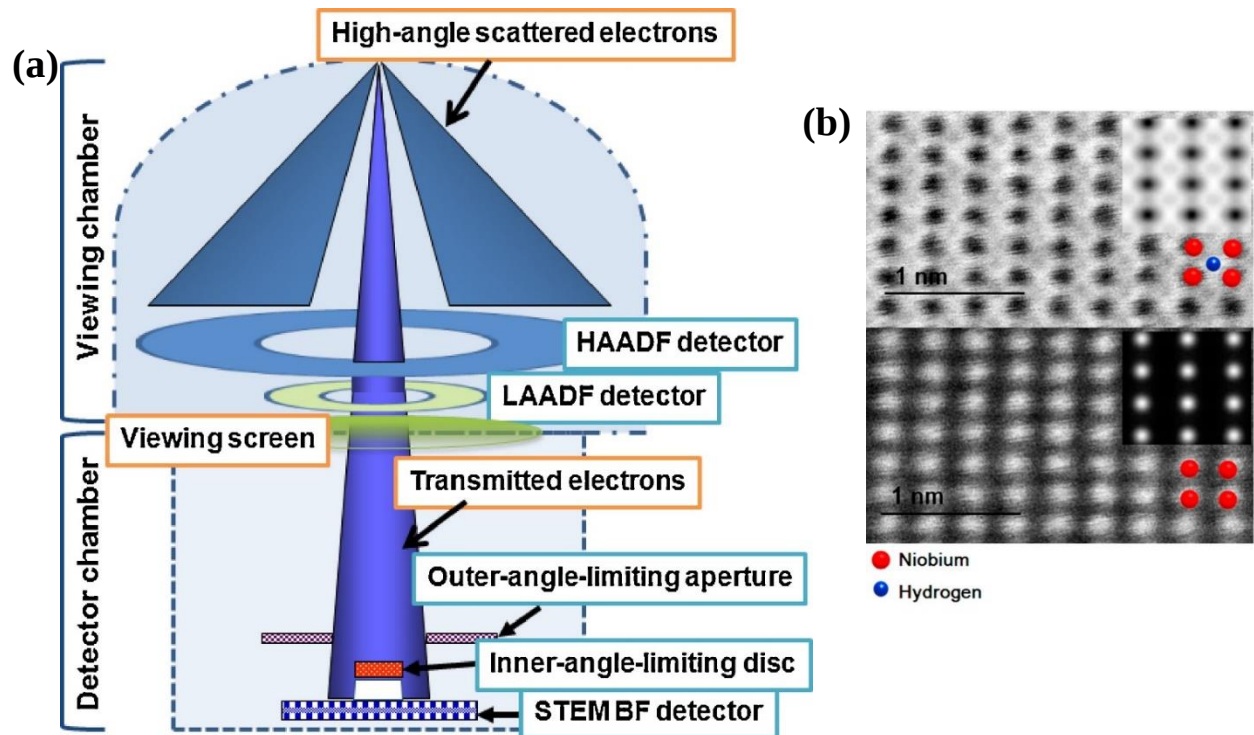
The chief advantage of this technique was found that being incoherent, the images did not reverse contrast with variations in thickness or defocus; thus it allowed for easily interpretable images. The theoretical explanation for this was provided by considering the Bloch wave method. The HAADF detector mainly collects the electrons scattered to high angles, which interact with the specimen nucleus where the 1s Bloch state is dominant. Thus the intensity seen in these Z-contrast images is primarily due to the 1s Bloch states and do not contain the effects of interference between different Bloch states. In addition, the intensities are integrated through the sample thickness, and since the 1s states are highly localized around the atomic columns, interference effects are to be minimal at the interfaces.<sup>44,45</sup>

## 2.4 Annular Bright Field (ABF) imaging

The ABF mode of imaging was introduced by Okunishi et al.<sup>46,47</sup> By introducing an inner angle limiting disk (referred to as a beam stop) and an outer angle limiting aperture (Bright field aperture) in the directly scattered region (usually  $< 28$  mrad) of the electron beam it was shown that light elements could be imaged. It was also established that by adjusting the distance between HAADF and ABF detectors, simultaneous acquisition for both types of images can be done, thus allowing for imaging of both heavy and light atomic columns at the same time.

Findlay et. al.<sup>48</sup> proposed a generalization of the ‘s-state’ model to explain the ABF image formation mechanism. According to this model, the dark contrast in the ABF images that clearly indicate atomic column locations arise from the deficit of scattered electrons in the 11-22 mrad angular range (the annular region that gives rise to the ABF signal). The s-state model assumes the incident electron probe excites the s state of the particular atomic column on which it is placed, and the reciprocal space wave function that describes the scattered electron distribution depends on the angular range defined by the apertures. In the middle region, ( $\sim 11$ -22 mrad), interference leads to reduction of electron density, leading to the contrast seen in ABF images. Systematic simulation studies have also shown that this ABF mode of imaging was thickness independent, similar to Z-contrast image, though the interpretable defocus range is somewhat narrow.<sup>48,49</sup>

While the ABF image in Fig. 2.4 (b) shows both heavy (Nb) as well as the light (H) atomic columns, the corresponding HAADF image only shows the heavier Nb atomic columns, and cannot image the H.<sup>50</sup> This example illustrates the usefulness of this imaging technique.



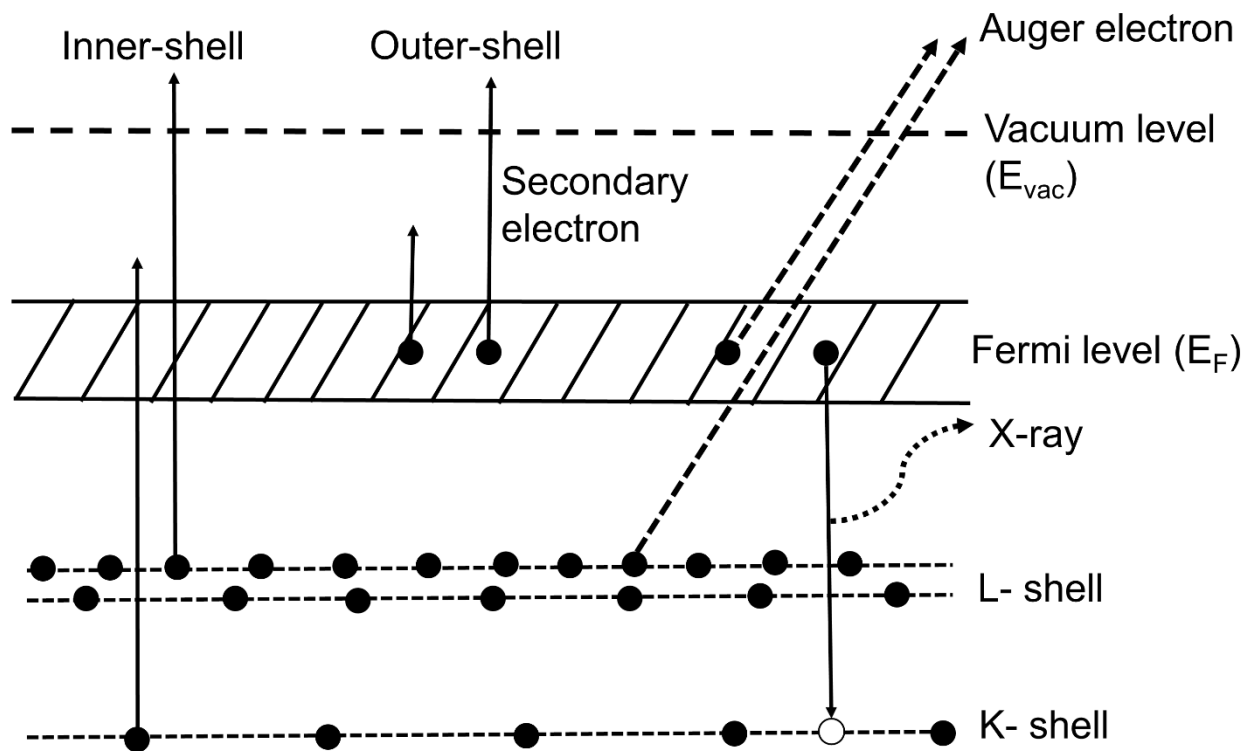
**Figure 2.4** (a) Configuration of detectors in a standard JEOL JEM ARM 200F transmission electron microscope that allows for simultaneous HAADF and ABF imaging. Adapted with permission from Okunishi *et. al.* [47]. (b) HAADF and ABF image pairs from NbH in [110] orientation, adapted with permission from Y. J Kim *et. al.* [50].

## 2.5 Electron Energy loss spectroscopy

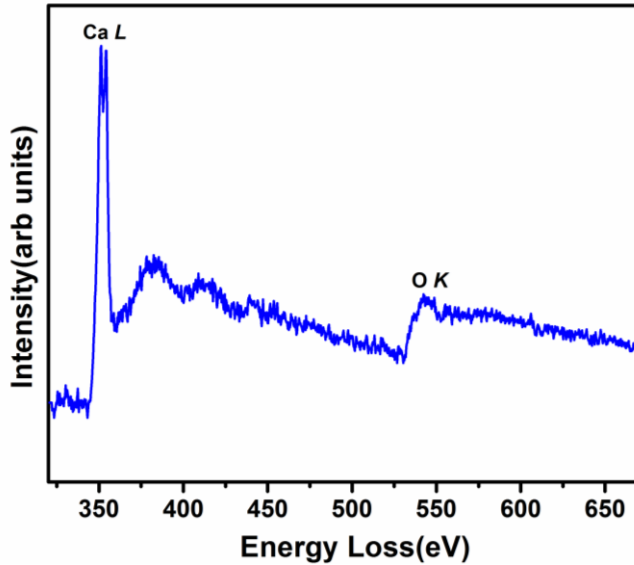
The primary electrons in the incident electron beam undergo *inelastic* scattering with the electrons of the specimen, and as a result are transmitted after losing some specific amount of energy, characteristic of the specimen. These transmitted electrons are then intercepted by the electron energy loss spectrometer, which classifies the electrons as a function of their kinetic energy. Fig. 2.5 below shows the energy level representation of the specimen.<sup>51</sup> Some of the incident electrons would excite the inner shell electrons of the solid (such as K or L shell electrons), which would then be excited to the unoccupied energy levels above Fermi level ( $E_F$ ) and the incident electron would lose an energy equal to the binding energy of the inner shell sample electron. Subsequently, the excited state electron would make a downward transition, emitting the excess energy as electromagnetic radiation (x-ray photon) or Auger electrons.

Since EELS measures transitions from inner shells to energy bands above Fermi level ( $E_F$ ), it can map out the local density of states in the outer bands/conduction band from a careful analysis of the near edge fine structure. Additionally, in case of transition metals, analyzing  $L_3/L_2$  ‘white line’ intensity ratio or computing the energy differences between certain edges, it is also possible to quantify valence states directly and therefore confirm Li/Mg intercalation into the cathode.

The EELS spectrometer functions both as a magnetic prism and a lens, the transmitted electrons go through an entrance aperture into the drift tube, and the magnetic field deflects them by different amounts in proportion to their energies. So the electrons that are scattered *elastically* by interacting with the atomic nucleus of the specimen lose minimal energy while the *in-elastically* scattered ones lose more energy. The latter are deflected by a greater amount and the spectrum on the dispersion plane compares this energy loss of the electrons versus intensity.



**Figure 2.5:** Energy band diagram of a solid showing the excitation of inner and outer-shell electrons and possible spectroscopic signals. Redrawn from [51].



**Figure 2.6:** An example of a core-loss EEL spectra acquired from a  $\text{Ca(OH)}_2$  phase that forms as a by-product of the conversion reaction during cycling of  $\alpha\text{-MnO}_2$  cathode with  $\text{Ca}^{2+}$  ion.

The spectrometer energy resolution is usually determined by the FWHM of the ZLP and depends on the electron source, for a cold FEG as in the ARM, it is  $\sim 0.3$  eV.

The typical EEL spectra consists of three regions; the most intense peak : “zero-loss peak” (ZLP) (0 eV). However, since the spectrometer has a finite energy resolution, it also contains those scattered electrons which interact with the phonons of the specimen, losing minimal energy ( $\sim 0.3$  eV). So it is possible to do vibrational spectroscopy using EELS, provided the spectrometer resolution is enough to distinguish these from the intense ZLP, so a monochromated EELS system is employed for such measurements.

The low loss region ( $\sim 0\text{-}50$  eV) contains the plasma peak originating due to the collective excitation of the weakly bound valence shell electrons, this region can be analyzed to determine the dielectric constant of the specimen.

The core-loss region ( $\sim >50$  eV) containing the in-elastically scattered electrons that lose most energy due to interaction with the tightly bound inner shell electrons of the specimen

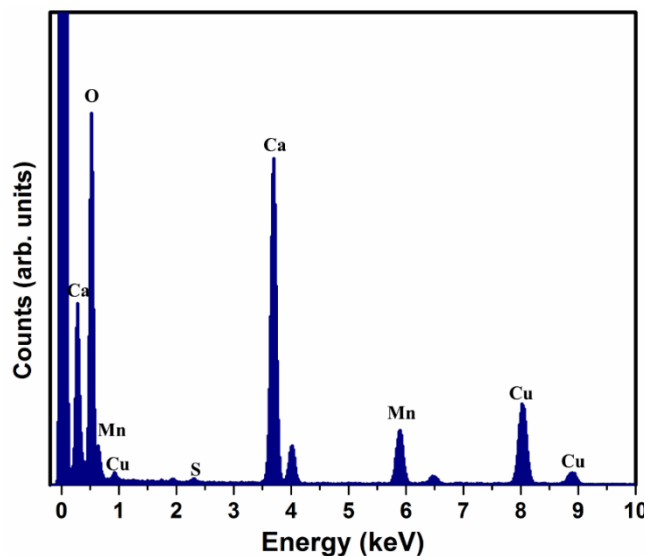
The ratio between the relative intensities of the ZLP and plasma peak can also estimate the specimen thickness.<sup>52</sup>

## **2.6 Energy Dispersive X ray spectroscopy (EDX)**

As illustrated in Fig. 2.5, the incident electrons may excite the inner shell electrons of the specimen into unfilled energy states above the Fermi level. Thus, there would be a hole (electron vacancy) in the inner shell, and the excited atom can return back to ground state where an outer shell electron makes a downward transition and occupies the hole. This downward transition is accompanied by emission of an Auger electron or X-ray photon.

The energy of the emitted X ray photon would be representative of the energy difference of the two states involved in the transition, and these are therefore termed as *characteristic X rays*.

In addition to these well-defined peaks, an EDX spectra also consists of a continuous background which results from the electrostatic interaction between the incident electrons and the nucleus of the specimen, this elastic scattering event causes a significant change in momentum for the incident electrons which then emit a X ray photon. These are collectively referred to as *Bremsstrahlung*.



**Figure 2.7** An example of an EDX spectra showing Ca, O and Mn signals, collected from the Ca-rich secondary phase that forms as a by-product of the conversion reaction during cycling of  $\alpha$ -MnO<sub>2</sub> cathode with Ca<sup>2+</sup> ion. The Cu signal is from the TEM grid.

Since the generation of X-ray photons is anisotropic, the EDX detector employed in the ARM is a large angle windowless silicon drift detector. The basic idea is that the X ray photons deposit energy creating electron-hole pairs, and a reverse bias is applied to measure the charge pulse. The Si drift detector, as the one in ARM, consists of concentric rings of p-doped Si on a single crystal of n-Si, high voltage applied across the n-Si layer collects the electrons generated by X-rays. Due to advances in Si fabrication technology, this kind of detector has much less noise due to thermally generated carriers, and can operate with minimal cooling, usually from a Peltier cooler.<sup>52</sup>

## 2.7 Beam damage

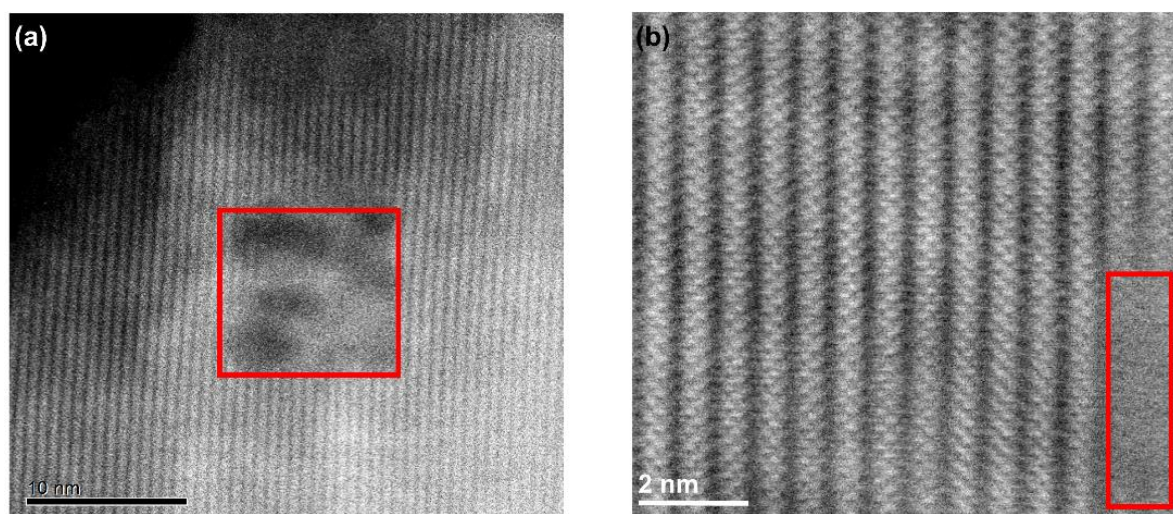
Specimen damage as a result of interaction with the electron beam is an unfortunate side-effect. The two common types of damage are (i) Knock on damage where the high energy electron beam displaces atoms in the specimen causing mass loss and (ii) Radiolysis/ ionization damage where the electrons break the chemical bonds in the specimen. The first type is worsened at

higher voltages whereas the latter is more severe at lower voltages. Eventually, all specimens are subject to damage, especially in STEM mode where a focused probe is incident on the sample resulting in higher current densities.

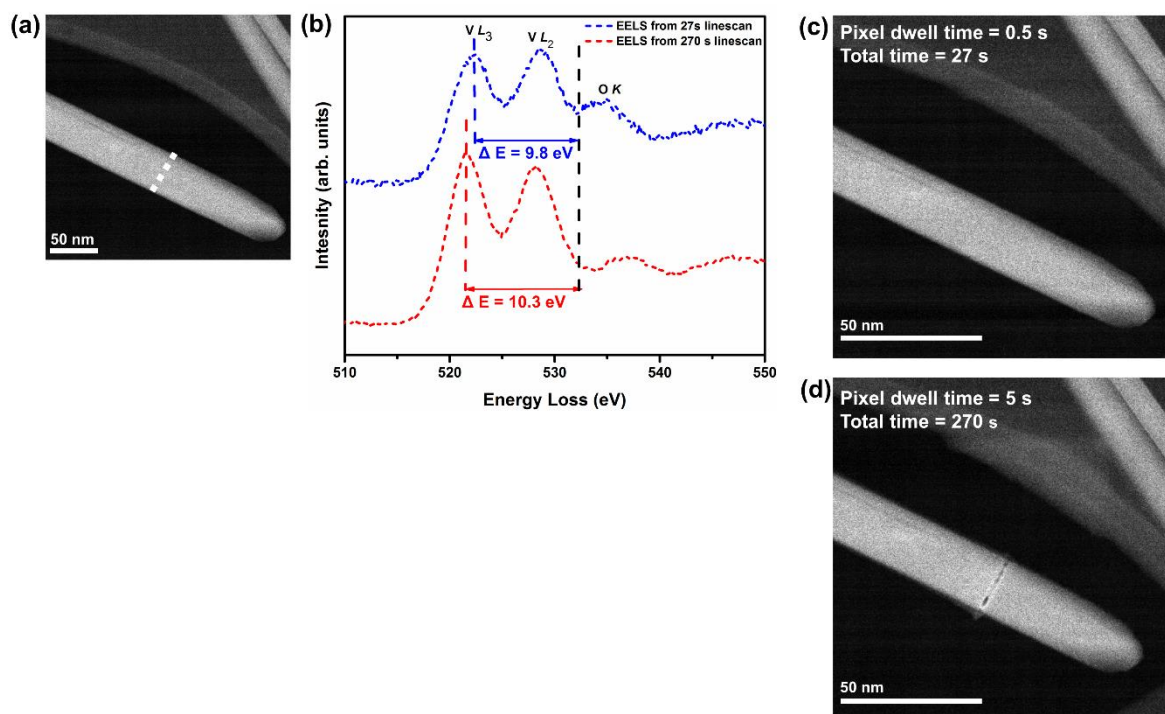
There are several traditional approaches employed to deal with electron beam damage. Firstly, if the damage mechanism for the specimen is well-understood, changing the accelerating voltage can work. As already discussed, knock on damage can be reduced at lower voltage, whereas radiolysis type damage is worse at higher voltages. In the case of metastable  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph lowering the voltage to 80 keV was tried, but was found to worsen the beam damage. The second way is to reduce total electron dose by possibly using a lower emission current. This was found to work for my experiments with the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph. All the data acquired from this sample was acquired at  $I_E = 7\text{-}8\ \mu\text{A}$ . STEM images acquired with the conventional conditions ( $I_E = 15\ \mu\text{A}$ ) show damage evident with the degradation of the crystalline structure as presented in Fig. 2.8 (a) and (b), the areas showing the most severe damage marked with red boxes. In fact, even under low dose conditions with a reduced  $I_E$ , electron beam damage is present, and techniques such as high-resolution EDX linescan burn holes in the sample. Therefore, those techniques have to be avoided.

Another important parameter that controls the electron dose during spectroscopy is the pixel dwell time which can be defined as the amount of time the probe spends per pixel of the specimen. For example, in the orthorhombic  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph, EELS linescans done with longer pixel dwell times (5s) were seen to damage the specimen, and resulted in a reduction of the Vanadium (V) oxidation state from V<sup>5+</sup> to V<sup>4+</sup>. Thus, while doing EELS analysis during *in-situ* lithiation experiments on  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires, (results from which are described in detail in Chapter 3) a short pixel dwell time (0.5 s) was employed which did not damage the specimen,

due to the low electron dose. This was done to ensure the observed change in V valence was due to Li intercalation and not beam-induced reduction. Thus, not only are beam-damage effects detrimental to atomic-resolution/high-resolution analysis, they can also lead to artifacts. Since most of the oxide cathodes that I worked with are beam-sensitive, I did careful analysis of the optimum parameters for each system as discussed above, so that electron beam damage can be minimized and the data is free from any damage related artifacts.



**Figure 2.8 :** Both (a) and (b) present snapshots of beam induced damage during STEM imaging/ EDX linescan seen in metastable  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph.



**Figure 2.9** (a) HAADF-STEM image of  $\alpha$ - $\text{V}_2\text{O}_5$  nanowire used for EELS line-scans (b) EEL spectra from  $\alpha$ - $\text{V}_2\text{O}_5$  nanowire acquired with shorter and longer pixel dwell times (c) Post-EELS snapshot from the nanowire after EELS line-scan with short pixel dwell time showing no damage (d) Post-EELS snapshot from the nanowire after EELS line-scan with longer pixel dwell time showing clear beam damage

Another conventional method to deal with beam-sensitive samples is to cool the specimen, this approach is commonly employed in the study of beam-sensitive biological materials by cryo-TEM. Since liquid samples are generally incompatible with high column vacuum inside the TEM, biological samples are frozen in amorphous ice followed by sectioning to produce thin TEM specimens. Another important reason for using ice is to freeze cellular functions, and image the specimen<sup>53, 54</sup>. One of the major limitations in this approach however, is that, the

samples are not in their native liquid state and are most likely both structurally and chemically altered.

A new method to deal with beam-sensitive materials by employing the graphene liquid cell (GLC) approach was developed in our group. Wang et. al. showed that using this GLC approach, biological samples, such as ferritin, could be imaged at high-resolution in their native liquid environment. Since the graphene layers enclosing the liquid cell are quite thin, they also allow EEL/EDX spectra to be obtained from the sample, thus yielding important chemical information. It was found that the area-averaged threshold dose rate for bubble formation (formation of gas bubbles indicates destruction of the liquid and is representative of radiolysis based beam-damage) was  $\sim 9 \text{ e}^-/\text{\AA}^2/\text{s}$ . It was also established that by controlling parameters such as the emission current, magnification, pixel dwell time etc. it is possible to get an accurate estimate of the electron dose rate. Below the threshold dose conditions, the beam energy would be dissipated by the graphene layers, protecting the enclosed biological samples.<sup>55</sup>

In some of the projects that I undertook during my PhD, I explored this method.

The following portions (till the end of Section 2.7 and Fig. 2.10) are partially reproduced from [A.R Riberio, A. Mukherjee, X. Hu, S. Shafiee, R. Ghodsi, K. He, S. Gemini-Piperni, C. Wang, R.F Klie, T. Shokhufar, R. S Yassar, R. Borojevic, L. A Rocha, Jose M. Granjerio , Bio-camouflage of anatase nanoparticles explored by in situ high-resolution electron microscopy, *Nanoscale*, **2017**, 10.1039/c7nr02239e ] published by The Royal Society of Chemistry (RSC) publishing (2017).

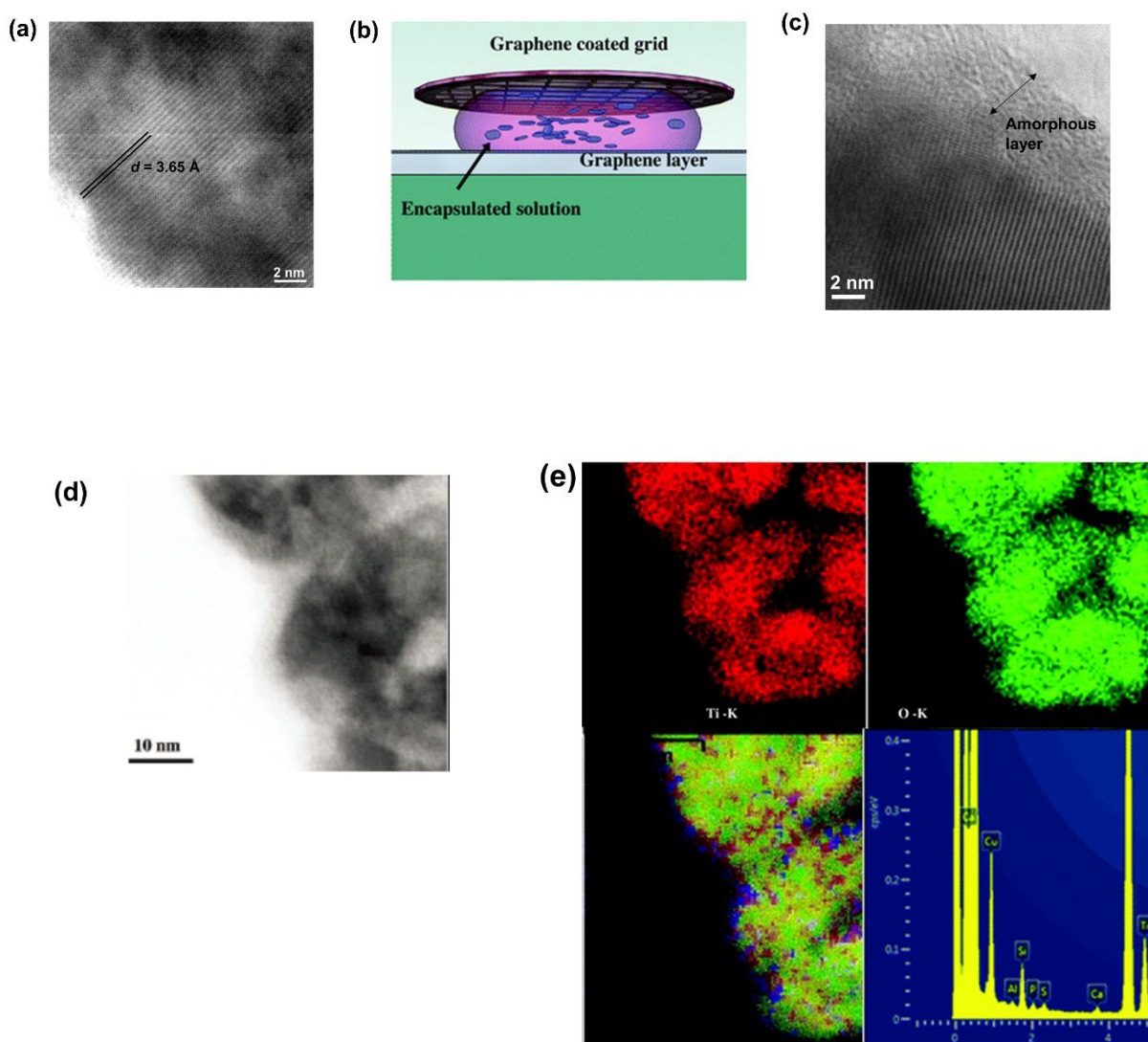
In the first of these projects, the goal was to study the interactions between Titanium dioxide ( $\text{TiO}_2$ ) nanoparticles and protein corona in the native liquid environment. These  $\text{TiO}_2$

nanoparticles find wide applications in dental implants and orthopedics since they are believed to be biocompatible. However, in several cases, nanoparticles have been detected in organs away from the implant site, thus leading researchers to explore the biocompatibility aspect in greater detail. One of the fundamental challenges in this regard is direct characterization of the TiO<sub>2</sub> nanoparticles in native cell culture media at high resolution. While the conventional method of TEM sample preparation for nanoparticles ( #2.8, Section I) can be applied for the TiO<sub>2</sub> system, the protein would be destroyed by direct electron beam exposure.

Therefore, the GLC method was applied in this case. The data from the ‘dry’ system, that comprised of TiO<sub>2</sub> nanoparticles prepared in the conventional way (Section 2.8, Part I) was compared with the ‘hydrated’ system, that comprised of GLC’s encapsulating TiO<sub>2</sub> nanoparticles in protein media. The sample preparation for GLC method has been explained in #2.8, Section IV.

Fig. 2.10 presents the major highlights from this study. Fig. 2.10 (a) shows the high-resolution ABF image from the ‘dry’ TiO<sub>2</sub> nanoparticles with lattice fringes extending till the edge of the particle, proving the crystallinity of the system. Fig. 2.10 (b) shows the schematic of the GLC experimental setup employed in this case.

Fig. 2.10 (c) shows the ABF image from the GLC system showing the TiO<sub>2</sub> nanoparticle cluster in the cell culture. An amorphous shell (around ~5 nm) can be clearly identified around the particle cluster which can be attributed to the protein and ionic corona. Verification of this hypothesis that the amorphous shell is representative of the protein corona comes from the subsequent EDX analysis on the system. Fig. 2.10 (d) shows the ABF image from the particle cluster used for EDX mapping, obtained from the GLC system. Fig. 2.10 (e) shows the EDX maps acquired from the TiO<sub>2</sub>-protein bio-complex.



**Figure 2.10** (a) High-resolution ABF image from TiO<sub>2</sub> nanoparticles in a dry system (b) Schematic of the GLC setup employed for this study (c) ABF image from the TiO<sub>2</sub>-protein system encapsulated in GLC (d) ABF image from the particle cluster used for EDX analysis (e) Individual and overlaid EDX maps showing distribution of different elements in the core-shell system.

While the Ti and O signals are present in the core, the overlaid map shows the adsorption of Ca and P ions along the shell. These elements (Ca and P), as also seen in the integrated EDX spectra, are the constituents of the protein. Thus, the shell identified in Fig. 2.10 (c) is representative of the nano-bio interface in this case and indicates the formation of the protein corona. These results indicate that this ‘bio-camouflage’ formation at the nanoparticle interface is likely responsible for their biological identity within bone cells and govern their properties and further internalization by cells. Thus, this project elucidates the relevance of the GLC approach in both structural and functional analysis of biological systems.<sup>56</sup>

## **2.8 Sample preparation methodologies**

### **I. Preparation of nanowire/nanoparticle samples**

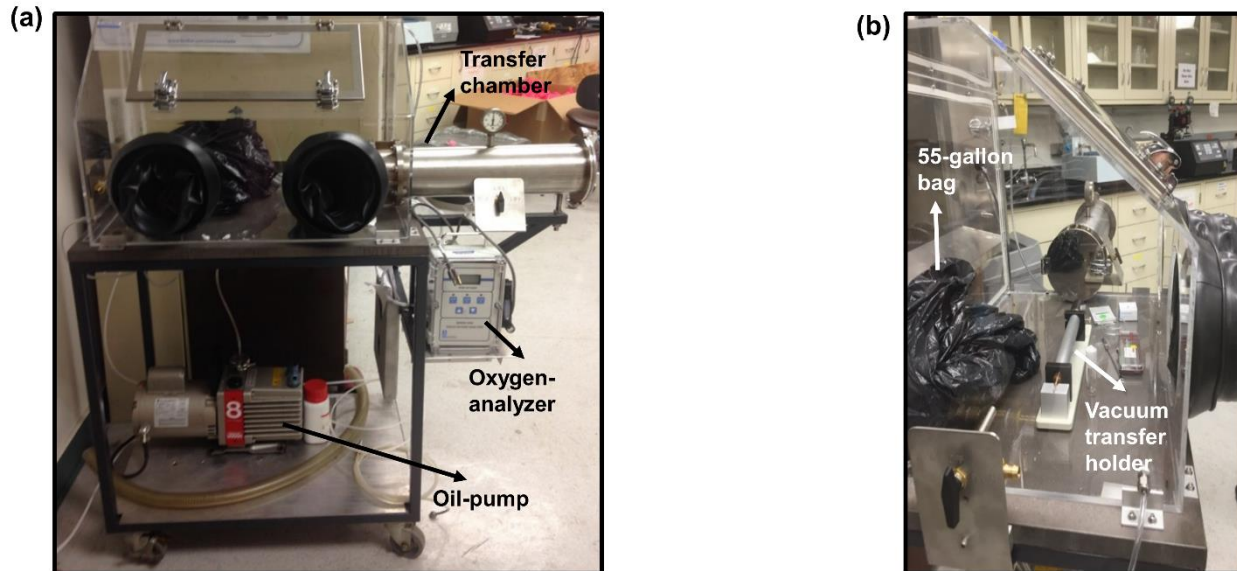
Traditionally, nanowires/nanoparticles, essentially samples that do not require any polishing/thinning and are already electron transparent can be prepared for TEM analysis in a relatively simple manner. The samples, which are usually in the form of powders, are suspended in Isopropyl alcohol (IPA) and sonicated for uniform dispersion. Then using a micropipette, usually 20-30  $\mu\text{L}$  of the sonicated solution is drop casted on a holey carbon coated TEM grid. The prepared grid is then put under the IR lamp for 20-25 min to reduce hydrocarbon contamination on the surface. The pristine samples, which are not usually air/moisture sensitive were prepared in this manner. Some electrochemically cycled samples which are sensitive to air exposure had to be prepared inside an inert environment, as discussed in the next section.

### **II. Development of portable glove box for handling of air/moisture sensitive samples**

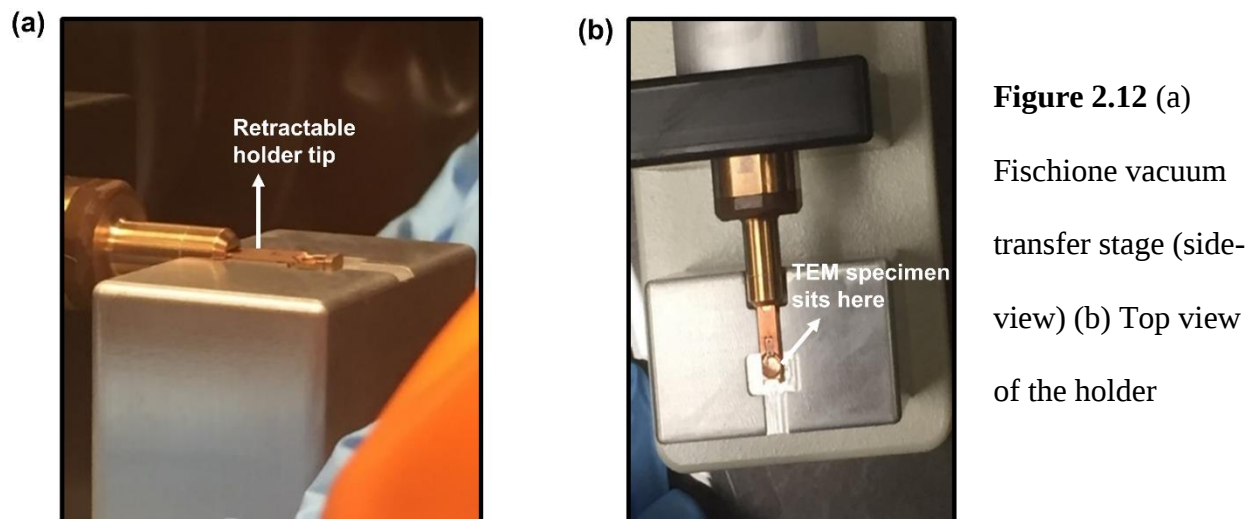
Electrochemically cycled cathodes are often oxygen/moisture sensitive, thereby limiting the amount of air exposure permissible for analysis of such samples. To handle such samples, a portable glove box was developed which provides an inert argon environment for sample

loading. Fig. 2.11 (a) and Fig. 2.11 (b) below present labelled pictures of this glove box. The glove box was purged and then filled with pure argon (Ar) several times employing the 55-gallon bag (as shown). Essentially the air inside was replaced with increasing amounts of Ar with subsequent purge and fill cycles till the moisture and oxygen levels reached below 10 ppm (<0.001% of atm. concentrations).

Air-sensitive samples were loaded into the glove box through the metallic transfer chamber along with a special vacuum transfer holder (Fischione Model 2560), which consists of a retractable tip. The samples were prepared for TEM analysis inside the glove box, loaded into the vacuum transfer holder and the tip was retracted. So, after loading, this special holder maintained the sample under the argon environment while transferring from the glove box to the microscope. Fig. 2.12 (a) and Fig. 2.12 (b) present pictures of this vacuum transfer holder.



**Figure 2.11** (a) Portable glove box-front view (b) Side view of the glove box with the vacuum transfer stage loaded



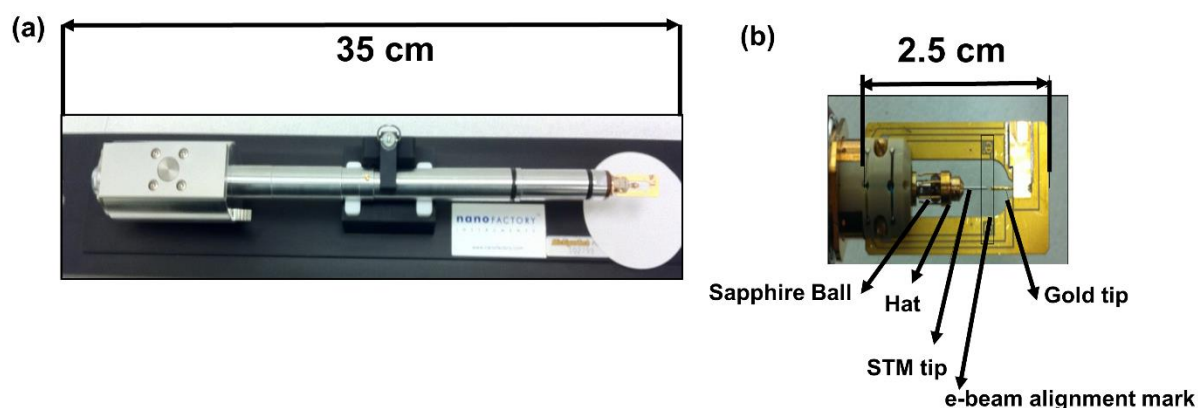
### III. Open cell battery setup for *in situ* lithiation experiments

The open cell battery setup<sup>57,58</sup> is implemented inside a transmission electron microscope using the Nanofactory TEM-STM biasing stage. The picture of this holder, emphasizing the holder tip is presented in Figs. 2.13 (a) and 2.13 (b) below. Fig. 2.14 (a) presents the schematic of the open cell nano-battery setup employed for my experiments while Fig.2.14 (b) present a representative BF-TEM image of the experimental setup. As we can see from Fig. 2.14 (b), the gold (Au) and the tungsten (W) tips both appear dark due to mass-thickness contrast, while the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode is chosen to be of appropriate length and orientation so it can achieve reliable contact with the Li metal anode side.

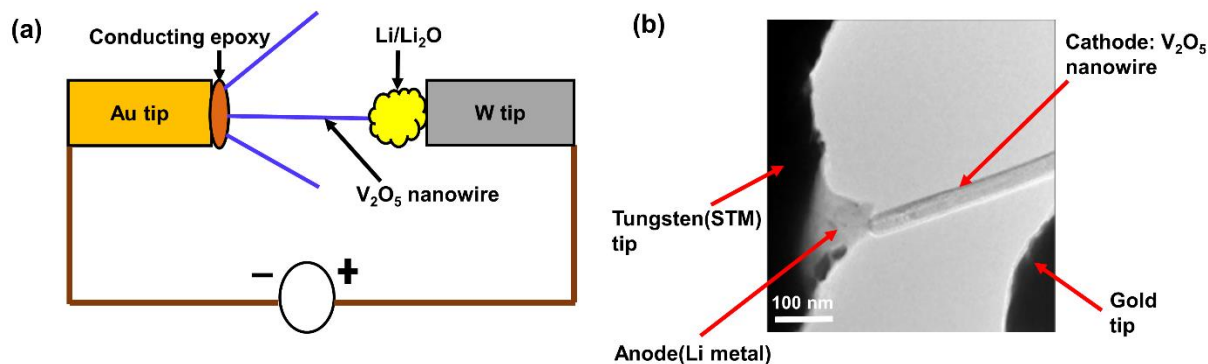
For the *in situ* lithiation experiments, the Li metal, which acts as the anode, is loaded on the STM W tip, while the cathode (which, in this case, are  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires) is glued to the Au tip using conducting epoxy. The Li metal anode is created by scratching the W tip against the corresponding metal foil in an Ar filled glove box, and then loaded onto the holder. The yellow

powder like  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires are dispersed in isopropyl alcohol (IPA), and sonicated for homogeneous dispersion (similar to the method described in Section I.) Then, a drop of the sonicated solution is put on a glass slide and allowed to dry, following which the Au tip is scratched against the slide, this attaches several nanowires to the gold tip. For use as cathode during the *in situ* lithiation experiments, the nanowire should be pointing out from the Au support, as shown in Fig. 2.14 (b), to achieve reliable contact with the Li metal source.

During loading of the holder into the TEM column, the Li metal forms Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) and Lithium hydroxide (LiOH) due to the brief air exposure. After successful loading, the piezo-controller of the STM-TEM stage can be used to move the W tip and bring the Li metal source in contact with the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires, subsequently a negative bias voltage is applied to the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires to initiate lithiation. The applied negative bias causes dielectric breakdown of the Li<sub>2</sub>CO<sub>3</sub> / LiOH layer on the Li metal, allowing diffusion of Li<sup>+</sup> ions and forms a Li<sub>2</sub>O shell on the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowire which acts as the solid state electrolyte. This experimental setup is commonly applied to study reaction mechanism of nanoscale electrode materials and more details of the setup as well as its applications can be found in these references.<sup>59,60,61,62</sup>



**Figure 2.13** (a) Nanofactory STM-TEM stage (b) Enlarged view of holder tip with parts labelled.



**Figure 2.14** (a) Schematic of open cell battery setup (b) TEM view of the experimental setup

#### IV. Graphene Liquid cell (GLC) preparation

The protocol employed for GLC preparation is explained, it was adapted with modifications from the methodology outlined by Wang et. al. (Supporting Information).<sup>55</sup> Commercially available, single layer graphene on copper (Cu) foil usually grown by chemical vapor deposition (CVD), is cut into several 1 cm× 1 cm pieces. These pieces are put under IR lamp for 20 min to remove surface hydrocarbon contamination and then floated on either 7% diluted Ferric chloride (FeCl<sub>3</sub>) or 15% diluted Ammonium persulphate (APS) Cu- etchant solutions. The choice of etchant is usually governed by the sample, and also total time of etching desired (fast vs slow etch). Post etching, the free standing graphene floats on the surface, and is usually stable for 20-30 min after all the Cu is gone. This free standing graphene is illuminated by a light source held below the surface of the etchant solution so as to create total internal reflection at the liquid-air interface, the evanescent waves at the surface interact with the graphene, allowing its visualization.

Using a home-made metal loop, the graphene is then transferred from the etchant to deionized water (DI-water) surface. The sample solution is usually put on the surface of a graphene grid or

a holey carbon coated gold (Au) TEM grid using a micropipette (usually 10- 15  $\mu\text{L}$ ) and dried thereafter to achieve a thin liquid layer on the grid surface. Then using reverse tweezers, the grid containing the sample solution, with the sample side facing the floating graphene layer, is put in contact with the floating graphene on water and held steady for 20-25 s. Then, the as-prepared grid is air-dried, and stored in a vacuum desiccator to dry any excess liquid before putting it inside the TEM for further analysis.

## **2.9 Other Sample Preparation Methods and Characterization Techniques**

### **Transmission Electron microscopy (TEM)**

The TEM images and selected area electron diffraction (SAED) data presented in Chapters 3, 4 and 5 were obtained from the JEOL JEM 3010 microscope operated at a primary energy of 300 keV. The JEOL JEM 3010 microscope was also employed for some of the *in situ* lithiation studies into  $\alpha\text{-V}_2\text{O}_5$  nanowires, for collecting the lithiation snapshots and SAED data presented in Chapter 3. In the TEM mode, the specimen is illuminated with a coherent, parallel beam of electrons, unlike the focused electron probe scanned in a raster across the sample as in the STEM mode. Another important difference is the placement of the objective lens, as shown in Fig. 2.1, for STEM mode this is a pre-specimen lens and provides the final demagnification step in forming the sharp, focused electron probe. However, in TEM mode, the objective lens is a post-specimen lens, focusing the transmitted electrons and forming the image.

### **X-ray Diffraction (XRD)**

The powder X-ray diffraction results presented in Chapters 3 and 4 were obtained using Bruker D8 Advance with LynxEye detector under Bragg-Brentano focusing, using Cu  $K\alpha$  ( $\lambda = 1.5406$  Å) radiation. The XRD results provide bulk/ensemble information about the phase of the sample,

and thus differs from the selected area electron diffraction (SAED) data which provides information on a local scale.

### **Synchrotron X-ray Diffraction and X-ray absorption near edge spectroscopy (XANES)**

High-resolution powder XRD data for the topochemically leached  $\zeta$ -V<sub>2</sub>O<sub>5</sub> (presented in Chapter 4) were obtained at beamline 11-BM of the Advanced Photon Source at Argonne National Laboratory ( $\lambda = 0.4136860$ ). The XANES data presented in Chapter 3 were obtained at the undulator beamline 6.3.1.2 at the Advanced Light Source at Lawrence Berkeley National Lab.

### **Cathode and electrolyte preparation and electrochemical cycling details**

For use as cathode for the Li intercalation experiments presented in Chapter 3, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> powder was first thoroughly mixed with acetylene black as a conductive agent using a mortar; then the solution of polymeric binder was added and mixed to get the slurry. The binder solution was 6 wt.% polyvinylidene fluoride (PVDF, Solvay) dissolved in 1-methyl-2-pyrrolidinone (NMP, Sigma Aldrich, >99%) solvent. The ratio of active material, conductive agent, and polymeric binder was adjusted to 6:2:2. The slurry was coated on aluminum foil substrates, followed by drying under infrared (IR)-lamp for 30 min. The area of electrodes was 1.27 cm<sup>2</sup> with mass loading of ca. 1.7 mg. The electrodes were dried under vacuum at 80 °C overnight before usage. Coin-type cells were used for the electrochemical intercalation of Li<sup>+</sup> into  $\zeta$ -V<sub>2</sub>O<sub>5</sub>. In the coin cell, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> electrode and a piece of lithium foil (Alfa Co., 99.9%, 0.75 mm thick) was separated by a glass fiber filter (VWR Co., grade 691, 210  $\mu$ m thick) soaked with Li<sup>+</sup> electrolyte (Selectilyte LP57, BASF Co., 1.0 M LiPF<sub>6</sub> in EC/EMC (3:7 w/w)). A multi-channel battery cycler (BCS-805, Bio-Logic) was used for the electrochemical tests. The (de)lithiated samples were prepared by opening the coin cells, washing the electrodes thoroughly with

dimethyl carbonate solvent, and drying under vacuum. The cells were fabricated or opened in a glove box (MBraun) under inert atmosphere filled with Ar gas, where water and oxygen levels were less than 0.1 ppm.

For use as cathode for the Mg intercalation experiments into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> presented in Chapter 4, the vanadium oxide laminates were prepared by mixing 8:1:1 weight ratio of vanadium oxide (Fluka, >99%), Timcal C45 carbon black and polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone (NMP). The as prepared laminate was casted onto 304 stainless steel current collector and then dried at 75°C overnight. Dried laminate was subsequently punched into 7/16" discs for further usage.

Magnesium bis(trifluoromethane sulfonyl)imide purchased from Solvionic (France, 99.5% purity) was obtained and further dried in a vacuum oven placed in a pure argon atmosphere with H<sub>2</sub>O and O<sub>2</sub> level under 1 ppm. The as received diglyme (Aldrich, anhydrous, 99.5%) solvent was further treated with dried molecular sieve (Aldrich, 3Å beads, 4-8 mesh) overnight, before mixing with the dried Mg(TFSI)<sub>2</sub> salt. The electrolyte was stirred overnight for complete mixing before being utilized in coin cells. Water levels of the as prepared electrolytes are under 20 ppm, as determined from Karl-Fischer measurement. All experiments were performed in an argon filled glovebox with H<sub>2</sub>O and O<sub>2</sub> level under 1 ppm.

Galvanostatic cycling of V<sub>2</sub>O<sub>5</sub> cathode against polished Mg metal anode in a coin cell configuration was carried on a Maccor series 4000 cycler at current density of 20  $\mu$ A/cm<sup>2</sup>.

For use as cathode for the Mg intercalation experiments into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> presented in Chapter 4, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> powder was first thoroughly mixed with acetylene black as a conductive agent and a polymeric binder to form a slurry. The slurry was coated on an aluminum foil substrate and dried

overnight. The electrolyte used was a mixture of 0.2 M Magnesium *bis* (trifluoromethylsulfonyl)imide ( $\text{Mg}(\text{TFSI})_2$ ) salt and propylene carbonate as the solvent. Activated carbon cloth was used as the anode for the electrochemical cells. The activated carbon cloth (ACC) was dried under vacuum at 80 °C overnight. The high specific surface area of ACC (ca. 2000 m<sup>2</sup> g<sup>-1</sup>) gives rise to sufficient double-layer charging within the electrolyte's voltage stability window to match the charge for the cycling of the cathodes. Coin-type cells were fabricated by stacking the cathode and anode separated by glass fiber (VWR, grade 691, 210 μm thick) soaked with the electrolyte. A multi-channel potentiostat (VMP3, Bio-Logic) was used for the electrochemical tests. The potential of the cathode was calibrated by considering the AC anode's potential, which is originally 2.2 V vs  $\text{Mg}/\text{Mg}^{2+}$  and linearly proportional to the state-of-charge. An oven with forced-convection (BINDER) was used to fix the temperature of the cells to 50 °C.

## CHAPTER 3

### Lithium intercalation into $V_2O_5$ polymorphs

#### 3.1 Introduction

The following portions (Section 3.1- 3.4 and Figure 3.1 - 3.8) are reproduced from [A.

Mukherjee, H. A. Ardakani, T.Yi, J. Cabana, R. S Yassar and R. F Klie, “Direct characterization of the Li intercalation mechanism into  $\alpha$ - $V_2O_5$  nanowires using *in-situ* Transmission Electron Microscopy”, Applied Physics Letters, 110, 213903, 2017] with permission from AIP Publishing, LLC.

Lithium-based rechargeable batteries are widely used in portable electronics and transportation sectors.<sup>63,64</sup> As already discussed in Chapter 1, Section 1.1, an ideal cathode candidate for Li-ion batteries needs to possess certain key features such as: having a cation that can be easily oxidized/reduced, having a high capacity and high voltage, which would lead to good energy storage capabilities, and good cycling ability through, preferably, an intercalation type reaction with lithium involving minimal structural transformation.<sup>4</sup>

The orthorhombic  $\alpha$ - $V_2O_5$  polymorph, with a layered framework, has been long known as a classical intercalation based cathode material for Li-ion batteries.<sup>8</sup> It demonstrates both high voltage (3.5 V),<sup>10, 11</sup> as well as high capacity (440 mAh/g) for Li intercalation, intercalating upto 3 Li ions/ $V_2O_5$  unit.<sup>12</sup> However, the performance at high current densities and cycling stability of Lithium cobalt oxide ( $LiCoO_2$ ), the standard commercial cathode, is better than that of  $V_2O_5$ .<sup>4</sup> Nevertheless, there has been renewed interest in  $V_2O_5$  in recent years since it shows potential as a versatile intercalation based cathode, with the ability to intercalate multivalent ions.

There has been a wide range of studies of the lithiation behavior of bulk  $V_2O_5$ . As discussed in Chapter 1 [Section 1.2], it has been established that Li insertion into orthorhombic  $\alpha - V_2O_5$  leads

to the formation of various intermediate phases depending on temperature, as well as the degree of Li intercalation.<sup>4,8</sup> However, nanoscale electrode materials for lithium ion batteries have several advantages including providing shorter Li diffusion path lengths and accommodating strain upon lithiation better which can lead to better cycling performance.<sup>65,66</sup> There have been some investigations into the lithiation mechanism of nanoscale  $V_2O_5$ .<sup>67</sup> In 2007, Chan *et al.* employed a systematic TEM investigation of chemically lithiated  $V_2O_5$  nanowires, and reported the formation of  $\gamma - Li_2V_2O_5$  and  $\omega - Li_3V_2O_5$  phases upon *ex-situ* chemical lithiation using electron diffraction and electron energy loss spectroscopy. It was found that the lithiated nanowire retained its structure, suggesting an intercalation type reaction and various lithiated phases, as well as pristine  $V_2O_5$  phase were found to co-exist in the different areas of the nanowires that were investigated.

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More recently, Strelcov *et al.* employed *in-situ* SEM and investigated the morphological changes in a  $V_2O_5$  nanobelt battery during *in-situ* lithiation using  $LiCoO_2$  counter electrode and ionic liquid electrolyte. These  $V_2O_5$  nanobelts were grown with a whisker like morphology on a palladium (Pd) wire substrate and had a flat cross-section. They found that the  $V_2O_5$  nanobelt can undergo reversible intercalation with Li showing minimal shape distortion and no fracture/crack formation.<sup>69</sup> However, the lithiated  $V_2O_5$  phases were inferred from the *ex-situ* cycling data, and no direct identification of the distribution or evolution of different phases was reported. It will, therefore, be of great scientific interest to use an *in-situ* TEM approach for investigating the lithiation process of  $V_2O_5$  nanowire and to directly determine the structural and phase evolution of the nanowire upon progressive lithiation.

Since its introduction by Huang *et al.*<sup>57</sup> and Wang *et al.*<sup>58</sup>, the “open-cell nano-battery” inside the transmission electron microscope has been extensively used to study the lithiation mechanism in

anode materials such as  $\text{SnO}_2$ <sup>70-59</sup>,  $\text{Si}$ <sup>71,72,73,74</sup>,  $\text{Ge}$ <sup>62</sup> as well as cathodes such as  $\text{MnO}_2$ <sup>75</sup> at the nanoscale. This method allows for real time observation of structural changes induced by *in-situ* lithiation, which can be captured via imaging and electron diffraction as well as get chemical information with electron energy loss spectroscopy (EELS). This method can, therefore, provide direct and unique insights into the lithiation mechanism of  $\alpha\text{-V}_2\text{O}_5$  nanowire cathode. The details of the open-cell battery setup, including the sample preparation methodology, have been discussed in detail in Chapter 2, (Section 2.8, Part III). *In-situ* lithiation studies of single crystalline  $\alpha\text{-V}_2\text{O}_5$  nanowires are performed using a combination of selected area electron diffraction and electron energy loss spectroscopy to investigate phase changes and structural evolution upon progressive lithiation.

### **3.2 Electron Diffraction analysis elucidating phase evolution in $\alpha\text{-V}_2\text{O}_5$ nanowires as a consequence of *in situ* lithiation**

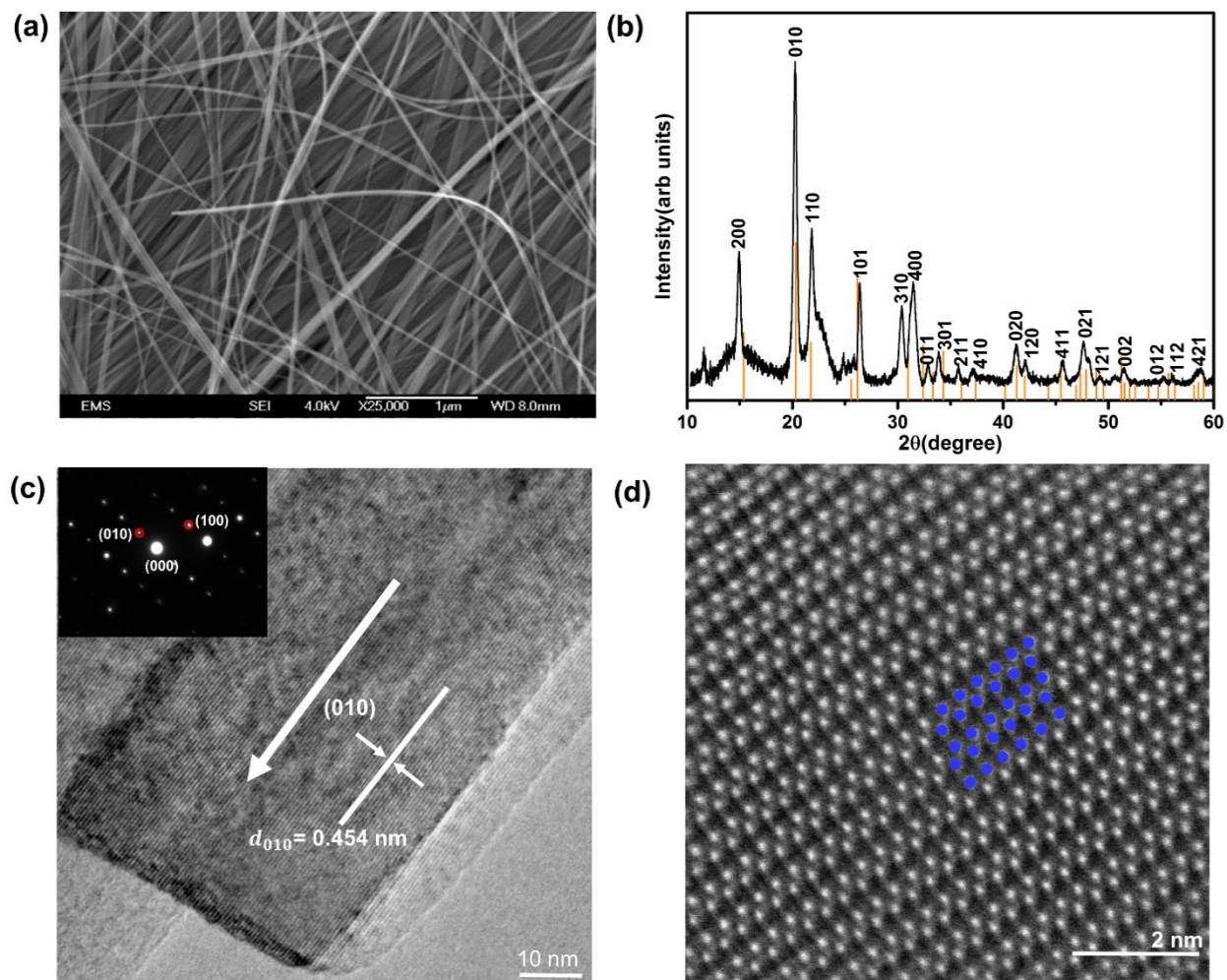
As already described in Chapter 2, (Section 2.8, Part III), the *in-situ* lithiation experiments are performed using a Nanofactory TEM-STM biasing holder that has Li metal placed on the STM tungsten tip and the  $\text{V}_2\text{O}_5$  nanowires glued to a gold tip using conducting epoxy. The Li metal anode was formed by scratching the corresponding foil with a tungsten (W) tip inside an Ar filled glove box and transferred to the holder under an Ar environment. During loading of the tips and subsequent transfer to the TEM, the Li metal reacts with air to form Lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and lithium hydroxide ( $\text{LiOH}$ ). Before the tips are brought in contact, EELS spectra were collected from the  $\text{V}_2\text{O}_5$  nanowire representative of the pristine (unlithiated) phase. Using the piezo-control of the TEM-STM sample stage, the  $\text{V}_2\text{O}_5$  nanowire was then brought in contact with the Li source and a negative bias was applied on the  $\text{V}_2\text{O}_5$  nanowire to initiate lithiation. This applied negative bias causes dielectric breakdown of the  $\text{Li}_2\text{CO}_3/\text{LiOH}$  layer on the Li metal surface driving  $\text{Li}^+$

ions into the  $V_2O_5$  nanowire. The initial condition was 0 V bias and subsequently bias voltages of -0.5 V, -1 V and -1.3 V were applied. At every intermediate bias step, the system was allowed to reach equilibrium by waiting for around 20 minutes and, then, electron diffraction pattern from the  $V_2O_5$  nanowire was captured. At -1.3V, EEL spectra was collected from the nanowire which is representative of the dominant lithiated phase at that bias condition. Results from the *in situ* EELS analysis are presented in the next section.

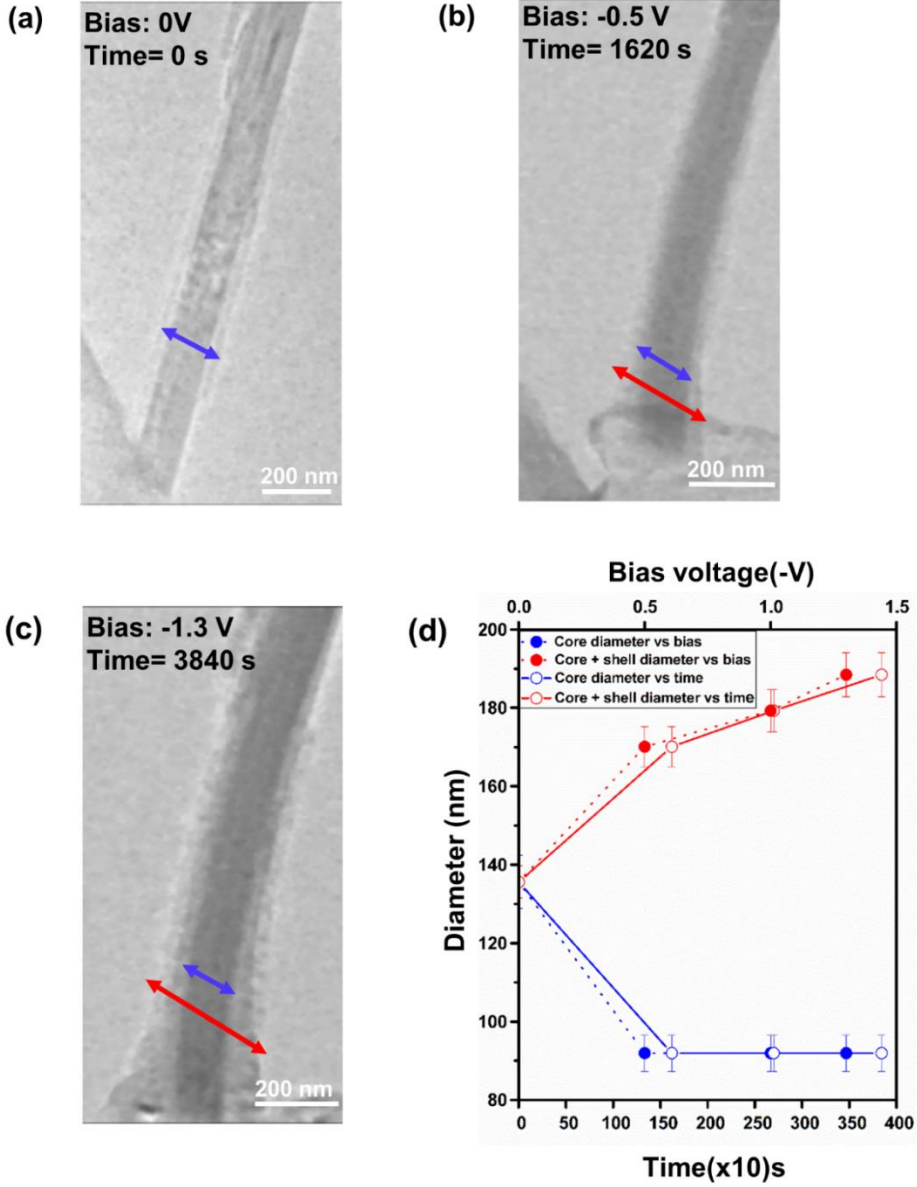
The synthesized  $\alpha$ - $V_2O_5$  nanowires typically range in diameter from 50 nm to 130 nm and can be up to several centimeters in length [as presented in Figure 3.1(a)]. For the *in-situ* experiments, we typically choose  $\sim 600$  nm long nanowires so we can establish reliable contact with the tungsten (W) tip containing Li metal source. The X-ray diffraction (XRD) data [Figure 3.1(b)] can be indexed according to  $\alpha$ - $V_2O_5$  [PDF # 01-072-0433]. The high-resolution TEM image in Figure 3.1 (c) shows distinct lattice fringes with 0.454 nm spacing which are consistent with the spacing between (010) planes of orthorhombic  $\alpha$ - $V_2O_5$ . The inset in Fig 3.1 (c) shows the indexed selected area electron diffraction pattern. In Figure 3.1 (d), the atomic-resolution high angle annular dark field (HAADF) image clearly shows the vanadium atomic columns, again, confirming the single crystalline nature of the nanowires.

Figure 3.2 shows snapshots taken during the *in-situ* lithiation process. More specifically, the TEM images shown in Figure 3.2 (b) – (c) clearly demonstrate the formation of a surface layer/coating on the  $V_2O_5$  nanowire. It can be seen that the diameter of the nanowire core and shell taken together grows with applied bias voltage and time [Figure 3.2 (d)]. This core-shell formation for nanowire electrodes during *in-situ* lithiation has been previously reported in case of Si and Ge anodes, and was identified as a combination of  $Li_xSi$  or  $Li_xGe$  alloy and lithium oxide.<sup>72,74,62</sup> Since  $V_2O_5$  is an intercalation compound, we do not expect any alloying to occur in our experiments. However, we

can also identify a very thin crystalline layer around the pristine  $\text{V}_2\text{O}_5$  nanowire in Fig. 3.2 (a) which is most likely very thin  $\text{V}_2\text{O}_5$ . This hypothesis was also verified by EELS analysis on a pristine  $\text{V}_2\text{O}_5$  nanowire having similar core-shell appearance (Fig. 3.3). So it is possible that the surface shell that grows with bias voltage and time is a mixture of  $\text{Li}_2\text{O}$  and lithiated  $\text{V}_2\text{O}_5$  phases. The  $\text{Li}_2\text{O}$  serves as a solid state electrolyte, facilitating movement of  $\text{Li}^+$  ions into the nanowire core, so the lithiation proceeds radially in this case.



**Figure 3.1:** Characterization of pristine  $V_2O_5$  nanowire (a) SEM image (b) XRD spectra of  $V_2O_5$  nanowire showing peak positions of orthorhombic  $V_2O_5$  (ICDD PDF# 01-072-0433) with orange lines (c) High Resolution TEM image showing distinct lattice fringes with lattice spacing 0.454 nm, inset showing indexed selected area electron diffraction (d) Atomic resolution (filtered) High angle annular dark field (HAADF) image clearly showing the V atoms in  $[010]$  zone.



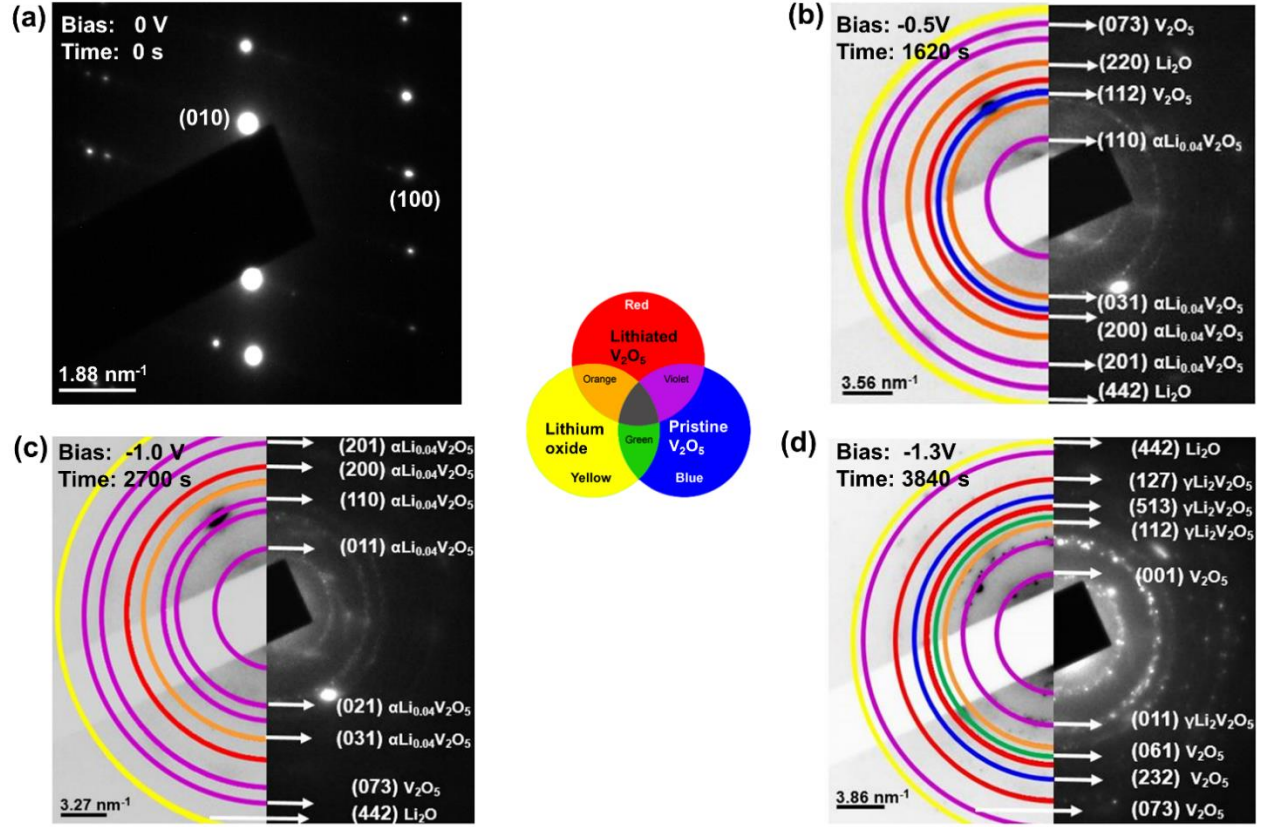
**Figure 3. 2:** Serial snapshot images capturing *in situ* lithiation progression of an individual V<sub>2</sub>O<sub>5</sub> nanowire cathode (a)-(c) The same nanowire monitored over a period of 0s-3840s with the blue and red arrows indicating nanowire diameter without and with surface layer. (d) Plot of nanowire diameter vs time and bias voltage. Blue solid line showing nanowire core diameter vs time, blue dotted line shows the same vs bias voltage. Red solid line shows nanowire core+ shell diameter vs time, red dotted line shows the same vs bias voltage.

The raw electron diffraction data has been presented in Fig. 3.3 while Fig. 3.4 presents the corresponding rotationally averaged line-profiles. The raw diffraction data was converted to rotationally averaged line-profiles using the plug-in to the DigitalMicrograph Software Suite.<sup>76</sup>

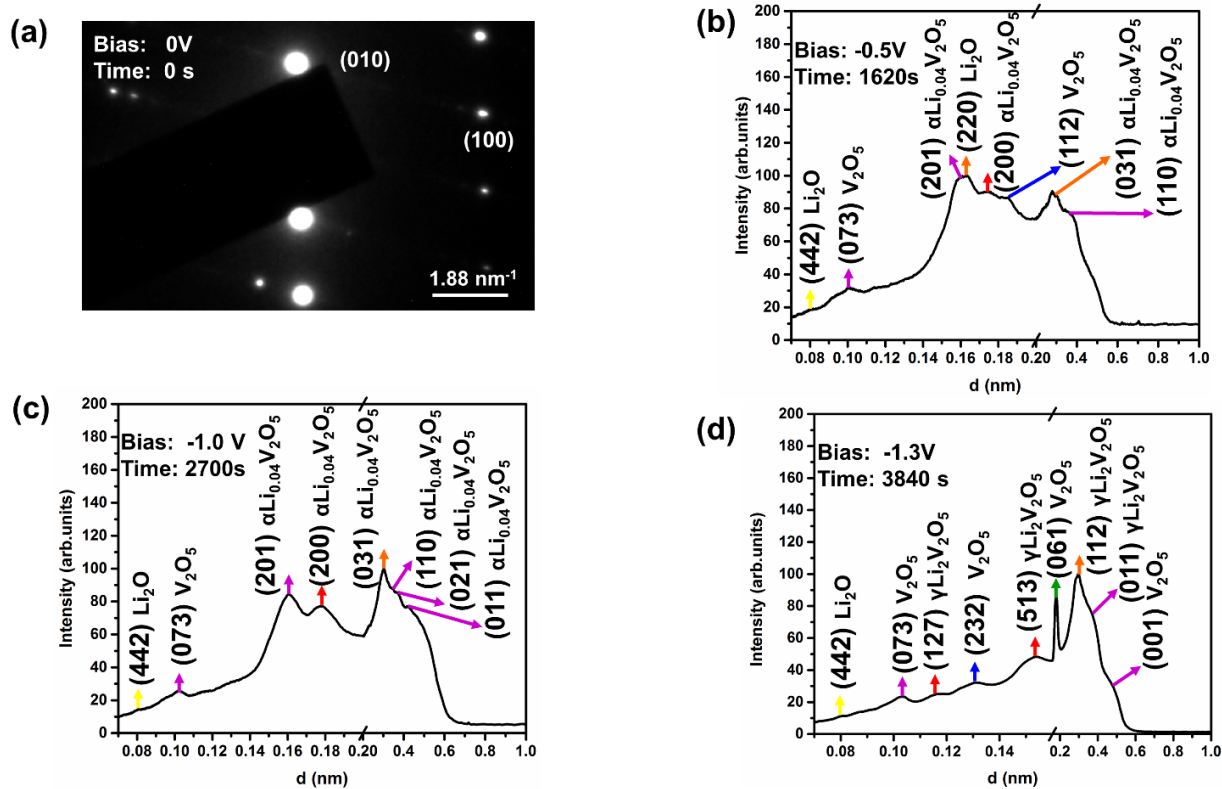
Fig. 3.3 (a) presents the single-crystalline electron diffraction data obtained from the  $V_2O_5$  nanowire at the beginning of the experiment which is representative of the pristine phase. Fig. 3.3 (b)- (d) show the polycrystalline diffraction rings at different bias voltage points that can be indexed according to lithium oxide ( $Li_2O$ ), lithiated  $V_2O_5$  ( $\alpha - Li_{0.04}V_2O_5$  at -0.5 V and -1 V, and  $\gamma - Li_2V_2O_5$  at -1.3 V) as well as unreacted, pristine  $V_2O_5$ . The small amount of lithium initially intercalated could be due to the smaller bias voltage, most likely, the lithiation reaction needs to overcome some threshold bias to successfully drive the  $Li^+$  through the  $Li_2O$  layer, and in this case, with the  $V_2O_5$  nanowire cathode, it can be seen that application of a more negative bias voltage of -1.3 V drove the lithiation reaction further. As the bias voltage decreases from -0.5V to -1.3V, the dominant lithiated phase changes from  $\alpha - Li_{0.04}V_2O_5$  to  $\gamma - Li_2V_2O_5$ . Due to the overlap of phases, primary colors were chosen to indicate the three dominant phases (Pristine  $V_2O_5$ , lithiated  $V_2O_5$  and lithium oxide) and secondary colors mark the overlapped phases. Overlapped phases, in this context mean the phases that could not be uniquely assigned to any of the three dominant ones, rather represent a superposition of two/more primary phases. [Fig 3.3 (b)-3.3 (d)]. The color wheel shown further elucidates this color scheme. In each case, the ring color represents the phase and the (hkl) value is indicated which represents the corresponding lattice plane in case of primary phases, or the more intense reflection in case of secondary/overlapped phases.

Likewise, the diffraction profiles presented in Fig. 3.4 (b)-(d) are derived from the polycrystalline electron diffraction data presented in Fig. 3.3 (b) – (d). Fig. 3.4 (a) is essentially the same as Fig. 3.3 (a). In each case, the arrowhead color represents the phase and the (hkl) value is indicated

which represents the corresponding lattice plane in case of primary phases, or the more intense reflection in case of secondary/overlapped phases.



**Figure 3.3 :** Diffraction Pattern captured during in situ lithiation (a)-(d) Diffraction Patterns at 0V (before bias), -0.5V, -1V and -1.3V respectively. Color scheme: Red (lithiated phase) [ $\alpha - \text{Li}_{0.04}\text{V}_2\text{O}_5$  phase for diffractions patterns at -0.5V and -1V and  $\gamma - \text{Li}_2\text{V}_2\text{O}_5$  phase for diffraction pattern at -1.3V] Blue: Pristine  $\text{V}_2\text{O}_5$ , Yellow: Lithium oxide. Overlap of two phases is marked by a secondary color. Color wheel explaining the color scheme used for phase identification also shown.



**Figure 3.4 :** Electron Diffraction data captured during *in situ* lithiation (a) Diffraction Patterns at 0V (before bias) (b)-(d) Rotationally averaged line-profiles of diffraction patterns at -0.5V, -1V and -1.3V respectively, plotted with a break in x-axis to emphasize the peaks at lower  $d$  values; corresponding raw diffraction data shown in Fig. 3.3; ( $hkl$ ) values and corresponding phase for each peak indicated, the arrowhead color follows the scheme, Blue: Pristine  $V_2O_5$ , Red: Lithiated  $V_2O_5$  and Yellow: Lithium oxide.

### 3.3 EELS analysis on pristine and lithiated V<sub>2</sub>O<sub>5</sub> nanowires

The evolution of the vanadium valence state as a consequence of the *in-situ* lithiation is quantified using the V *L*- and O *K*-edges, however, the overlap of these edges makes it difficult to use the conventional white line ratio method<sup>77</sup> for quantification of the vanadium valence. Previous work by Laffont *et al.*<sup>78</sup> and Gallasch *et al.*<sup>79,80</sup> have established a linear relationship of the V *L*- and O *K*-edge energy onsets with the vanadium valence state, in accordance with Kunzl's law.<sup>81</sup> This makes it straightforward to compare the experimentally obtained difference in the energies between V *L*<sub>3</sub> and O *K*-edge for pristine and lithiated V<sub>2</sub>O<sub>5</sub> nanowires and extract information about the Vanadium valence state. In this study, we use both of the previously published reference data sets<sup>79,80</sup> to calibrate our vanadium valence measurements.

As already discussed in Chapter 2 (Section 2.7 and Fig. 2.9), the EELS measurements on  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires were performed with the appropriate low electron-dose conditions so as to avoid inducing any electron beam damage. All the EELS data presented here (Fig. 3.6 – Fig. 3.8 ) were acquired with the short (0.5 s) pixel dwell time which was shown in Fig. 2.9 to produce the optimal electron dose and not induce any beam-damage or electron beam induced reduction in V valence state.

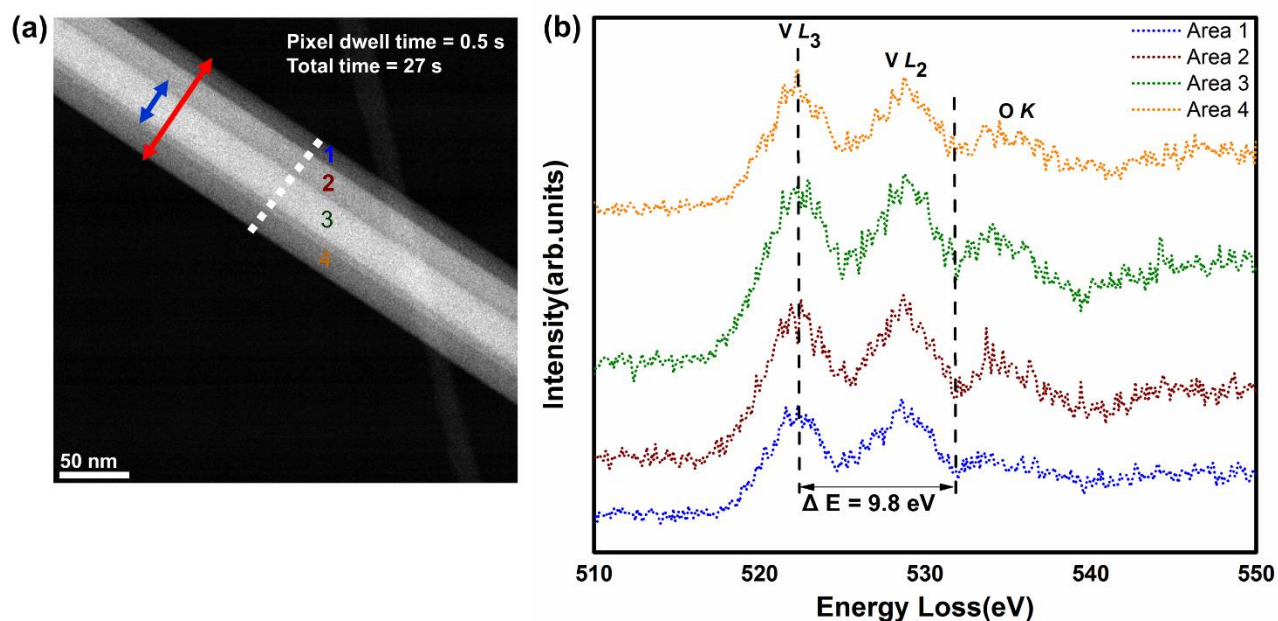
It was mentioned in Section 3.2 that the starting  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowire for the in situ lithiation experiment [as seen in Fig. 3.2 (a)] has a somewhat core-shell appearance, with a very thin layer surrounding the central nanowire. This kind of structure is quite commonly seen in nanowires, and is usually a result of a thinner nanowire growing around the central one, so essentially the entire structure represents homogeneous phase of the pristine material. However, in these experiments, growth of a surface layer around the pristine V<sub>2</sub>O<sub>5</sub> nanowire with increasing bias voltage is seen,

which the signature of the *in situ* lithiation reaction is. Thus, it is crucial to verify the phase of the starting material, and ensure that the surrounding thin layer is also pristine  $V_2O_5$ .

Fig. 3.5 presents EELS data from a pristine  $\alpha$ -  $V_2O_5$  nanowire having a core-shell appearance.

Fig 3.5 (a) shows the ADF image of the nanowire used for the EELS linescan (area of the linescan highlighted with white dotted line) while Fig 3.5 (b) presents the EELS comparison plot, essentially comparing EELS data from the apparent core and shell regions to check their chemical composition.

The energy difference between the V  $L_3$  - edge and O  $K$ - edge onset (peak to trough) in each case is found to be 9.8 eV, which according to the calibration data in these references,<sup>79,82</sup> corresponds to a V valence state of  $V^{5+}$ , thus consistent with the composition  $V_2O_5$ . This analysis therefore establishes that such nanowires with a core-shell appearance represent the uniform  $V_2O_5$  phase, as also true for the case presented in Fig. 3.2 (a).

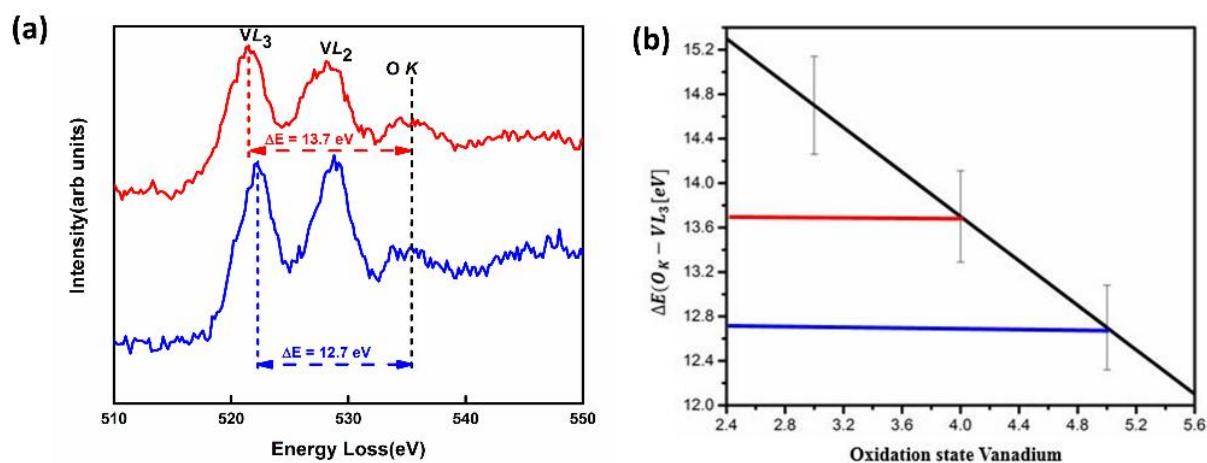


**Figure 3.5:** EEL spectra captured from a pristine  $\alpha$ -  $\text{V}_2\text{O}_5$  nanowire having a core-shell appearance (a) ADF image showing the nanowire on which EELS line scan was performed indicating the four areas from which EELS data was extracted, blue and red arrows mark the apparent core and shell regions (b) Comparison of EEL spectra from the four indicated areas on the nanowire.

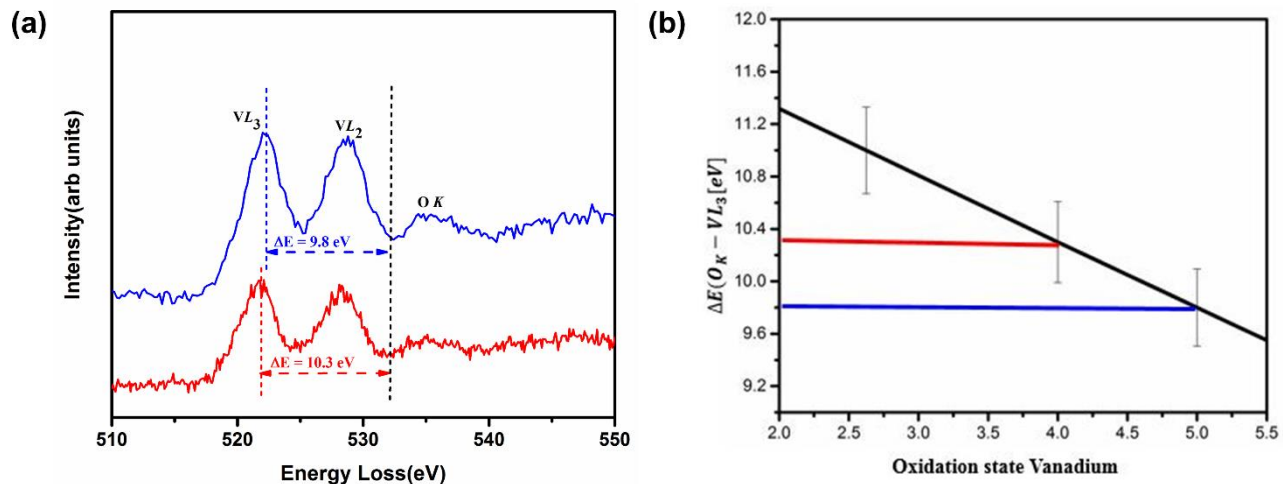
EELS analysis of the pristine  $V_2O_5$  nanowire, and during the *in-situ* lithiation at -1.3V is shown in Figure 3.6. Fig 3.6 (a) shows comparison between the EELS spectra collected from pristine  $V_2O_5$  nanowire (blue) and EELS spectra collected from the nanowire after *in-situ* lithiation (red). The V  $L_3$ -edge shifts to a lower energy value upon lithiation suggesting a reduction of Vanadium valence state. The energy difference between V  $L_3$ - and O  $K$ -edge is found to be 12.7 eV for pristine spectra (shown in blue) and 13.7 eV for lithiated spectra.(shown in red).

The experimentally measured energy difference between the V  $L_3$ - and O  $K$ - edge, determined by EELS spectra is presented in Fig 3.6 (a) and can be directly correlated to the valence state of vanadium. The calibration data from literature<sup>80</sup> has been shown in Fig 3.6 (b) and we find that the energy difference of 12.7 eV corresponds to  $V^{5+}$  valence state (highlighted in Fig 3.6 (b) with a blue line) consistent with pristine  $V_2O_5$  and the energy difference of 13.7 eV (highlighted in Fig 3.6 (b) with a red line) corresponds to  $V^{4+}$  valence state, consistent with  $\gamma - Li_2V_2O_5$ . In these *in situ* lithiation experiments, I did not find any evidence of the formation of higher lithiated phases, such as the  $\omega$ - $Li_3V_2O_5$  phase that has been previously reported to form during lithiation of bulk  $\alpha$ - $V_2O_5$ .<sup>11, 4</sup> However, it cannot be said that the nanowire is fully lithiated since I do find evidence of unlithiated zones that show up as pristine  $V_2O_5$  in the electron diffraction data [Fig. 3.3 and Fig. 3.4]. The schematic for the *in situ* lithiation reaction [Fig. 3.8] also reflects this, with the final product at -1.3 V showing presence of pristine, unlithiated  $V_2O_5$  as one of the phases.

Another set of EELS dataset acquired from a different *in situ* lithiation experiment was analyzed using a different calibration method, comparing the energy difference between the V  $L_3$ - edge and O  $K$ - edge onset (peak to trough)<sup>83,84,85</sup>. This EELS data and the corresponding calibration dataset has been presented Fig. 3.7 (a) and (b) respectively.



**Figure 3.6** EEL spectra captured from the nanowire before and after *in situ* lithiation (a) Comparison of EELS spectra collected from pristine (blue) and lithiated (red) nanowire showing energy difference between V  $L_3$ - and O  $K$ - edge change from 12.7 eV (blue spectra) to 13.7 eV (red spectra) (b) Reference calibration data from literature.

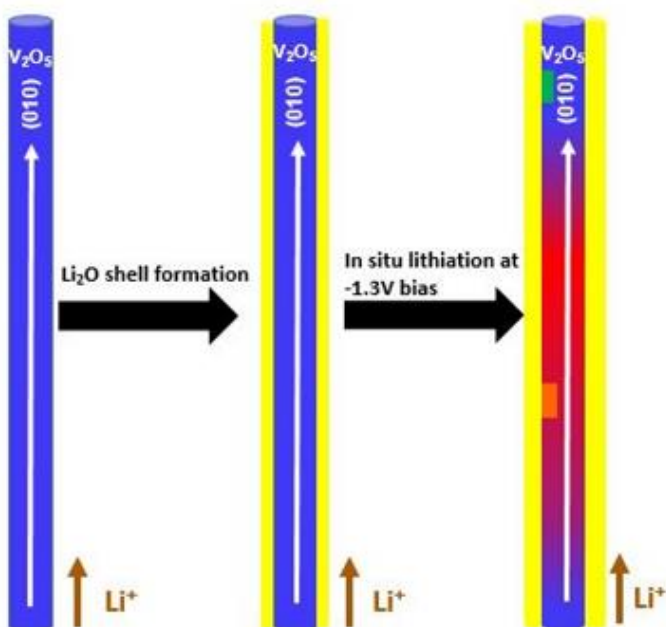


**Figure 3.7** EEL spectra captured from the nanowire before and after *in situ* lithiation (a) Comparison of EEL spectra collected from pristine (blue) and lithiated (red) nanowire, energy difference between V  $L_3$ - and O  $K$ - edge changes from 9.8 eV (blue spectra) to 10.3 eV (red spectra) (b) Reference calibration data from literature quantifying change in energy difference to corresponding change in Vanadium valence state.

### 3.4 Conclusions from the *in situ* lithiation experiments for $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowire

From the results and analysis presented here, it can be concluded that the *in-situ* lithiation mechanism of single-crystal  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires can be explained by the following scheme (Figure 3.8). The surface layer of Li<sub>2</sub>O, which forms on the nanowire, acts as a solid state electrolyte that facilitates Li ion diffusion into the center of the nanowire electrode, and bulk of the nanowire undergoes transformation to the  $\gamma$  -  $Li_2V_2O_5$  phase at -1.3V bias voltage that can be identified using electron diffraction. Furthermore, EELS verifies the valence change of Vanadium from V<sup>5+</sup> to V<sup>4+</sup>, consistent with the transformation from pristine V<sub>2</sub>O<sub>5</sub> to lithiated phase  $\gamma$  -  $Li_2V_2O_5$  at -1.3V. I did not find any evidence suggesting the formation of higher lithiated phases such as  $\omega$  -  $Li_3V_2O_5$  phase that has been previously reported to form upon *ex-situ* lithiation of V<sub>2</sub>O<sub>5</sub><sup>11,86</sup> in these *in-situ* lithiation experiments.

These findings are consistent with previous studies of *in-situ* SEM observation of V<sub>2</sub>O<sub>5</sub> nanobelts<sup>69</sup> and TEM characterization of chemically lithiated V<sub>2</sub>O<sub>5</sub> nanowires<sup>68</sup> as amorphization or fracturing of the lithiated V<sub>2</sub>O<sub>5</sub> nanowires at several hundred nanometers scale were not seen. Importantly this study elucidates the lithiation scheme of V<sub>2</sub>O<sub>5</sub> nanowire cathode dynamically and provides direct identification of lithiated phases by combining structural and spectroscopic characterization techniques. The conclusions suggest that the V<sub>2</sub>O<sub>5</sub> nanowires can accommodate the lithium ions without loss of structural integrity which should lead to stable cycling performance and longer cycling lifetimes for the battery. Such *in-situ* lithiation experiments with  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires could also further pave the way for *in-situ* experiments with Mg employing a suitable ionic liquid electrolyte which would be explored in future studies.



**Figure 3.8** Schematic elucidating the *in situ* lithiation of  $\alpha$ - $\text{V}_2\text{O}_5$  nanowire cathode. Primary colors: Blue  $\rightarrow$  Pristine  $\text{V}_2\text{O}_5$  nanowire, Yellow  $\rightarrow$  lithium oxide ( $\text{Li}_2\text{O}$ ), Red  $\rightarrow \gamma - \text{Li}_2\text{V}_2\text{O}_5$ . Secondary colors: Green  $\rightarrow$  overlap of blue and yellow, Orange  $\rightarrow$  overlap of red and yellow, Violet  $\rightarrow$  overlap of red and blue.

### 3.5 Metastable $\zeta$ -V<sub>2</sub>O<sub>5</sub> as potential oxide cathode for Li ion based batteries

This section is reproduced from [A. Mukherjee, H. D. Yoo, G. Nolis, J. Andrews, S. Banerjee, J. Cabana and R. F. Klie, Multimodal investigation of electrochemical lithium intercalation in tunnel structure  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode (*in preparation*)]

Li ion battery technology has been immensely successful, especially in the personal portable electronics market. However, ever increasing demands for more efficient rechargeable energy storage options has led many researchers and companies to focus on developing alternatives to conventional lithium ion battery technology. One of the possible pathways towards development of advanced Li ion batteries require identification and implementation of novel cathode materials that can incorporate critical features such as having a cation that can be easily oxidized/reduced, having high capacity and high voltage, which would lead to good energy storage capabilities, and good cycling ability through, preferably, an intercalation type reaction with lithium involving minimal structural transformation as well as provide better performance with regards to crucial parameters such as energy density, cycle life, charge-discharge rates, cost and safety.<sup>87</sup> Among several parameters, one of the important ones to consider while evaluating novel cathodes in the reaction mechanism, as already discussed it is desirable to have an intercalation type reaction with Li which ideally leads to minimum structural strain/distortion upon Li insertion, and hence, can lead to good cyclability. Usually, these properties are exhibited by oxide-based cathodes which are the only commercialized positive electrode systems for Li-ion batteries.<sup>15,20</sup> Thus, it is only natural to further explore the phase space of oxide materials while searching for novel cathodes for Li ion based batteries.

Recently, a metastable polymorph of V<sub>2</sub>O<sub>5</sub>, termed as the zeta phase ( $\zeta$ ), was reported to be stabilized.<sup>23</sup> This polymorph was synthesized in the nanowire form, starting from  $\beta$ -Ag<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub>

phase. Upon chemical deintercalation of  $\text{Ag}^+$  cations from the tunnel sites, the resulting phase, termed as  $\zeta\text{-V}_2\text{O}_5$ , was found to retain the tunnel framework, thus being quite stable. This  $\zeta\text{-V}_2\text{O}_5$  polymorph consists of a one dimensional tunnel framework as opposed to the two dimensional layered framework of  $\alpha\text{-V}_2\text{O}_5$ . This polymorph has the space group  $C2/m$  and its structure consists of three distinct vanadium centered polyhedra which enclose 1D tunnels along the ‘b’ direction. More details about this structure can be found here.<sup>23,22</sup> First principles calculations estimate that migration barriers for ionic intercalation are lower in this  $\zeta$  phase compared to the conventional  $\alpha$  phase, owing to its favorable anion framework along the intercalation path. While it has been shown that this polymorph could intercalate both  $\text{Li}^+$  and  $\text{Mg}^{2+}$  cations chemically,<sup>23</sup> electrochemical intercalation, especially for Li and Mg ions and associated structural evolution has not been investigated.

Electrochemical reactions with oxide based cathodes, especially with multivalent cations can be quite complicated. Therefore, it is imperative to fully understand the electrochemistry and associated chemical and structural changes with the, potentially simpler case, of Li intercalation. The lithiation mechanism of  $\alpha\text{-V}_2\text{O}_5$  is quite well studied.<sup>8</sup> It has been established that lithiation in  $\alpha\text{-V}_2\text{O}_5$  proceeds through the formation of several intermediate phases, with the insertion of increasing amounts of lithium. The  $\alpha$  phase exhibits high capacity in a Li cell, intercalating up to 3 Li/unit cell, forming the  $\omega\text{-Li}_3\text{V}_2\text{O}_5$  phase upon discharge to  $\sim 1.5$  V.<sup>11,86</sup> However, the transformation to  $\omega\text{-Li}_3\text{V}_2\text{O}_5$  is irreversible; thus, rendering the cathode useless for recharge purposes. It is understood that the Li intercalation in  $\alpha\text{-V}_2\text{O}_5$  is reversible only till the  $\delta\text{-LiV}_2\text{O}_5$  composition, upon discharge to  $\sim 2.3$  V insertion of more than 1 Li/unit cell leads to the formation of the  $\gamma\text{-Li}_2\text{V}_2\text{O}_5$  phase. This  $\gamma\text{-Li}_2\text{V}_2\text{O}_5$  phase shows significant distortion in the layered framework with severe puckering of the layers and the  $\text{VO}_5$  square pyramidal units

alternate in a different sequence in the  $\gamma$ - $\text{Li}_2\text{V}_2\text{O}_5$  phase compared to the pristine material,  $\alpha$ - $\text{V}_2\text{O}_5$ . Thus while lithiation in bulk  $\alpha$ - $\text{V}_2\text{O}_5$  is quite well understood, studies focusing on extensive multimodal characterization upon ionic intercalation are somewhat rare. In this context, what is presented here is a systematic study of the electrochemical lithiation in this novel  $\zeta$ - $\text{V}_2\text{O}_5$  cathode material, accompanied by structural and spectroscopic characterization to fully comprehend the Li intercalation mechanism in this material. Also, it would be of great scientific interest to contrast the electrochemical performance and associated structural changes in  $\zeta$ - $\text{V}_2\text{O}_5$  with that seen in  $\alpha$ - $\text{V}_2\text{O}_5$ .

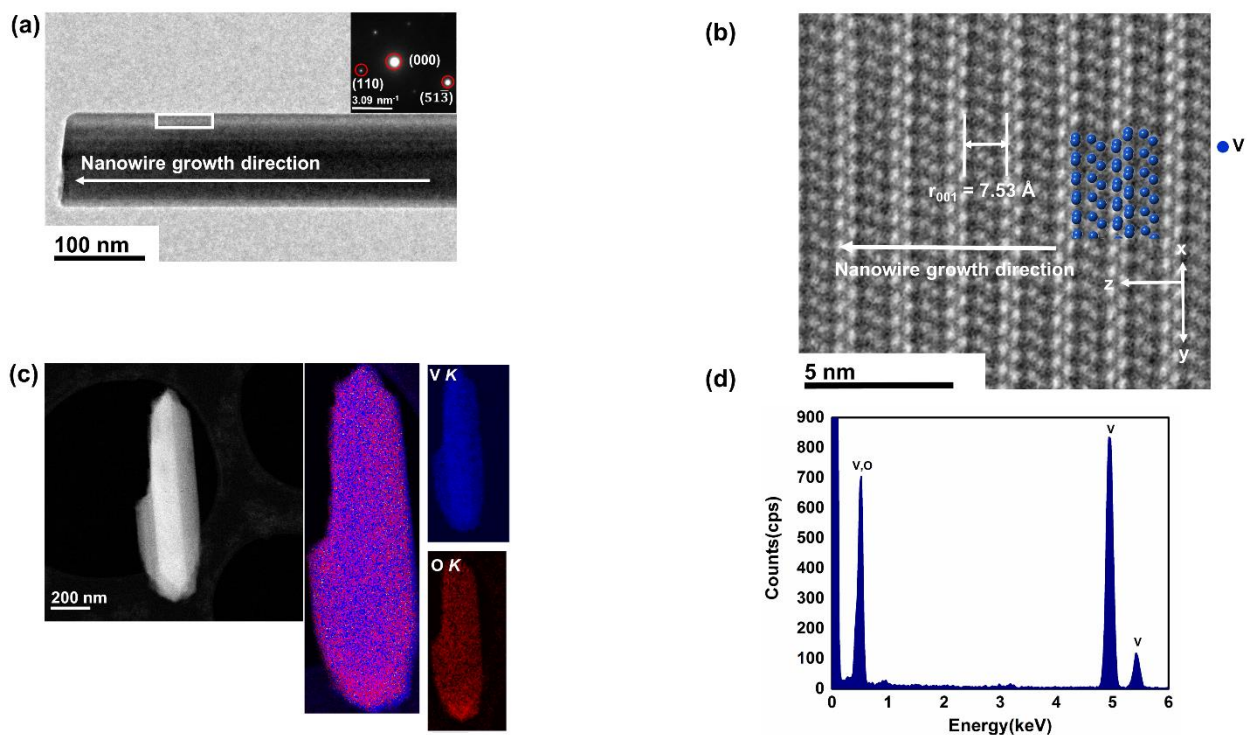
In the following work, a systematic study of electrochemical lithiation of this novel  $\zeta$ - $\text{V}_2\text{O}_5$  polymorph is completed by combining electrochemical cycling with extensive multimodal characterization techniques, such as aberration corrected scanning transmission electron microscopy (STEM) imaging, X ray diffraction (XRD), X ray absorption spectroscopy (XAS), electron energy loss spectroscopy (EELS) and energy dispersive X ray spectroscopy (EDX). We provide direct evidence by atomic-resolution High angle annular dark field (HAADF) imaging that the electrochemically lithiated  $\zeta$ - $\text{V}_2\text{O}_5$  cathode retains the V atomic framework of the pristine material upon intercalation of  $1.5 < x_{\text{Li}} < 2$  unit cell, thus showing evidence of topotactic lithiation at an atomic scale.

### 3.6 STEM/EDX characterization of pristine $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires

Figure 3.9 presents STEM/EDX characterization data for pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire sample. The low magnification TEM image in Fig. 3.9 (a) illustrates the nanowire morphology, also indicating the growth direction for these nanowires. The thin area from which the atomic-resolution HAADF image was acquired has been marked in Fig. 3.9 (a). Fig. 3.9 (a) inset shows the selected area electron diffraction pattern, with (110) and (51 $\bar{3}$ ) planes indexed, confirming the single crystalline nature of these nanowires. The atomic-resolution high-angle annular dark field (HAADF) STEM image presented in Fig 3.9 (b) identified V atomic positions. This can be seen to correspond with the structural model for pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> presented along the [110] zone axis, showing only V atoms, overlaid on the experimentally acquired image. The nanowire growth direction as well as the spacing between V atomic columns have been clearly indicated on Fig. 3.9 (b).

Fig. 3.9 (c) presents EDX mapping data from a representative pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire. The HAADF- STEM image shows the nanowire used for EDX mapping, and both individual elemental maps for Vanadium (V) and oxygen (O) as well as the overlaid EDX map is shown. As can be seen, this pristine nanowire exhibits a homogeneous phase, with a uniform distribution for both V and O, as expected. Finally, the integrated EDX spectra for the pristine sample collected from a large field of view is presented in Fig. 3.9 (d). This shows V at% of ~29.4% and O with ~70.6 at%, thus consistent with the V<sub>2</sub>O<sub>5</sub> composition.

More details on the synthesis methodology and structure of the metastable  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires are provided in Chapter 4 [Section 4.9].

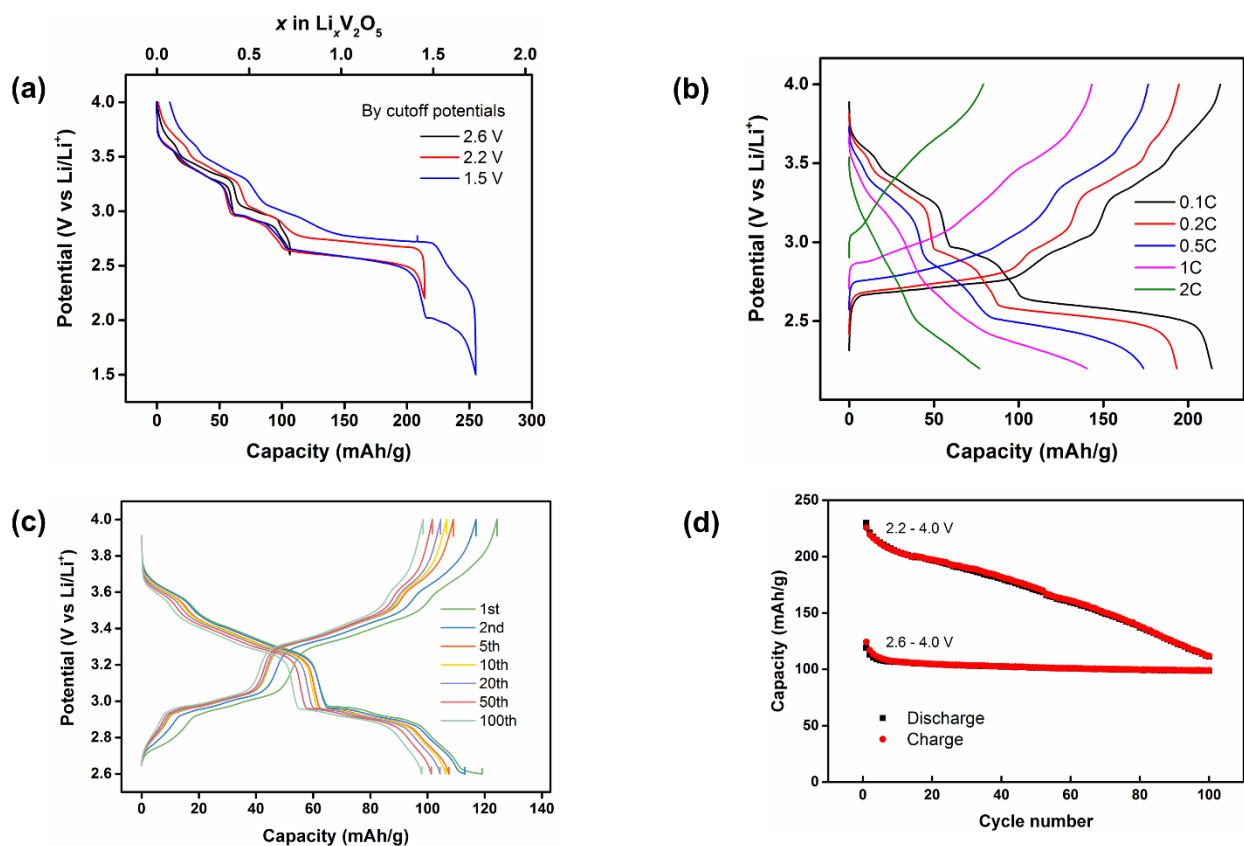


**Figure 3.9** STEM/EDX characterization of pristine  $\zeta - V_2O_5$  nanowire (a) Low magnification TEM image showing the nanowire morphology, inset showing indexed selected area electron diffraction. (b) Atomic-resolution HAADF (filtered) image in [110] zone confirming the tunnel structure of these nanowires (c) EDX map data showing nanowire used for EDX mapping, V K and O K individual and overlaid maps (d) Integrated EDX spectra clearly showing V and O signals.

### 3.7 Electrochemical lithiation into $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode

Figure 3.10 presents the electrochemical characteristics of Li<sup>+</sup> intercalation into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode. Fig. 3.10 (a) shows the voltage profiles with different cutoff potentials, 2.6 V, 2.2 V and 1.5 V vs Li/Li<sup>+</sup>. For the sample discharged to 1.5 V, the capacity of 250 mAh g<sup>-1</sup> corresponds to the intercalation of  $\sim 2$  Li<sup>+</sup> per  $\zeta$ -V<sub>2</sub>O<sub>5</sub> unit. It is important to note that 96.0 % of the discharge capacity was retained upon recharge to 4 V. The electrochemical performance of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> is significantly different from the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph, which is irreversibly transformed to  $\omega$  - Li<sub>3</sub>V<sub>2</sub>O<sub>5</sub> phase at 1.5 V vs Li/Li<sup>+</sup>.<sup>4</sup>

Fig. 3.10 (b) shows the rate capability of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> within a potential range of 4.0 - 2.2 V vs Li/Li<sup>+</sup>. High reversible capacity values of 193.2, 173.8, 140.3, and 77.0 mAh g<sup>-1</sup> were utilizable at 0.2C, 0.5C, 1C, and 2C rates, respectively. Fig. 3.10 (c) shows stable cycling of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> with reversible Li<sup>+</sup> intercalation for 100 cycles. The almost unchanged voltage profiles reflect the good structural reversibility upon repeated Li<sup>+</sup> intercalation. Fig. 3.10 (d) represents profiles of discharging and charging capacity vs cycle number, which exhibit 49.5% and 79.7% retention after 100 cycles for discharging cutoff potentials of 2.2 V and 2.6 V vs Li/Li<sup>+</sup>, respectively. This result indicates that discharging to deeper voltages facilitates the degradation of the material upon Li<sup>+</sup> cation insertion.



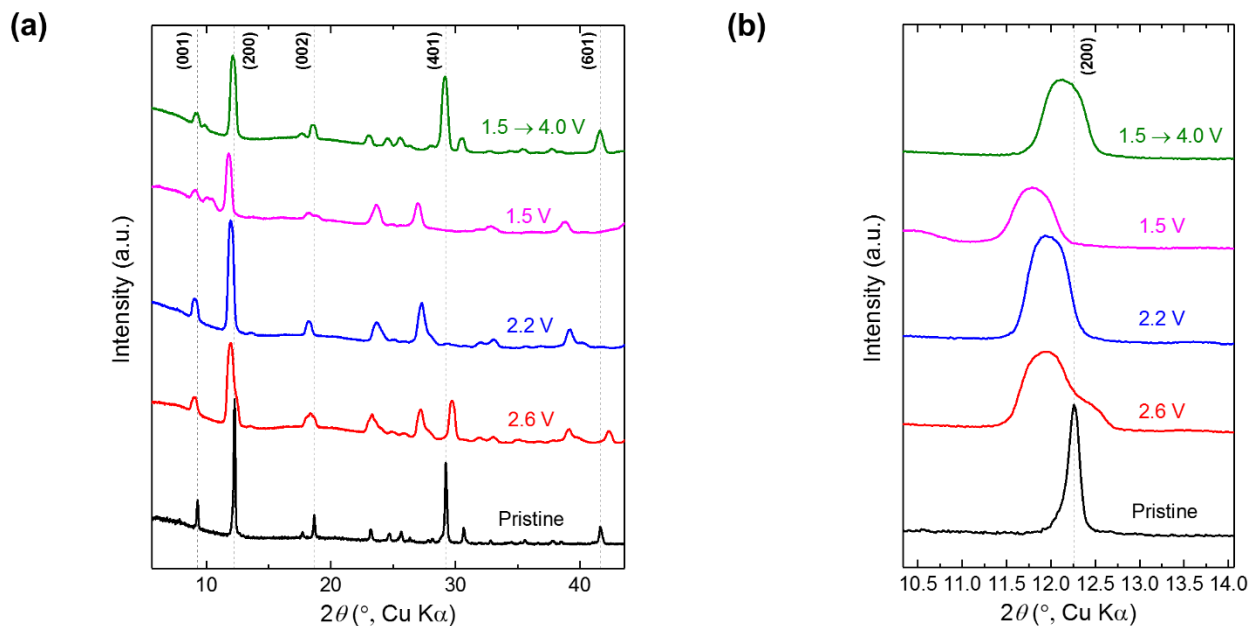
**Figure 3.10** Electrochemical characterizations of  $\zeta - V_2O_5$  nanowires for  $Li^+$  intercalation. (a) Comparison of voltage profiles with different discharging cutoff potentials. (b) Rate performance measured with the discharging cutoff potential of 2.2 V vs  $Li/Li^+$ . (c) Voltage profiles with cutoff potential of 2.6 V vs  $Li/Li^+$  during 100 cycles. (d) Cycling retention with respect to different discharging cutoff potentials of 2.2 and 2.6 V vs  $Li/Li^+$ .

### 3.8 Structural characterization of lithiated $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode

To understand the structural changes occurring upon Li<sup>+</sup> intercalation, XRD was performed for the pristine and lithiated samples (Fig.3.11). The (001) and (002) peaks shift to the left upon discharge compared to the pristine material, suggesting a slight increase in the *d* spacing upon Li<sup>+</sup> intercalation. At 2.6 V vs Li/Li<sup>+</sup>, new peaks evolve at 12.0°, 23.3°, 27.2°, 29.8°, 39.2°, and 42.4° as the peaks of pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> are diminished, signifying the characteristics of two-phase reactions. The remaining pristine phase is almost disappeared as the intercalation proceeds to 2.2 V vs Li/Li<sup>+</sup>; additionally, all the peaks shift slightly whereas the peak at 29.8° completely disappears. At 1.5 V vs Li/Li<sup>+</sup>, new peaks at 10.2° and 18.9° newly appear and all the peaks of previous phase shift to the lower angle, reflecting a significant expansion of the unit cell parameters. Upon deintercalation of Li<sup>+</sup> by recharging from 1.5 V to 4.0 V vs Li/Li<sup>+</sup>, most of pristine peaks are restored, indicating that structural changes of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> are mostly reversible. However, we can also see that the peaks are not fully restored, that would indicate a small part of the intercalated Li ion are not removed. This can also explain the hysteresis seen in the electrochemical cycling data upon 1.5 V discharge, as noted before this deeper discharge possibly leads to some structural changes that hinders complete recovery of the pristine structure upon Li deintercalation.

It is also noteworthy that the diffraction peaks are significantly broadened by lithiation. The peak broadening seen in the XRD spectra upon discharge would point to inhomogeneous lithiation along the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode, which would result in formation of smaller localized lithiated domains. That would mean the lithiated nanowire no longer exhibits the uniform phase, seen in the pristine case [Fig. 3.9 (c)] which is why the XRD peaks are sharp in the pristine case, but get broadened upon subsequent lithiation. The appearance of several plateaus in the voltage

profiles for cycling of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> vs Li [Fig. 3.10 (a)] indicate that the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph go through several phase transitions, with increasing amounts of Li ions in the structure for the range  $0 < x_{Li} < 2$ . It has been previously reported that lithiation in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires exhibit domains with lithiation gradients along the nanowires by stabilization of small polarons. Scanning transmission X ray (STXM) measurements done on lithiated  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires revealed that inhomogeneous lithiation led to formation of distinct domains.<sup>88</sup> So it is possible that nanowire cathodes exhibit this kind of inhomogeneous lithiation. It can also be seen that the XRD peaks remain broadened after delithiation, charging back to 4 V, which would also support this domain formation hypothesis. Once the smaller lithiation domains are formed, they cannot join back together even after removal of Li<sup>+</sup> ion, and hence cannot regain the homogeneous phase as found in the pristine nanowire, [Fig. 3.9 (c)] prior to lithiation. This could also be the reason behind the subtle structural deformation upon deep discharge of the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode to 1.5 V discussed before.



**Figure 3.11** X-ray diffraction (XRD) data for pristine vs lithiated samples (a) XRD data of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire samples with different levels of electrochemical lithiation; pristine (black), discharged to 2.6 V (red), 2.2 V (blue) and 1.5 V (magenta) vs Li/Li<sup>+</sup> and charged back to 4.0 V after discharge to 1.5 V (green) (b) Comparison of (200) peak showing good structural reversibility.

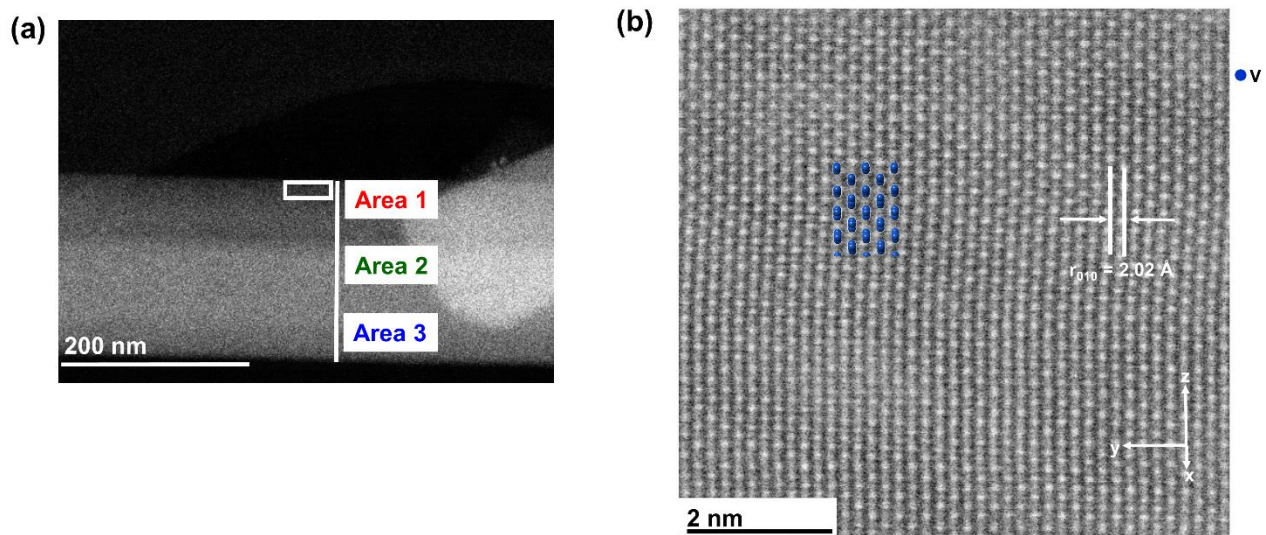
Figure 3.12 presents STEM characterization of the electrochemically lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire, discharged to 1.5V. Fig. 3.12 (a) shows the low-magnification HAADF image from the lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire, the thin area used for atomic-resolution imaging has been marked. Also, the area from which EELS linescan data was acquired [presented in Fig. 3.14 (a) and Fig. 3.14 (b)] has been indicated with a white line, with the three specific areas from which the core-loss EELS data was extracted highlighted as Area 1, 2 and 3, using the same color scheme as that employed in Fig. 3.14 (b).

The atomic-resolution HAADF-STEM image from the lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode has been presented in Fig 3.12 (b). To understand the structural change upon Li intercalation, we compare this with the structural model for pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub>. As can be seen, the experimentally observed structure can be seen to match the pristine structural model in  $[30\bar{1}]$  zone, showing only V atoms, which is directly overlaid on the image.

This implies that the V framework is preserved, at an atomic scale, upon intercalation of  $\sim 2$  Li ions/unit cell for the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph. The good reversibility observed in electrochemical cycling [Fig. 3.10 (a)] may be explained by this structural stability at an atomic scale. However, as noted before in the discussion for the XRD data (Fig. 3.11), in this case, it is possible that lithiation gives rise to smaller domains along the nanowire. The atomic-resolution imaging probes a very small region of the lithiated nanowire at the few nm scale, thus what we see could be the snapshot of a small lithiated domain. In fact, prior STXM experiments probing lithiation in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires found existence of highly lithiated domains along the nanowire that were fairly large in size.<sup>88</sup>

Measurements, such as XRD, electrochemical cycling or STXM would evaluate the lithiation at the more average scale (several hundred nm or more), and thus are representative of the bulk

behavior. So atomic-resolution STEM imaging would be capturing a particular lithiated domain (or maybe even a section of it), while XRD/electrochemical cycling would sample the whole nanowire considering all the phase inhomogeneity that may exist. The atomic-resolution image in Fig. 3.12 (b) does indicate that the small lithiated domain that we captured during STEM/EELS measurements preserves the V framework of the pristine structure locally. These observations also establish the importance of combining multi-modal techniques that can probe significantly different length scales to fully understand intercalation, especially in novel cathodes.



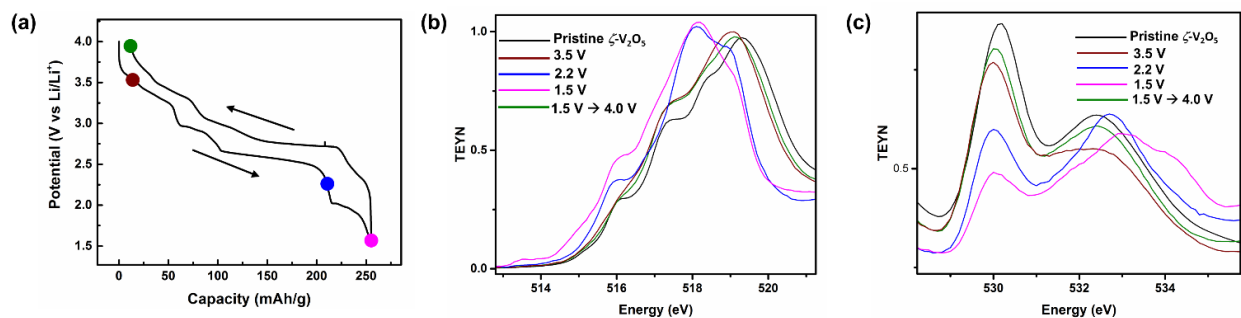
**Figure 3.12:** STEM characterization data for electrochemically lithiated  $\zeta$ - $\text{V}_2\text{O}_5$  (a) Low-magnification HAADF image of lithiated  $\zeta$ - $\text{V}_2\text{O}_5$  nanowire highlighting the area from which atomic-resolution HAADF image and EELS linescan data were acquired and (b) Atomic-resolution HAADF (filtered) image in  $[30\bar{1}]$  zone with the structural model overlaid, spacing between V atomic columns indicated.

### 3.9 Spectroscopic characterization of lithiated $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode

XANES was taken of the electrodes' V *L*- and O *K*-edges as a function of charge state and is shown in Figure 3.13 (b) and 3.13 (c). Fig. 3.13 (a) presents the electrochemical profile of the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode vs lithium highlighting the phases for which XANES data was acquired. The spectrum of pristine V<sub>2</sub>O<sub>5</sub> is in good agreement with previously reported  $\zeta$ -V<sub>2</sub>O<sub>5</sub> structure, and the V *L*<sub>3</sub> spectral feature at 519.2 eV is corresponding to the electron transition from V 2p<sub>3/2</sub> orbital directly to the unoccupied 3d states.<sup>88</sup> Upon discharge to 3.5 V vs. Li, V *L*<sub>3</sub> feature decreased by about 0.1 eV. Further discharges to 2.2 and 1.5 V vs. Li resulted in the V *L*<sub>3</sub> generally decreasing by 1 eV. At discharge states lower than 3.5 V vs. Li, the *L*<sub>3</sub> feature broadens with the genesis of a more intense feature at 518.1 eV while the original feature at ~ 519 eV remains with reduced intensity. This 1 eV change is likely related to the formation of V<sup>4+</sup> species and is indicative of insertion of ~ 2 Li/  $\zeta$ -V<sub>2</sub>O<sub>5</sub> unit, as also consistent with the electrochemical capacity data presented in Fig. 2a for discharge to 1.5 V. Following a recharge to 3.5 V vs Li, the V *L*<sub>3</sub> feature recovers to 519.1 eV, indicating that the V redox activity is reversible.

O *K* features were also scanned in conjunction with V *L* edges (shown in Figure 4c). The O *K*-edge features originate from O 1s→O 2p transitions, where the O 2p orbitals have hybridized with V 3d orbitals. Pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> shows characteristic *t*<sub>2g</sub> and *e*<sub>g</sub> features at 530.2 eV and 532.4 eV, respectively. Due to the hybridization between V 3d-O 2p orbitals, two distinct sets of resonances are observed, owing to the crystal field splitting of V 3d orbitals. A description of the orthorhombic V<sub>2</sub>O<sub>5</sub> structure is to consider highly distorted [VO<sub>6</sub>] octahedra building units joined together to form the layered anisotropic structure.<sup>89</sup> In this sense, the vanadium and the vanadyl oxygen atoms are shifted from the octahedral centers to give rise to a short V-O bond (about 1.577 Å) and a longer V-O bond to an apical oxygen in the next layer with a bond length of

approximately 2.791 Å).<sup>90</sup> Therefore, the splitting of the O K-edge region into two features is attributed to the roughly octahedral coordination of VO<sub>6</sub>, the low- and high-energy peaks are  $t_{2g}$  and  $e_g$ , respectively. Since V is  $d^0$  in  $\zeta$ -V<sub>2</sub>O<sub>5</sub>, electron transitions into those unfilled orbitals is clear and evident.<sup>88</sup> The lowest energy feature (530.2 eV) stems from weaker (pi) interactions between O  $2p_x$  and  $2p_y$  and  $t_{2g}$  V  $3d_{xy}$ ,  $3d_{xz}$  and  $3d_{yz}$  orbitals. Overlapping stronger (sigma) bonds between O  $2p_x$  and  $2p_y$  and V  $d_{x^2-y^2}$  represent the spectral feature at 532 eV. Upon discharging to 1.5 V vs. Li, the  $t_{2g}$  and  $e_g$  peaks lose intensity, peak ratios and the  $e_g$  feature experiences a blue chemical shift. Deeper discharge states as also seen in the previous study by De Jesus et al.<sup>88</sup> observed a diminution of the  $t_{2g}$  and  $e_g$  peak ratio at the O K-edge with increasing Li intercalation. Upon recharging the cathode to 4 V vs. Li, these two features reform close to the pristine state. As Li is inserted into the structure, V will reduce from V<sup>5+</sup> to V<sup>4+</sup> which coincides with 2 electrons populating antibonding  $t_{2g}$  orbitals. Since more electrons are present, the number of allowed electron transitions to those orbitals decreases and the intensities also decrease. This oxidation change is reversible since the  $t_{2g}$  and  $e_g$  features are recovered upon recharge (Li de-insertion).

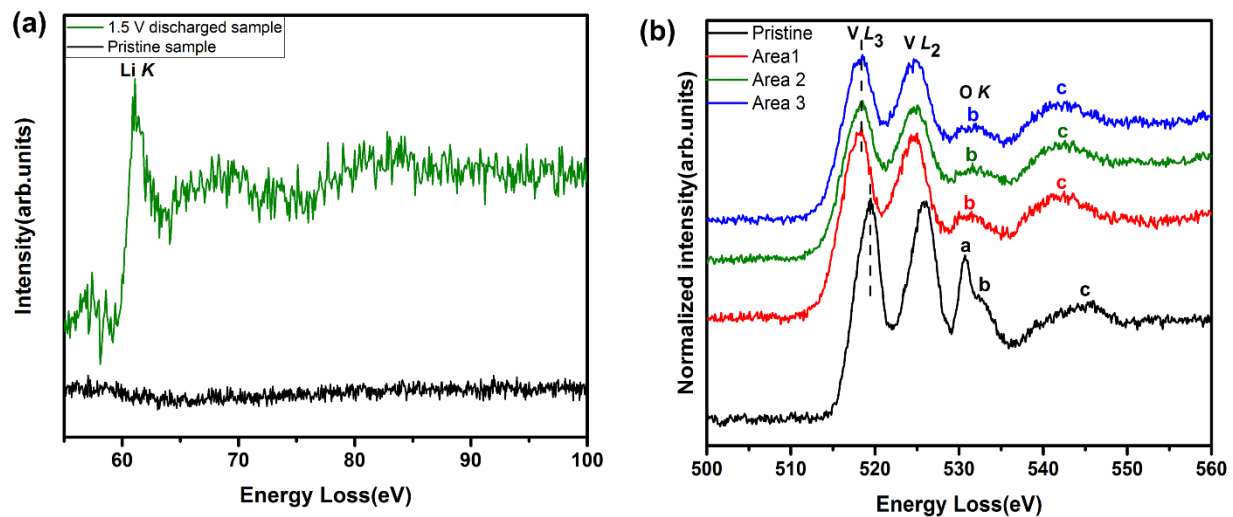


**Figure 3.13** XANES characterization of  $\zeta - V_2O_5$  nanowire sample discharged to 1.5 V vs lithium (a) C/V curve for  $\zeta - V_2O_5$  against Li highlighting the lithiated phases for which XANES data was acquired (b) XANES data comparing V  $L_3$  edges of pristine, charged and discharged samples. (c) XANES data comparing O  $K$  edges of pristine, charged and discharged samples.

The EELS data from this lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> sample are presented in Fig 3.14 (a) and Fig. 3.14 (b). The area for EELS linescan data acquisition has been shown in Fig. 3.12 (a). This EELS data is collected very close to the same area of the nanowire that was used for atomic-resolution HAADF imaging, so as to ensure that it is representative of insertion of  $\sim 2$  Li/ unit cell, and as discussed before, it captures the same lithiated domain that was used for HAADF imaging. Low-loss EELS measurements were also done in the same area [Fig. 3.14 (a)] directly identifying the Li K edge in this case, once again confirming Li intercalation. It is important to note that our XANES analysis of the V  $L_3$  edge and O K edge between the pristine and lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> sample, discharged to 1.5V, [black and magenta data in Fig 3.13 (b) and Fig. 3.13 (c)] are consistent with the EELS results. The core-loss EELS data presented in Fig. 3.14 (b) shows a comparison of EEL spectra from pristine and lithiated sample, data for lithiated sample extracted from EELS line-scan across the nanowire. The HAADF image showing the lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire used for EELS linescan has been presented in Fig. 3.12 (a). Lithiation is found to be homogeneous across the nanowire, in the radial direction, since the spectra along the line-scan [designated as area 1, area 2 and area 3 as shown in Fig. 3.12 (a)] are found to converge. We can identify two main features going from the pristine to lithiated samples. As is also seen in the XANES data presented in Figure 3.13 (b), the V  $L_3$  edge shifts to a lower energy in the lithiated sample compared to the pristine case, which is indicative of a reduction in the V valence state, consistent with Li intercalation.

The O K part of the core-loss EEL spectra can be subdivided into three regions, ‘a’, ‘b’ and ‘c’. The regions ‘a’ and ‘b’ seen in the pristine EEL spectra can be attributed to the  $t_{2g}$  and  $e_g$  features. Going from pristine to lithiated sample the feature labelled as ‘a’ shows a significant decay, as also seen in the XANES data in Fig. 3.13 (c). In transition metal oxides, such as V<sub>2</sub>O<sub>5</sub>,

the V 3d and the O 2p states hybridize and O *K* edge reflects the transition probability to the unfilled states that result from this hybridization. The additional electrons coming from Li intercalation occupy the higher V 3d orbitals, thereby reducing the weight of the  $t_{2g}$  manifold of the O *K* edge, which results in the decay of the O *K* pre edge. Thus, the intensity of the O *K* pre edge is linearly related with the valence of Vanadium, and the decrease in intensity going from pristine to lithiated case, once again, suggests a reduction in V valence.<sup>91</sup> The core-loss and low-loss EELS data prove that we do see true Li intercalation in this case, and not just a surface reaction.



**Figure 3.14** EELS data for electrochemically lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> (a) Low loss EEL spectra showing Li K edge for the lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire. (b) Comparison of core-loss EEL spectra from lithiated and pristine sample, data for lithiated sample collected from EELS line-scan, area of EELS linescan highlighted in Fig. 3.12 (a).

### 3.10 Conclusions from experiments investigating Li intercalation into metastable $\zeta$ -V<sub>2</sub>O<sub>5</sub>

In conclusion, this study has combined electrochemical cycling along with systematic characterization such as aberration corrected scanning transmission electron microscopy (STEM) imaging, X ray diffraction (XRD), X ray absorption spectroscopy (XAS), electron energy loss spectroscopy (EELS) and energy dispersive X ray spectroscopy (EDX) to directly probe the structural evolution upon electrochemical lithiation in the novel  $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode. At the bulk scale, the XRD results point to inhomogeneous lithiation possibly leading to smaller lithiated domains along the nanowire. At the nanoscale, using atomic-resolution HAADF imaging, we see the preservation of the V framework upon intercalation of  $\sim 2$  Li/unit cell. The spectroscopy techniques including XAS and core-loss EELS provide consistent results relating to shift of the V  $L_3$  edge upon lithiation as well as a decay in the O  $K$  pre edge both of which verify Li intercalation. Furthermore, low loss EELS directly captures the Li  $K$  edge in the lithiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires.

It is notable that previous theoretical work evaluating the electrochemical performance metrics for the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph set intercalation limit of  $x_{Li} = 0.66$ ,<sup>22</sup> however experimentally we have intercalated  $1.5 < x_{Li} < 2$  per formula unit of  $\zeta$ -V<sub>2</sub>O<sub>5</sub>, which induces significant strain on the lattice. Even so, we see significantly better reversibility than the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph for deep discharge conditions to  $\sim 1.5$  V. As discussed in Chapter 1, Section 1.2, the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph undergoes irreversible structural transformation upon intercalation of more than 1 Li ion/ V<sub>2</sub>O<sub>5</sub> unit. Previous work exploring lithiation of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> for different potential windows reported decrease in specific capacity from initial discharge value of 280 mAh/g to 230 mAh/g after 40 cycles. The authors attributed the capacity fading to the severe and repeated structural transformations involved in Li insertion from the empty  $\alpha$  to  $\gamma$ -phase.<sup>86</sup>

In case of the metastable  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph, even after deep discharge to 1.5 V, subsequent charging brings out the last Li ion at almost the same voltage ( $\sim 4$  V) as the voltage at which the first Li ion was inserted into the empty  $\zeta$ -V<sub>2</sub>O<sub>5</sub> structure, whereas in case of the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph, there is a clear difference for the removal of last Li ion after subsequent charging back from the  $\gamma$  or  $\omega$ -phases.<sup>11,86,8</sup> This, along with the XRD data, especially the evolution of the (200) peak [Fig. 3.11 (b)] indicates much better structural reversibility for the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph. Furthermore, the atomic-resolution HAADF image [Fig. 3.12 (b)] shows preservation of the V atomic structure of pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> for the lithiated (discharged to  $\sim 1.5$  V) material. So the phase transitions upon successive lithiation in the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> material are certainly much more subtle than the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> case. Especially it is important to note that the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph exhibits excellent structural reversibility upon lithiation, as evidenced from the XRD and atomic-resolution STEM data. It might be interesting to study if the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanoparticles (presented in Chapter 4, Section 4.14) with their shorter diffusion lengths can provide better capacities for Li intercalation. In any case, the phase transitions for an ideal intercalation cathode should not be so dramatic to cause irreversible structural changes, since that would lead to cycling instabilities. Thus, in this regard, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph presents new opportunities as a possible Li-ion battery cathode material.

Interestingly, the two Vanadium pentoxide cathodes ( $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\zeta$ -V<sub>2</sub>O<sub>5</sub>) that were discussed here also show potential as an intercalation cathode for Mg-ion batteries, results on experiments exploring Mg-ion intercalation into these cathodes are presented in Chapter 4 of this thesis. We believe discovery of such metastable vanadium oxide phases as  $\zeta$ -V<sub>2</sub>O<sub>5</sub> and systematic understanding of ionic intercalation and associated structural changes into them could open

exciting new avenues in the ongoing search and development for better intercalation based cathodes for lithium ion as well as multivalent battery systems.

## CHAPTER 4

### Magnesium intercalation into V<sub>2</sub>O<sub>5</sub> polymorphs

#### 4.1 Introduction

This following portions (Section 4.1- 4.6 and Figure 4.1 – 4.12) are reproduced from [A. Mukherjee, N. Sa, P. J. Phillips, A. Burrell, J. Vaughey and R. F. Klie, Direct investigation of Mg intercalation into orthorhombic V<sub>2</sub>O<sub>5</sub> cathode using atomic resolution transmission electron microscopy, *Chemistry of Materials*, **2017**, 29, 2218-2226 with permission from American Chemical Society (ACS Publications). Copyright (2017) American Chemical Society.]

Lithium ion batteries have been very successful in the consumer electronics market, even finding applications in electric vehicles.<sup>2,92</sup> However, as explained in Chapter 1, Section 1.2, they fall short in providing the high energy density required for next-generation energy storage, necessitating the need for an alternative energy storage technology.<sup>63,87</sup> As already outlined in Chapter 1, Section 1.3, multivalent battery technology is an exciting prospect, and of all the candidates, Mg-ion based batteries appear to be the most promising option.<sup>93,94,13,95,96</sup>

The first example of a prototype Mg battery utilizes the chevrel phase Mo<sub>6</sub>S<sub>8</sub> cathode.<sup>97</sup> However, this is a low voltage material (1.1 V vs Mg). Therefore, it is desirable to seek high voltage cathodes for Mg batteries. Research is underway to explore new potential cathode hosts for Mg intercalation.<sup>98</sup> Oxide materials are possible candidates for high voltage intercalation cathodes for Mg.<sup>99,100,101,15</sup> However, the nature of intercalation reactions with Mg, in particular in oxide cathodes, can be quite complicated. Questions regarding the pathways for Mg intercalation and a better understanding of the intercalated structures need to be addressed for further development. While several experimental reports claim reversible Mg intercalation based on electrochemistry data, there is a lack of systematic characterization work, which can provide

insights into Mg insertion sites or the phase formation upon Mg intercalation. One notable exception is the recent paper by Kim et al.,<sup>102</sup> that investigated Mg intercalation into a spinel oxide cathode host by using techniques such as atomic-resolution STEM imaging, EDX, nuclear magnetic resonance (NMR) to directly prove Mg intercalation. The work reported here presents a similar combination of techniques, including aberration-corrected STEM, EELS and EDX, to directly investigate the Mg intercalation with  $V_2O_5$  and thus providing information about the intercalation mechanisms. As already discussed in Chapter 3, orthorhombic  $V_2O_5$  is a well-known cathode candidate for Li ion batteries. The layered framework of  $V_2O_5$ , consisting of  $VO_5$  pyramids sharing corners and edges and connected by weak interlayer bonding, allows for ionic intercalation between the layers.<sup>4,8</sup> Furthermore,  $V_2O_5$  is a high capacity material (440 mAh/g) and can incorporate up to 3 Li ions per unit cell.<sup>12</sup> More recent simulation efforts have shown that orthorhombic  $V_2O_5$  is also a potential intercalation host for Mg ion batteries.<sup>103,104,105</sup> It is generally seen in the experimental reports investigating Mg insertion into orthorhombic  $V_2O_5$  that reversible insertion of Mg has an upper limit of  $x_{Mg} \sim 0.5$ , as opposed to Li intercalation, where  $x_{Li} \sim 3$  is more commonly reported.<sup>101,11,106</sup> Additionally, several experimental reports claim necessity of high water-content electrolytes to demonstrate significant capacities for Mg intercalation.<sup>106,107,108</sup> However, such electrolytes are not compatible with Mg metal anode, use of which is one of the major advantages of switching to a Mg ion based battery.<sup>109,110</sup> These reports also do not present any data directly proving true Mg intercalation in case of orthorhombic  $V_2O_5$  cathode. Furthermore, in the case of Li intercalation the formation of intermediate lithiated phases as well as structural evolution upon progressive lithiation has been relatively well studied, but questions regarding phase formation upon Mg intercalation remain

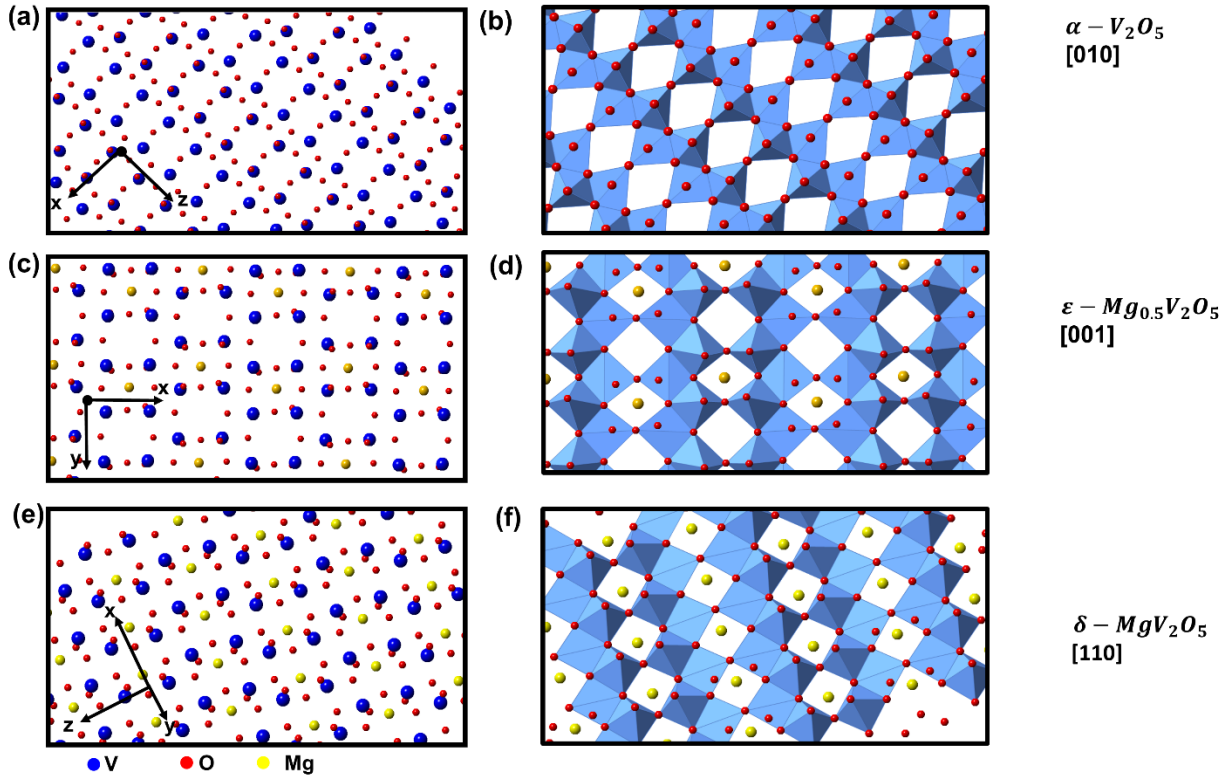
unanswered. Therefore, an in-depth understanding of Mg intercalation into  $V_2O_5$  is required for further development of stable Mg-intercalation cathode materials.

In this study, the approach that is put forth combines techniques, such as aberration-corrected STEM imaging, which can directly reveal Mg intercalation/insertion sites, EELS, which can verify Vanadium valence as well as quantify valence change upon Mg intercalation, EDX, which can provide compositional maps as well as quantify Mg insertion amounts and electron diffraction for phase identification to systematically probe the intercalation of Mg into orthorhombic  $V_2O_5$  cathodes. It is important to note that the sample I investigate is an electrochemically-cycled  $V_2O_5$  cathode in a full-cell configuration with a Mg metal anode and low water content 1.0 M  $Mg(TFSI)_2/G2$  electrolyte.<sup>111</sup> For comparison, and to develop an in depth understanding of Mg insertion pathways into orthorhombic  $V_2O_5$ , I also study a chemically synthesized  $MgV_2O_5$  sample, which represents a structure with full Mg insertion. In the case of electrochemically-cycled  $V_2O_5$ , though the intercalation levels are low, I provide, for the first time, direct evidence of true Mg intercalation into orthorhombic  $V_2O_5$  cathode and discover that the electrochemically intercalated sample forms a phase distinctive from the phase observed in the chemically synthesized sample  $MgV_2O_5$ .

## **4.2 Structural models of the phases and electrochemical data for Mg cycling into $\alpha - V_2O_5$ cathode**

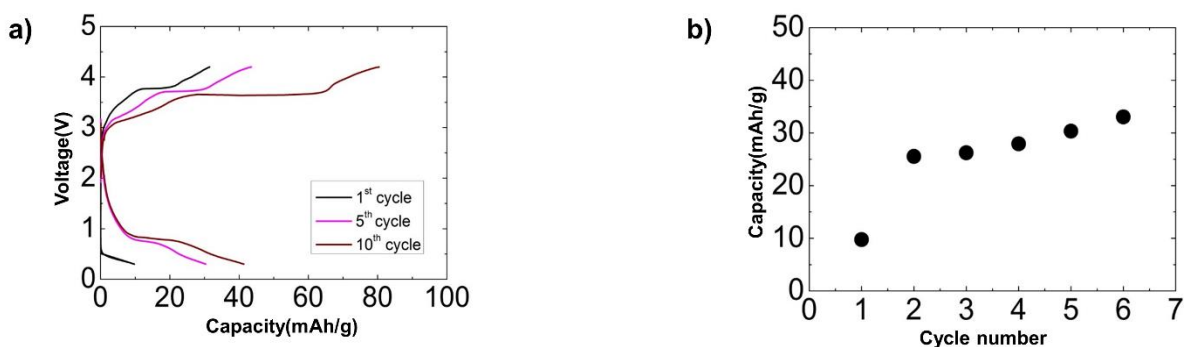
The structural models for the three phases that were investigated to gain a systematic understanding of Mg insertion into orthorhombic  $\alpha - V_2O_5$  have been presented in Figure 4.1. Fig 4.1(a) and Fig 4.1(b) present pristine  $\alpha - V_2O_5$  in [010] orientation with unmixed V and O atomic columns (PDF# 00-001-0359). Of course, this phase represents zero Mg occupancy. Fig 4.1 (c) and Fig 4.1 (d) present partially magnesiated phase,  $\epsilon - Mg_{0.5}V_2O_5$  in [001] orientation,

obtained by electrochemical cycling of  $\alpha - V_2O_5$  with Mg metal anode. This phase,  $\epsilon - Mg_{0.5}V_2O_5$  has been theoretically predicted to form upon electrochemical cycling of  $\alpha - V_2O_5$  with Mg.<sup>24</sup> Finally, Fig 4.1 (e) and Fig 4.1 (f) present fully magnesiated phase,  $\delta - MgV_2O_5$  in [110] orientation (PDF# 01-089-4728). This phase is expected to form for a chemically synthesized sample. To verify the expected phase formation in each of the three cases presented, a systematic study employing aberration-corrected STEM imaging, electron diffraction, EDX and EEL spectroscopies has been presented in this paper aiming to directly probe magnesium intercalation into orthorhombic  $V_2O_5$ .



**Figure 4.1** Structural models of three phases. Left panels show ball and stick models while right panels include conventional polyhedral representation. (a), (b) Pristine phase  $-V_2O_5$  ; (c),(d) Electrochemically cycled phase  $\epsilon - Mg_{0.5}V_2O_5$  ; (e),(f) Chemically synthesized phase  $\delta - MgV_2O_5$ .

Fig 4.2 (a) and Fig 4.2 (b) present the electrochemical cycling results for a representative  $V_2O_5$  cathode versus Mg metal anode full cell configuration. The cycling was done in a conventional coin cell with a  $\alpha - V_2O_5$  cathode, 1.0 M  $Mg(TFSI)_2/G2$  electrolyte and a freshly polished Mg metal anode. The low cell capacity presented in Fig 4.2 (a) points to low intercalation levels for Mg under experimental cycling conditions. It is important to point out that the cycling was done with a ‘dry’ electrolyte, [15 ppm water] so as to rule out any proton co-intercalation in this case and ensure true Mg intercalation, albeit with low levels of intercalation.

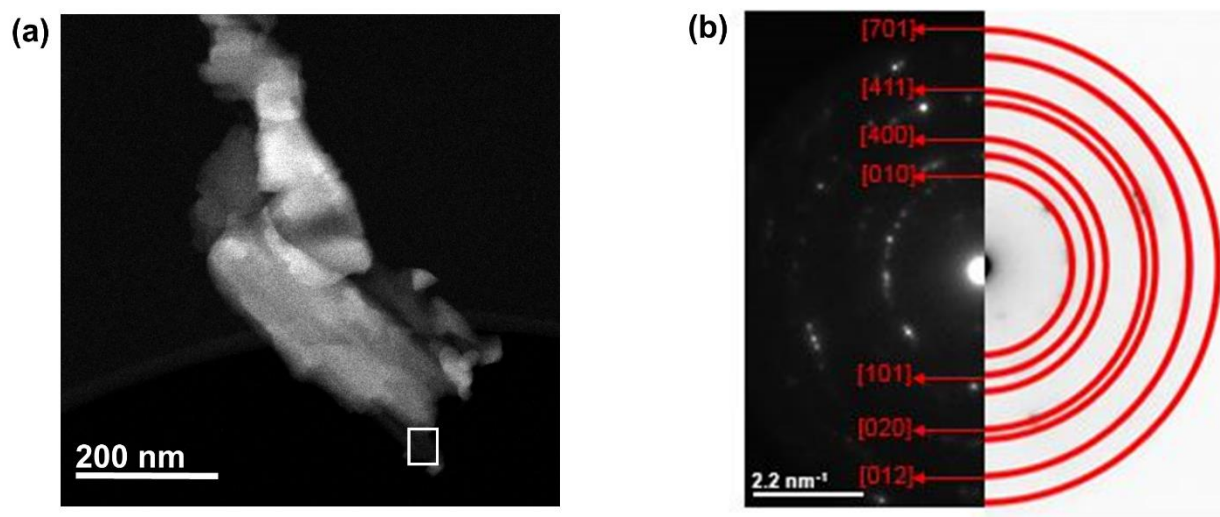


**Figure 4.2** Electrochemical cycling data for the full cell (a) represents the first 10 cycles of galvanostatic charge-discharge curves for  $V_2O_5$  against a Mg disk anode (b) Capacities versus cycle number plot for the two electrode coin cell.

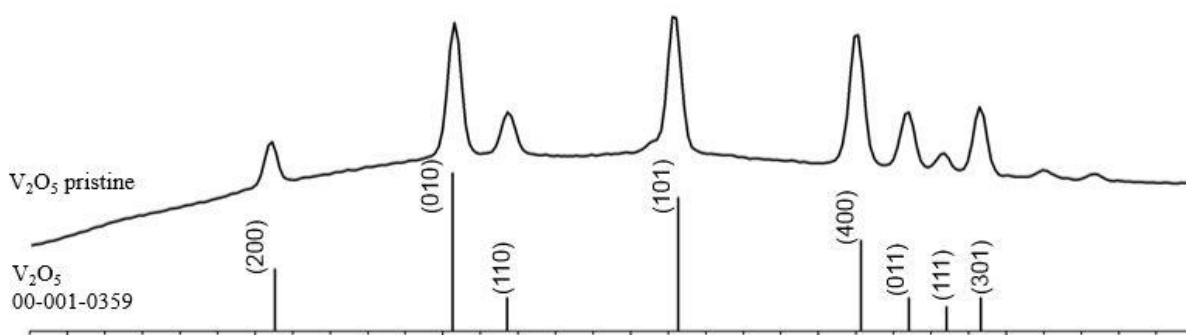
### 4.3 STEM/EELS data of pristine orthorhombic $\alpha$ - $V_2O_5$ phase

First, a pristine  $V_2O_5$  sample was characterized using STEM and EELS as presented in Figure 3. Fig. 4.3 (a) presents a low-magnification HAADF-STEM image showing a typical particle of the  $\alpha - V_2O_5$  cathode that was used, the thin area used for atomic-resolution imaging has been highlighted with a small rectangle. Fig. 4.3 (b) presents the polycrystalline electron diffraction data obtained from this sample, the rings can be systemically indexed according to orthorhombic  $\alpha$ - $V_2O_5$  (ICDD PDF# 00-001-0359), thus confirming the phase of this sample. Also, Fig. 4.4 presents the X-ray diffraction (XRD) data obtained from this pristine sample, which can also be indexed according to the same phase (ICDD PDF# 00-001-0359). The agreement of the XRD data with the orthorhombic  $\alpha$ - $V_2O_5$  phase points to the homogeneity of the phase at the bulk/ensemble scale, because while the electron diffraction data is collected from a small area of the sample, XRD gives information about the average phase the sample represents.

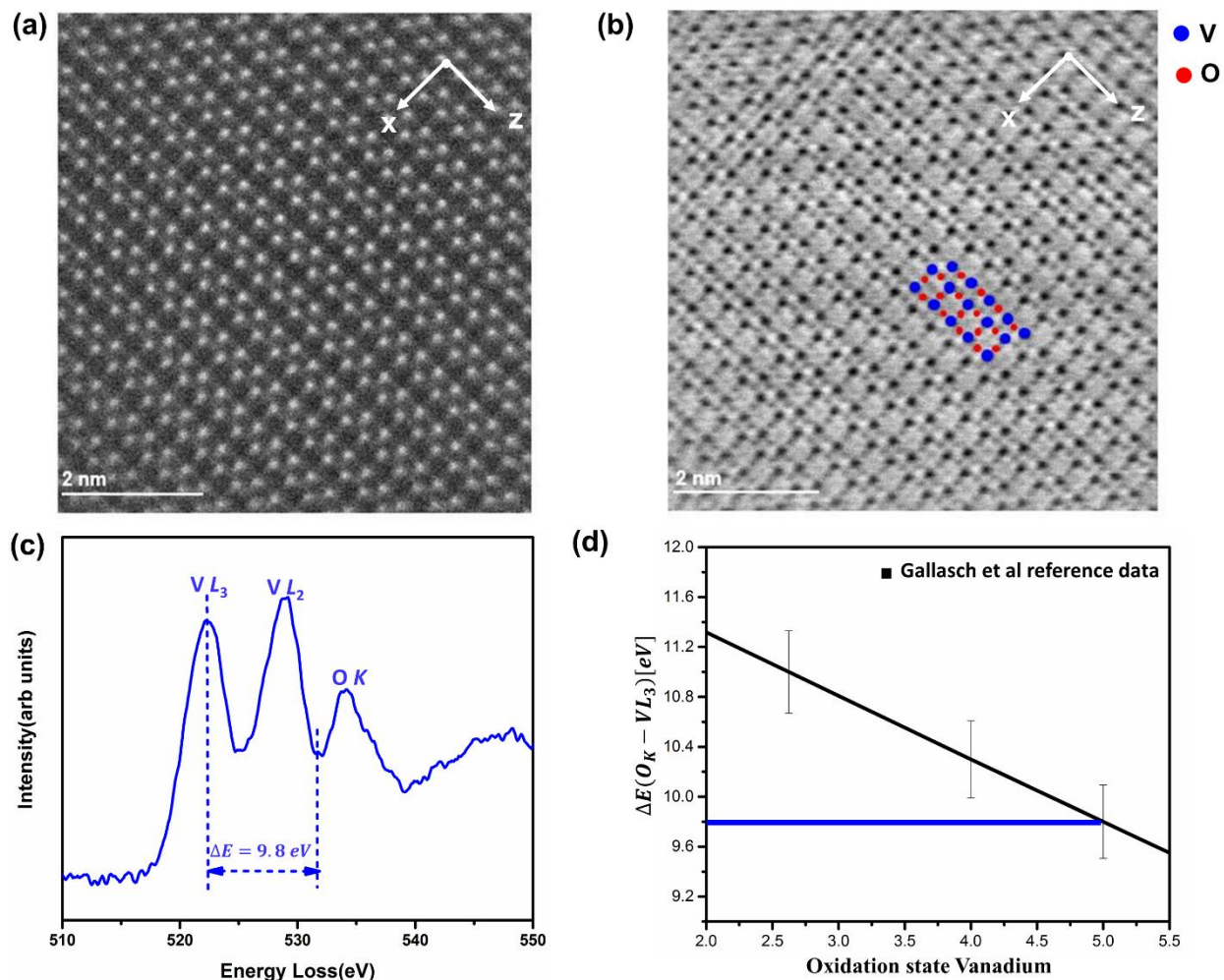
Atomic resolution STEM images from this sample are shown in Fig. 4.5 (a) and Fig. 4.5 (b) where V atomic columns are identified clearly in the HAADF image [Fig. 4.5 (a)] and the ABF image can capture lighter elements, such as O [Fig. 4.5 (b)]. The experimental STEM images can be seen to correspond with the structural model of  $\alpha - V_2O_5$  shown in the [010] projection [Fig. 4.1 (a)]. It is clear that both the V and O atomic columns can be identified in the ABF image [Fig. 4.5 (b)] in this zone axis. To further illustrate the structure, representative V and O atomic positions have been highlighted with blue and red spheres in the ABF image [Fig. 4.5 (b)] respectively. EEL spectra, shown in Fig. 4.5 (c), confirm the  $V^{5+}$  valence state as expected from pristine  $V_2O_5$  by comparing the energy difference between the V  $L_3$  edge and the O  $K$  edge onset. In this case, the energy difference of 9.8 eV corresponds to the valence state of  $V^{5+}$  as verified from the calibration data [Fig. 4.5 (d)].<sup>79,82</sup>



**Figure 4.3** STEM image and electron diffraction data from pristine orthorhombic  $\alpha$ - $V_2O_5$  sample (a) Low magnification HAADF-STEM image showing a typical particle cluster, the thin area used for atomic-resolution imaging [Fig. 4.5 (a) and (b)] has been highlighted. (b) Polycrystalline electron diffraction data for pristine  $\alpha - V_2O_5$  sample.



**Figure 4.4** XRD of pristine sample indexed according to orthorhombic  $\alpha - V_2O_5$  (PDF# 00-001-0359).



**Figure 4.5** Atomic resolution STEM images and EELS for pristine  $V_2O_5$  (a) High angle annular dark field (HAADF)(filtered)image showing V atomic positions(b) Annular Bright field(ABF)(filtered) image clearly showing both V and O atomic columns with some representative atomic positions highlighted (c) EELS spectra showing energy shift between  $V L_3$  and  $O K$  edge 9.8 eV (d) Calibration graph from literature correlating oxidation state of Vanadium with the energy shift between  $V L_3$  and  $O K$  edge with the relevant data point highlighted with blue line.

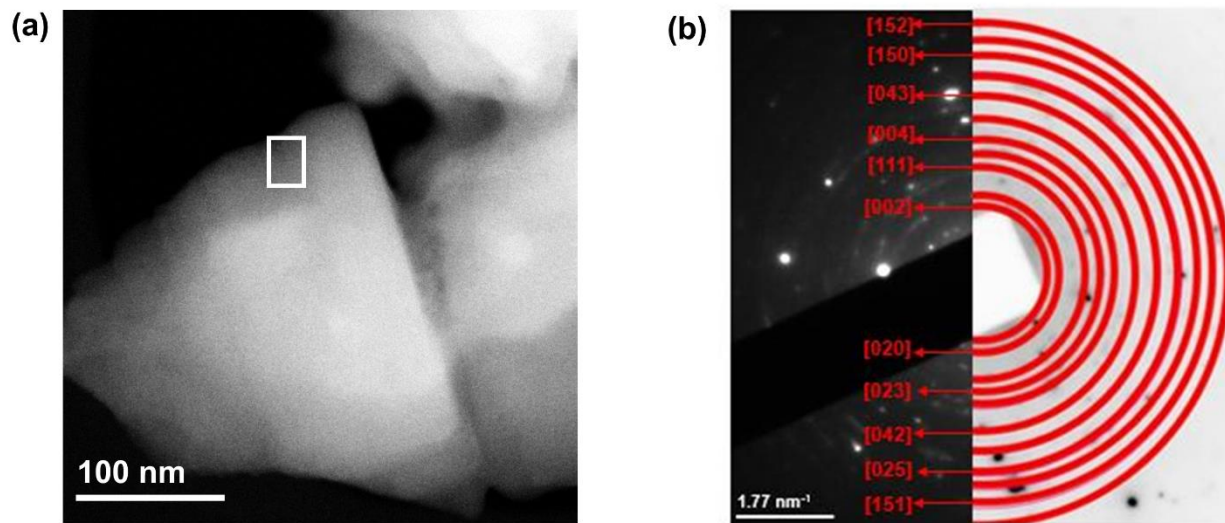
#### 4.4 STEM/EELS/EDX data from chemically synthesized phase

To explore the Mg insertion mechanism into  $V_2O_5$ , I first investigated a chemically synthesized sample representative of full Mg insertion. Fig. 4.6 (a) a low-magnification HAADF-STEM image showing a typical particle of the chemically synthesized  $MgV_2O_5$  sample, the thin area used for atomic-resolution imaging has been highlighted with a small rectangle. Fig. 4.6 (b) presents the polycrystalline electron diffraction data obtained from this sample, the rings can be systemically indexed according to  $\delta - MgV_2O_5$  (PDF #01-089-4728). This, once again, confirms the phase of this chemically synthesized sample.

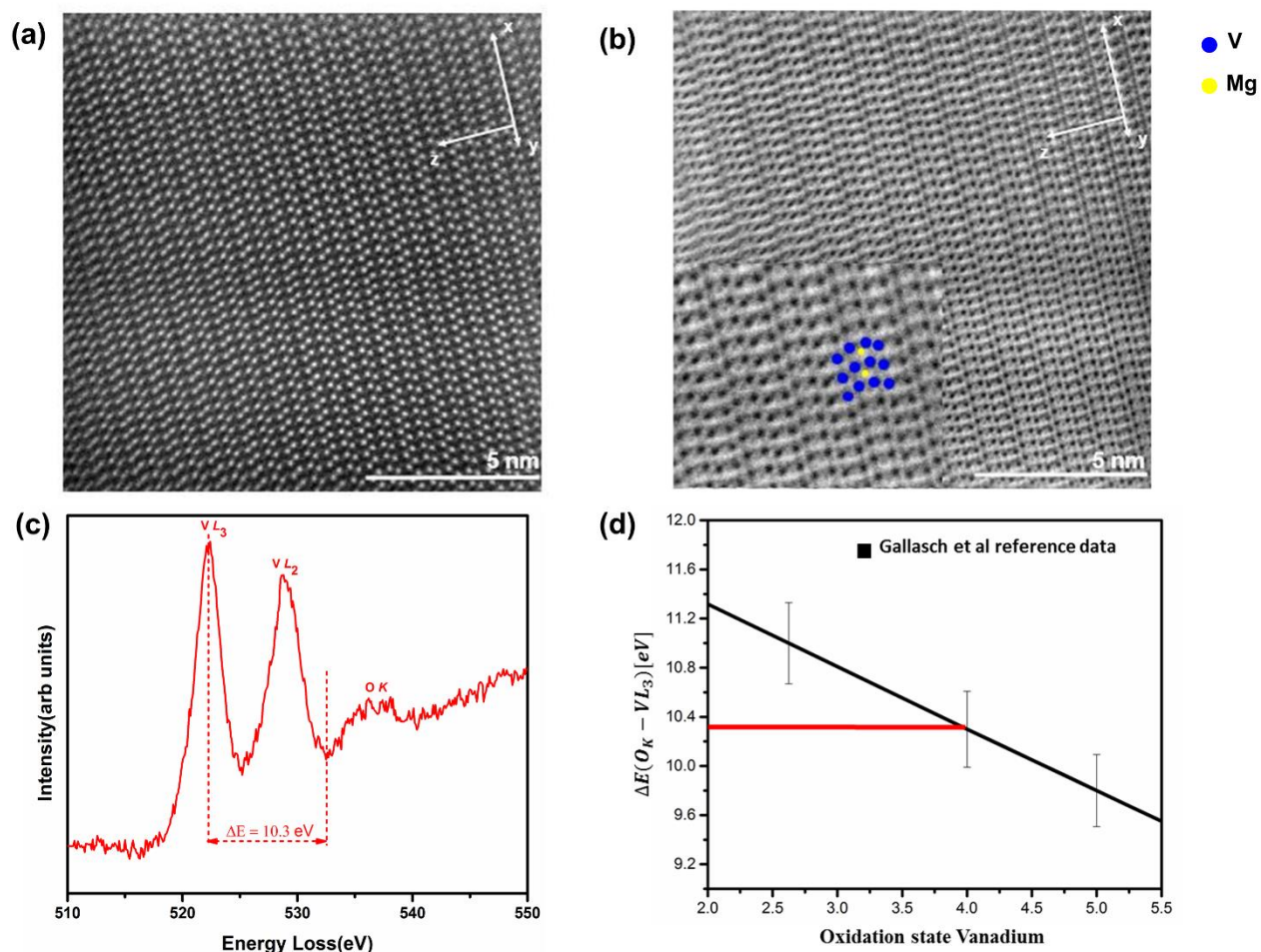
Figure 4.7 (a) and 4.7 (b) present the atomic-resolution HAADF and ABF images of the chemically synthesized  $MgV_2O_5$  sample. V atomic columns can be directly imaged in the HAADF image [Fig. 4.7 a)] and both V and Mg atomic columns in ABF image [Fig. 4.7 (b)]. Several representative V and Mg atomic positions have been illustrated on the blown up section of the ABF image [Fig. 4.7 (b) inset] with blue and yellow spheres, respectively, to elucidate the structure. By directly comparing the experimentally acquired atomic-resolution STEM images with the structural model for  $\delta - MgV_2O_5$ , [Fig 4.1 (e)] I confirm that the images represent  $\delta - MgV_2O_5$  phase in the [110] zone axis. Thus, it can be directly demonstrated that the chemically synthesized sample is distinctive from the  $\epsilon - Mg_{0.5}V_2O_5$  phase that is theoretically predicted to form upon electrochemical cycling of Mg with  $\alpha - V_2O_5$ . EELS [Fig 4.7 (c)] shows experimentally measured energy difference between the V  $L_3$  edge and the O  $K$  edge onset as 10.3 eV. Comparing this value with previously published data<sup>79, 82</sup> [Fig 4.7 (d)] confirms the presence of the  $V^{4+}$  valence state consistent with the phase  $\delta - MgV_2O_5$ .

In Fig 4.8 (a), an EDX intensity line-scan data of the chemically synthesized sample shows clear V and Mg signals. The EDX spectrum integrated over the entire region is presented in Figure 4.8

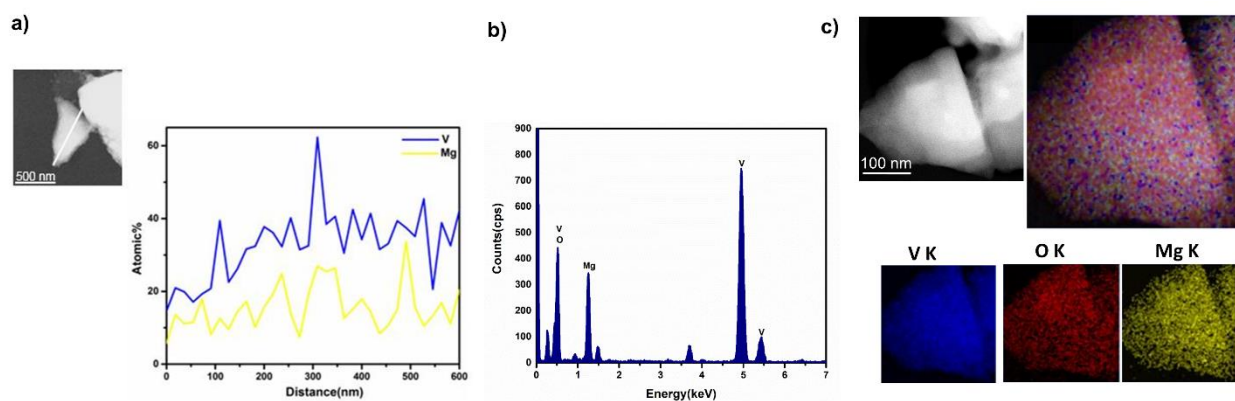
(b) which contains  $\sim 14.3$  atomic% of Mg. Fig 4.8 (c) presents EDX mapping data showing both overlaid and individual elemental maps. It can be concluded from the EDX analysis that the chemically synthesized sample [Fig 4.8 (a) and Fig 4.8 (c)] exhibited a homogeneous Mg distribution.



**Figure 4.6** STEM image and electron diffraction data from chemically synthesized sample  
 (a) Low magnification HAADF-STEM image showing a typical particle cluster, the thin area used for atomic-resolution imaging [Fig. 4.7 (a) and (b)] has been highlighted. (b) Polycrystalline electron diffraction data for chemically synthesized sample.



**Figure 4.7** Atomic-resolution STEM images and EELS for chemically synthesized sample (a) High angle annular dark field (HAADF) (filtered) image showing V atomic positions (b) Annular Bright field (ABF) (filtered) image showing both V and Mg atomic positions, with some representative atomic positions highlighted (c) EEL spectra showing energy shift between  $V L_3$  and  $O K$  edge as 10.3 eV (d) Calibration graph from literature correlating oxidation state of Vanadium with the energy shift between  $V L_3$  and  $O K$  edge with the relevant point highlighted with red line.



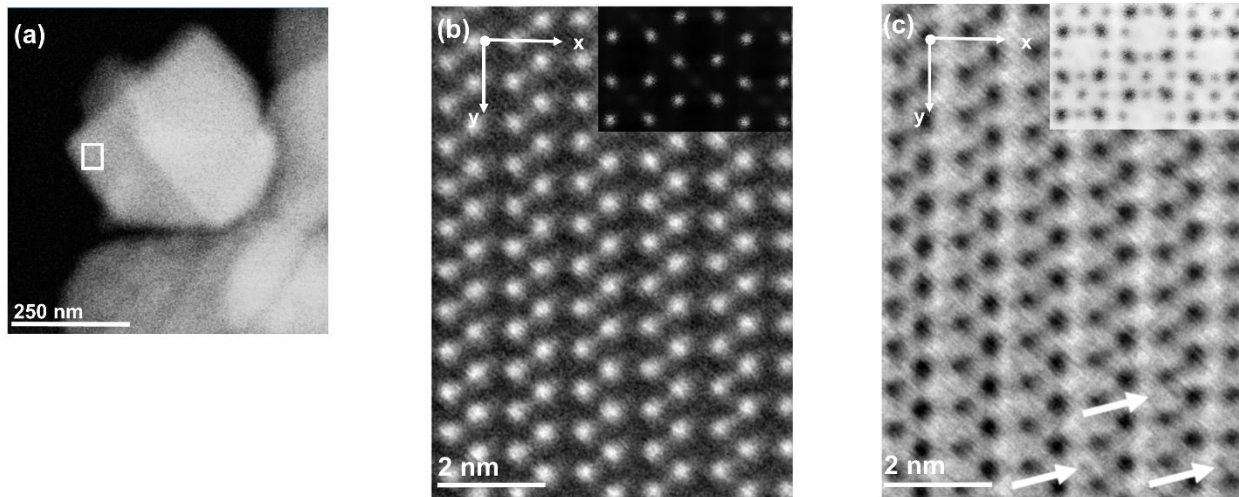
**Figure 4.8** EDX data for chemically synthesized sample (a) EDX line-scan shows V and Mg signal, particle on which EDX line-scan done shown highlighting area of acquisition; (b) Integrated EDX spectrum collected from a large field of view with Mg atomic%  $\sim 14.13\%$ ; (c) EDX map data showing homogeneous Mg distribution

#### 4.5 STEM/EDX data for electrochemically cycled sample

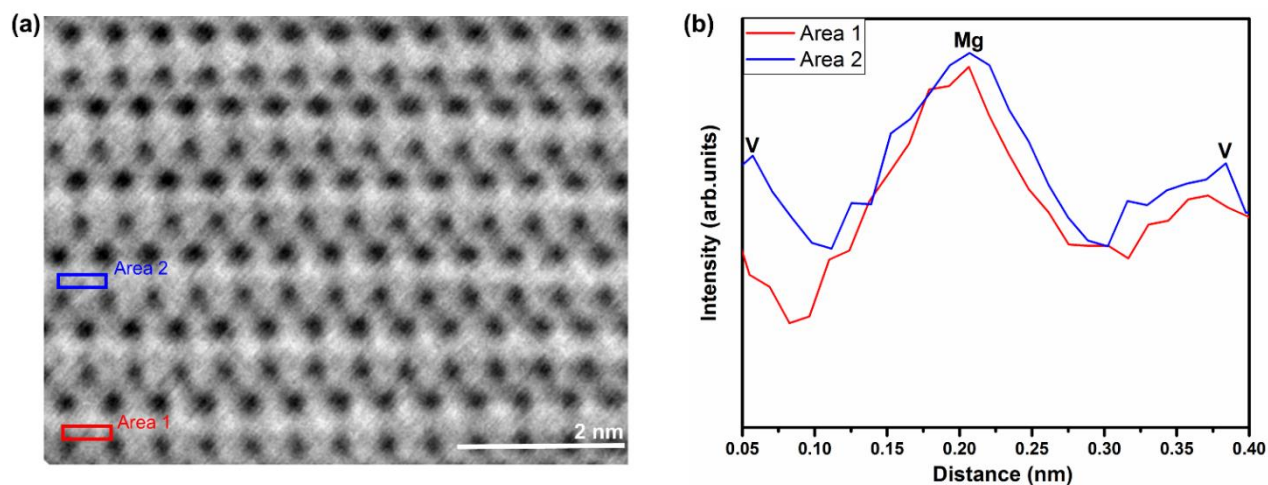
Fig. 4.9 presents the STEM characterization results from the electrochemically cycled orthorhombic  $V_2O_5$  cathode. Fig. 4.9 (a) shows the low-magnification HAADF-STEM image of the particle which was employed for analysis, the thin area used for atomic-resolution imaging has been highlighted with a white box. Atomic-resolution HAADF and ABF images of the electrochemically cycled orthorhombic  $\alpha - V_2O_5$  cathode are presented in Fig 4.9 (b) and Fig 4.9 (c). Heavier V atoms can be identified in the Z-contrast HAADF image, [Fig 4.9 (b)] while simultaneously acquired ABF image clearly shows Mg occupancy [Fig 4.9 (c)] (along with V atoms which appear dark due to the inverse contrast). The positions where Mg ion intercalation into  $V_2O_5$  was clearly identified has been labelled with white arrows in Fig 4.9 (c). Comparing the experimentally acquired STEM images with the previously published model structure for  $\epsilon - Mg_{0.5}V_2O_5$  in the [001] orientation [shown in Fig 4.1 (c)], it can be seen that V atomic positions match. The Mg positions in the experimental ABF image and the structural model do match in site occupancy, however it appears that Mg intercalation levels are lower experimentally than what is predicted by first principles calculations. To gain more insight into the phase formation upon electrochemical Mg intercalation into orthorhombic  $V_2O_5$ , multislice image simulations were performed with the theoretically predicted structure  $\epsilon - Mg_{0.5}V_2O_5$  in the [001] orientation. Simulated HAADF and ABF images are overlaid on the experimental images. Comparing the experimental and simulated ABF images it can be seen that V atomic positions transition almost continuously whereas Mg atomic positions match at a local scale, implying the Mg intercalation levels are lower in the experimental image compared to the predicted structure. This conclusion is also in agreement with the results from other experimental methods, such as cell capacity and XANES that have characterized the level of electrochemical

Mg intercalation in orthorhombic  $V_2O_5$ . Despite the lower Mg intercalation concentrations, it is important to note that the position of the Mg occupancy does match with the DFT predicted phase, which leads us to conclude that the formation of the DFT predicted  $\epsilon - Mg_{0.5}V_2O_5$  phase occurs locally within the  $V_2O_5$  cathode materials. A section of the experimentally acquired ABF STEM image has been presented in Fig 4.10 (a) [90° rotated]. Intensity line profiles done across the two regions where Mg occupancy was clearly identified (designated as Area 1 and Area 2) show a distinct peak indicating stronger contrast due to presence of Mg in those two areas [Fig 4.10 (b)]. The background peaks in the intensity profile originate from the probe tails of neighboring V atoms.

The  $\epsilon - Mg_{0.5}V_2O_5$  phase was recently predicted by Sai Gautam *et al.*<sup>24</sup> using first principles calculations, which also identified an intercalation pathway of Mg into the orthorhombic  $\alpha - V_2O_5$  structure. In orthorhombic  $V_2O_5$  ( $\alpha - V_2O_5$ ) the  $b$ -axis lattice parameter is considered to be indicative of the vanadium interlayer spacing and Mg intercalation sites are located between the two layers, near the middle of the  $VO_5$  pyramids. The diffusion path is, therefore, along the  $a$ -axis. Comparing the migration energies along the diffusion path, the thermodynamically stable phase corresponds to a specific ordering of Mg within the  $\alpha - V_2O_5$  lattice. The most thermodynamically stable configuration is predicted to be the  $\epsilon - Mg_{0.5}V_2O_5$  phase, which represents occupation of alternate intercalant sites along the  $a$ -axis. Therefore, this  $\epsilon - Mg_{0.5}V_2O_5$  phase represents the half intercalated or half magnesiated phase which is theoretically predicted to form upon electrochemical cycling of  $\alpha - V_2O_5$  with Mg under experimental conditions. The structural models of this phase have been presented in Fig 4.1 (c) and Fig 4.1 (d) and this structure was used in our multislice STEM image simulations presented in Figure 4.9 (b) and Fig 4.9 (c).



**Figure 4.9** STEM images of electrochemically cycled orthorhombic  $V_2O_5$  cathode (a) Low magnification HAADF-STEM image showing a typical particle cluster, the thin area used for atomic-resolution imaging has been highlighted (b) High angle annular dark field(HAADF)(filtered) image, simulated image overlaid (c) Annular Bright field(ABF)(filtered),some locations where Mg occupancy is clear has been marked with white arrows; simulated image for the theoretically predicted  $\epsilon - Mg_{0.5}V_2O_5$  structure overlaid on experimental image.

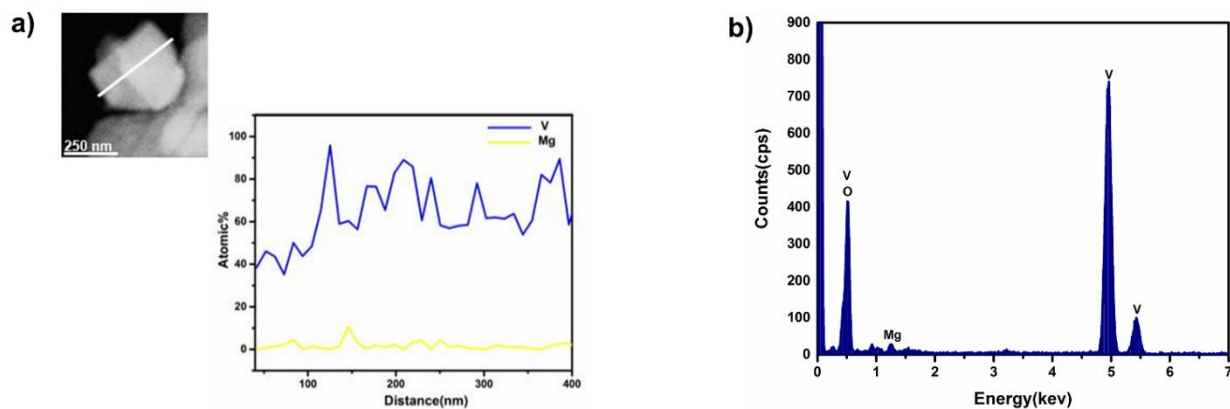


**Figure 4.10** Intensity line profiles done on ABF image of electrochemically cycled  $V_2O_5$  cathode (a) Portion of the ABF image(rotated 90°) showing the areas for the intensity line profiles with Mg occupancy (b) Intensity line profiles across the two marked areas showing clear Mg occupancy.

Figure 4.11 (a) presents the EDX line scan data where the Mg signal within the particle was presented with a low atomic concentration of Mg. The location of the EDX linescan within the sample is also shown. For easier comparison, only V and Mg linescan data have been presented. The EDX data coupled with the experimental ABF STEM image [Fig 4.9 (c)] are consistent with the local formation of the  $\epsilon - Mg_{0.5}V_2O_5$  phase,<sup>24</sup> particularly Mg occupancy in the DFT predicted sites within the  $V_2O_5$  lattice point to true Mg intercalation in this case. Importantly, the EDX analysis did not reveal any secondary phase formation which rules out any conversion type reaction in this case and further proves an intercalation type reaction of Mg with  $\alpha - V_2O_5$ , albeit with low Mg intercalation levels.

Comparing with the EDX data for the chemically synthesized sample [Fig 4.8 (a) and Fig 4.8 (b)], it can be seen that the Mg atomic% is much lower in the case of the electrochemically cycled sample. Specifically, the integrated EDX spectra [Fig 4.11 (b)] for the electrochemically cycled orthorhombic  $\alpha - V_2O_5$  cathode collected from a large field of view identifies Mg at a low atomic concentration ( $\sim 2.2$  atomic% Mg). While the theoretically predicted  $\epsilon - Mg_{0.5}V_2O_5$  phase<sup>24</sup> requires  $\sim 6.25$  atomic% Mg, in our experiments we see much lower Mg intercalation levels. The EDX quantification indicates that the electrochemically cycled sample represents  $\sim Mg_{0.17}V_2O_5$ . Previously published work investigating electrochemical behavior of the same sample has established that in case of a dry electrolyte system (same as the one used in our study), which is compatible with Mg metal anode, the capacities are lower (indicating low Mg intercalation levels) however this demonstrates true Mg intercalation as proved by X ray absorption near edge spectroscopy (XANES), NMR and EDX.<sup>111</sup> Recent first principles simulation work investigating Mg intercalation into nano-crystalline xerogel  $V_2O_5$  has also established that solvent co-intercalation in case of a wet electrolyte system is directly responsible

for higher capacities.<sup>26</sup> Also experimental reports have shown improved capacities for Mg as well as Zn intercalation with nanostructured cathode system bilayered  $V_2O_5$  which incorporates water molecules within the host structure.<sup>28,31</sup>



**Figure 4.11** EDX data for electrochemically cycled sample (a) EDX linescan shows V and Mg signal and particle on which EDX linescan was done with the area of acquisition highlighted (b) Integrated EDX spectrum collected from a large field of view with Mg atomic%  $\sim 2.2\%$

#### 4.6 Conclusions from STEM/EELS/EDX experiments investigating Mg intercalation into orthorhombic $\alpha$ - $V_2O_5$ cathode

In conclusion, this study combines atomic-resolution STEM imaging, EELS, electron diffraction and EDX to systematically study and directly demonstrate Mg intercalation in orthorhombic  $\alpha - V_2O_5$ . Importantly, the work presented here reveals Mg intercalation in orthorhombic  $V_2O_5$  by directly imaging the intercalated Mg atomic positions using aberration-corrected STEM imaging. From the electrochemically cycled orthorhombic  $V_2O_5$  cathode, representing the partially magnesiated phase, it has been established that Mg intercalated into  $\alpha - V_2O_5$  at low levels. However, the sites of Mg insertion appear to be consistent with the  $\epsilon - Mg_{0.5}V_2O_5$  phase as previously predicted by first-principles modeling.<sup>24</sup> Importantly, I need to point out here that the phase separation seen in the experimental STEM data [Fig 4.9 (c)] between Mg deficient and Mg containing domains is in agreement with previous DFT calculations for Mg intercalation with a ‘superdry’ electrolyte system.<sup>26</sup> As explained by Sai Gautam and co-workers here, in case of Mg intercalation into  $\alpha - V_2O_5$  with a ‘superdry’ electrolyte, phases with intermediate Mg concentrations [ $0 < x_{Mg} < 0.5$ ] are not stable. That is primarily why Mg intercalation occurs as a two phase reaction between ‘Mg rich’ [ $x_{Mg} = 0.5$ ] and ‘Mg poor’ [ $x_{Mg} = 0$ ] domains. The experimental ABF STEM image [Fig 4.9 (c)] confirms these predications, and we see a clear phase separation leading to a local formation of the theoretically predicted  $\epsilon - Mg_{0.5}V_2O_5$  phase.<sup>24</sup> On the other hand, the chemically synthesized sample, which represents full Mg insertion, exhibits the  $\delta - MgV_2O_5$  phase with a decrease in the vanadium valance state from  $V^{5+}$  (for pristine  $V_2O_5$ ) to  $V^{4+}$  [consistent with  $\delta - MgV_2O_5$ ]. Recent first principles modelling studies have established that the migration barriers for Mg intercalation strongly depends on the change in the anion coordination environment along the diffusion path. For example, in the  $\alpha -$

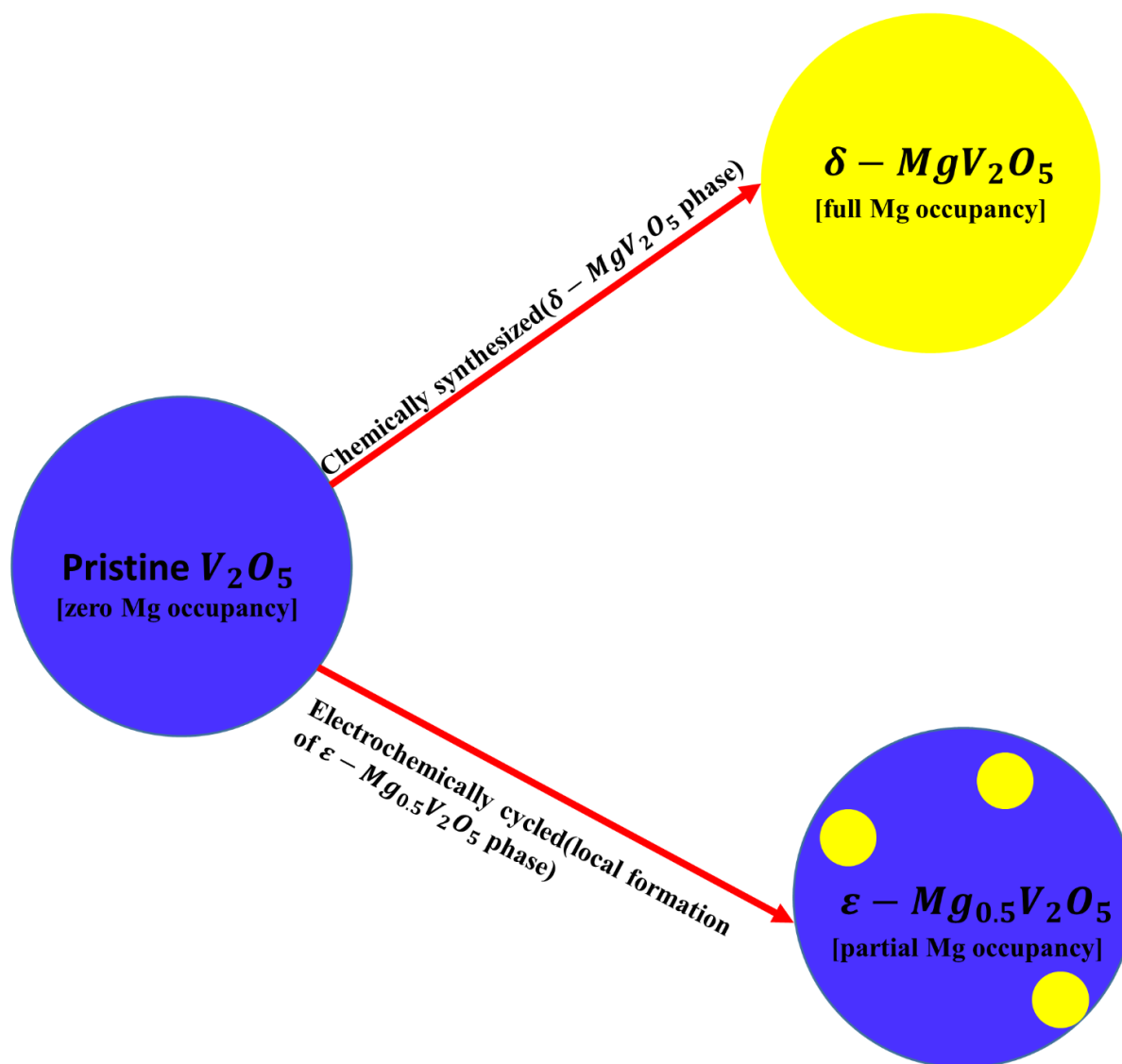
$V_2O_5$  polymorph, the anion coordination changes from 8-3-8 from one Mg insertion site to the next. So the migration barrier is higher in this case due to the steep change in the coordination environment. On the contrary, in the  $\delta - V_2O_5$  polymorph, the change in the anion coordination environment is much smaller [“4+2”-3-5-3-“4+2”] resulting in lower migration energy barriers.

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My understanding of the Mg intercalation/insertion mechanism in  $\alpha - V_2O_5$  has been summarized in the schematic presented in Fig 4.12. Starting from the pristine sample which shows no Mg occupancy, two independent routes of Mg insertion into  $\alpha - V_2O_5$  were systematically investigated. It can be concluded from our results that the chemically synthesized sample represents the  $\delta - MgV_2O_5$  phase. However, in the case of electrochemically cycled sample, we see local formation of the theoretically predicted  $\epsilon - Mg_{0.5}V_2O_5$  phase.<sup>24</sup>

These results provide direct proof of Mg intercalation in orthorhombic  $\alpha - V_2O_5$ , with low Mg intercalation levels. I have conclusively shown that the  $\delta - MgV_2O_5$  phase exhibited by the chemically synthesized sample is different from the locally observed  $\epsilon - Mg_{0.5}V_2O_5$  phase in the case of electrochemically cycled sample. Further work needs to be done to improve the cell capacity and voltage, including the development of better electrolyte systems that are compatible with the oxide cathode hosts, as well as thinner cathodes to increase intercalant ion mobility. Deeper understanding of the passivation layer on Mg metal anode that significantly slows down and ultimately stops cycling is also very important. Also, as established by first principles modelling studies it may be possible to lower activation barriers for multivalent cation intercalation by exploiting different coordination environments in metastable vanadium oxide bronzes.<sup>23,112,22</sup> I believe that the combination of techniques presented in this study outline a pathway to systematically investigate and directly probe the intercalation mechanism in different

polymorphs of  $V_2O_5$  cathodes (as well as other potential oxide cathode hosts) especially for Mg batteries. Such systematic understanding of the underlying intercalation mechanisms would be a key step in the design and development of future energy storage systems.



**Figure 4.12** Schematic elucidating Mg insertion mechanisms into orthorhombic  $\alpha - V_2O_5$  as seen from this study

In this context, it is interesting to note that more recent experiments exploring Mg-ion intercalation into the orthorhombic  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure at higher temperatures (110° C) reported much higher capacities (~295 mAh/g initial capacity), which would indicate formation of ~Mg<sub>1.0</sub>V<sub>2</sub>O<sub>5</sub>. It was found that the highly magnesiated V<sub>2</sub>O<sub>5</sub> nanostructures delaminated, which could be a consequence of the open layered architecture, and may also contribute to the high capacities observed, the delamination process exposed the whole structure to the intercalant ion and possibly greatly reduced the diffusion barrier. Further details on this study can be found here.<sup>113</sup>

#### **4.7 Mg insertion into metastable $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode**

The metastable tunnel structured polymorph  $\zeta$ -V<sub>2</sub>O<sub>5</sub> which was presented in Chapter 3 as an intercalation based cathode for Li-ion was also explored as a cathode for Mg-ion intercalation. The following experiments outline the results from these experiments, including electrochemical tests followed by XRD, X-ray spectroscopy and transmission electron microscopy (TEM) characterization such as STEM/EELS/EDX studies for Mg cycling with  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires as cathode at both room temperature as well as higher temperatures. Also, some results will be discussed exploring electrochemical performance with  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanoparticles, to compare the size/morphology effects (as in nanowires vs nanoparticles) on Mg ion intercalation behavior.

#### **4.8 Rationale for exploring metastable V<sub>2</sub>O<sub>5</sub> structures as Mg-ion cathodes**

The portions [Section 4.8 – 4.13 and Fig. 4.13 – 4.18] is partially reproduced from [J. Andrews, A. Mukherjee, H.D Yoo, A. Parija, P.M Marley, D.G Prendergast, J. Cabana, R.F Klie, S. Banerjee, Reversible Mg ion insertion in a metastable one dimensional polymorph of V<sub>2</sub>O<sub>5</sub>, *Chem*, (accepted for publication).]

While Mg-ion intercalation in the orthorhombic single-layer  $\text{V}_2\text{O}_5$  has been observed,<sup>101,111</sup> capacities are much lower than expected based on spatial or redox considerations ( $\sim 0.17$  Mg per  $\text{V}_2\text{O}_5$ ).<sup>14</sup> Relatively higher capacities have been observed for the xerogel phase of  $\text{V}_2\text{O}_5$ .<sup>28,30</sup> This xerogel phase is a bilayered  $\text{V}_2\text{O}_5$  polymorph, which incorporates interlayer and structural water molecules<sup>25</sup> and can more accurately be described as having a composition of  $\text{V}_2\text{O}_5 \cdot 1.8\text{H}_2\text{O}$ . There are two structural features of the xerogel phase which contribute to the increased intercalation capacities observed for  $\text{Mg}^{2+}$ . First, the water present within the structure greatly expands the interlayer spacing from 4.37 Å for  $\alpha\text{-V}_2\text{O}_5$  to 11.53 Å for the bilayered structure.<sup>25</sup> The water present in the interlayer spacing serves a second role when intercalating Mg-ions. The water molecules likely coordinate to the diffusing species and help to screen the cation charge, thereby facilitating diffusion. Li-ion intercalation has further been explored within a metastable puckered  $\gamma\text{-Li}_x\text{V}_2\text{O}_5$  phase;<sup>114</sup> wherein the puckered framework is retained upon reversible lithiation.<sup>115</sup> However, the intercalation of Mg-ions within this phase remains to be examined. A second example of the use of metastable  $\text{V}_2\text{O}_5$  phases as cathode materials is for lithium insertion into the quenched high-pressure  $\beta\text{-V}_2\text{O}_5$  phase, which comprises double-layered  $\text{V}_2\text{O}_5$  units incorporating corner-sharing motifs.<sup>116</sup> However, the ‘saw-tooth’ structure of this polymorph represents a particularly tortuous pathway for monovalent Li-ion diffusion; let-alone for divalent  $\text{Mg}^{2+}$  diffusion. To date, there have been no reports of metastable  $\text{V}_2\text{O}_5$  polymorphs being used as cathode materials for multivalent-ion batteries. This study thus provides a first example of using a metastable phase, namely  $\zeta\text{-V}_2\text{O}_5$ , as a multivalent ion cathode material.

The importance of evaluating metastable phases as cathode materials derives from recent reports which demonstrate that the crystal structure motifs of potential cathode materials are only one aspect of designing cathode materials to accommodate ions beyond Li specifically, the electronic

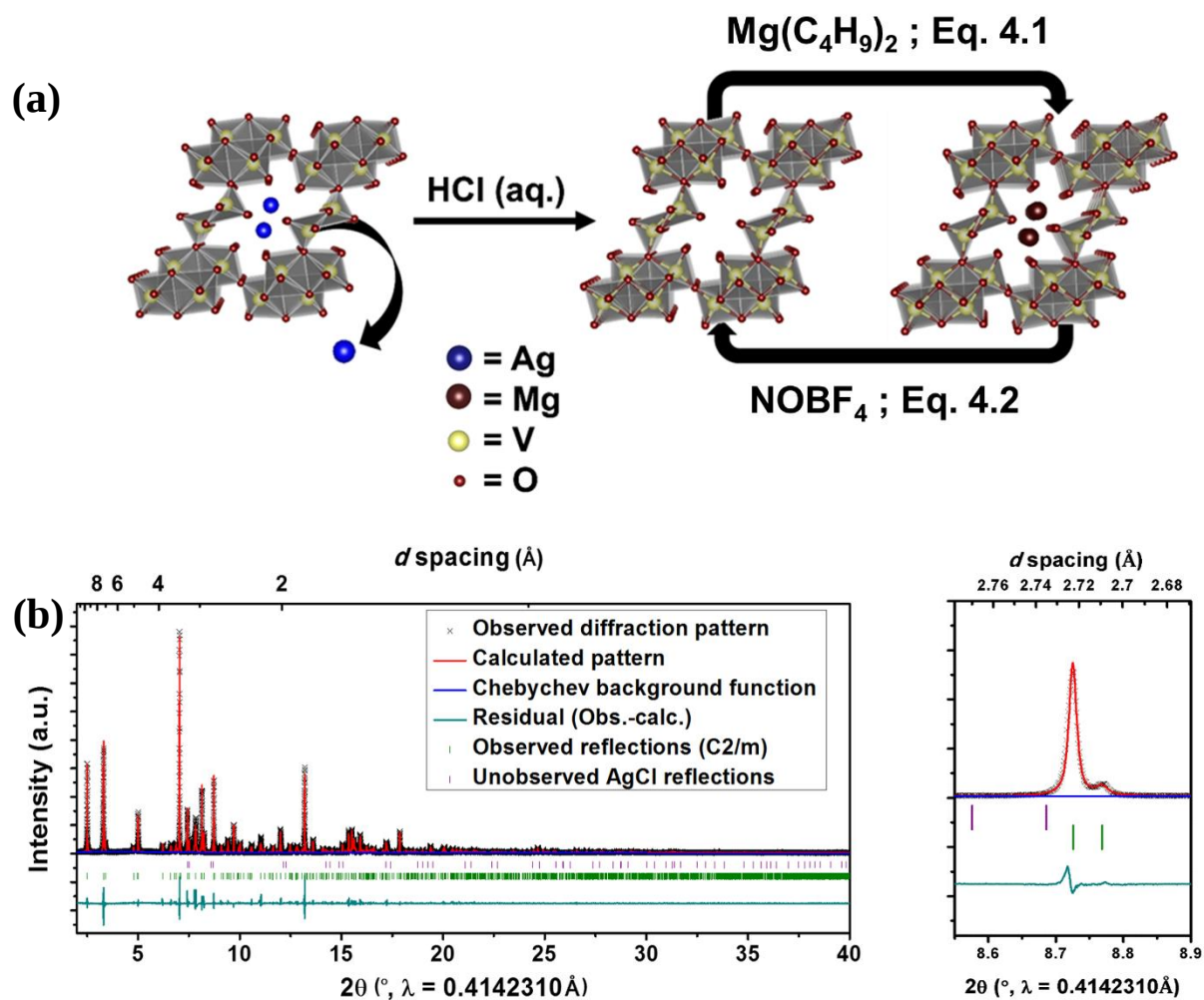
structure of such candidates is of equal importance in facilitating ion diffusion.<sup>22,117,118</sup> Consequently, for reasons of both crystallographic and electronic structure, many proposed cathode materials are not able to intercalate multivalent cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$ , because structural or electronic structure impediments that may be minor for the monovalent  $\text{Li}^+$  are exacerbated for di- and trivalent ions. In this context, metastable phases hold promise for allowing a broader range of structural motifs and connectivity but remain to be examined as viable cathode materials. Furthermore, utilizing an oxide cathode promises fundamentally greater operating potentials and improved gravimetric capacities; however, an oxide that combines the attributes necessary for reversible  $\text{Mg}^{2+}$  insertion from non-aqueous electrolytes with a high potential of operation remains elusive. Among the oxides studied so far,  $\text{Mg}^{2+}$  insertion with a reasonable voltage has been achieved in  $\alpha\text{-V}_2\text{O}_5$ <sup>101,119</sup> and in related xerogels containing water<sup>28,120</sup>; however, despite calculations which predict that the high-temperature  $\delta\text{-Mg}_{0.5}\text{V}_2\text{O}_5$  phase (isostructural with  $\delta\text{-LiV}_2\text{O}_5$ <sup>121</sup>) might be accessible upon magnesiation<sup>24</sup> as well as claims of capacities as large as  $\text{Mg}_{0.66}\text{V}_2\text{O}_5$ ,<sup>110,122</sup> it has been demonstrated by direct evidence that  $\text{Mg}^{2+}$  insertion levels are much smaller, around  $\text{Mg}_{0.17}\text{V}_2\text{O}_5$ ,<sup>14,101</sup> [as presented earlier in this chapter, Section 4.5] and as already mentioned earlier, NMR has established that the excess capacity observed in previous studies is due to proton intercalation.<sup>111</sup>

This study demonstrates that a metastable  $\zeta$ -phase of  $\text{V}_2\text{O}_5$ , stabilized by topochemical leaching of cations from  $\beta$ -phase ternary vanadium oxide bronzes, is capable of reversibly inserting Mg-ions up to 0.33 Mg-ions per  $\text{V}_2\text{O}_5$  unit within its 1D tunnel framework. In this study, the electrochemical performance of the material in a coin cell was evaluated, demonstrating a moderately high average operating potential of 1.65 V vs.  $\text{Mg}^{2+}/\text{Mg}^0$  and a capacity retention of 90  $\text{mAhg}^{-1}$  after 50 cycles

and atomic-resolution STEM as well as EELS and EDX characterization for the pristine and magnesiated samples are also presented.

#### 4.9 Structure of the metastable $\zeta$ -V<sub>2</sub>O<sub>5</sub> phase

Figure 4.13 (a) illustrates the approach utilized in this work to synthesize the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> phase, as well as an approach to ‘topochemical cycling’ of the materials by first magnesiating the structure *via* reaction with di-*n*-butylmagnesium in heptane followed by demagnesiation *via* reaction with NOBF<sub>4</sub> in acetonitrile each with retention of the original oxide framework. The quasi-one-dimensional  $\zeta$ -V<sub>2</sub>O<sub>5</sub> phase is a metastable open framework that is obtained by topochemical leaching of Ag-ions from nanowires of a tunnel-structured  $\beta$ -Ag<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> phase and has thus far not been stabilized in the bulk. Leaching of Ag-ions with HCl yields a AgCl precipitate along with  $\zeta$ -V<sub>2</sub>O<sub>5</sub> with the remnant Ag content greatly reduced to about 0.04 per formula unit of V<sub>2</sub>O<sub>5</sub>. To obtain a phase-pure material for Mg-intercalation studies, the mixture is washed with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Figure 4.13 (b) depicts a high-resolution synchrotron powder diffraction pattern ( $\lambda=0.4136\text{\AA}$ ) for the pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> material, including a refinement of the crystal structure, and also a magnified region of the high-resolution synchrotron diffraction pattern. It is evident from the magnified region of the synchrotron powder diffraction pattern that the major reflections due to AgCl impurity, expected to occur at  $2\theta$  values of  $8.55^\circ$  and  $8.65^\circ$  are absent, indicating successful removal of the AgCl precipitate and establishing high phase-purity of the pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> material.

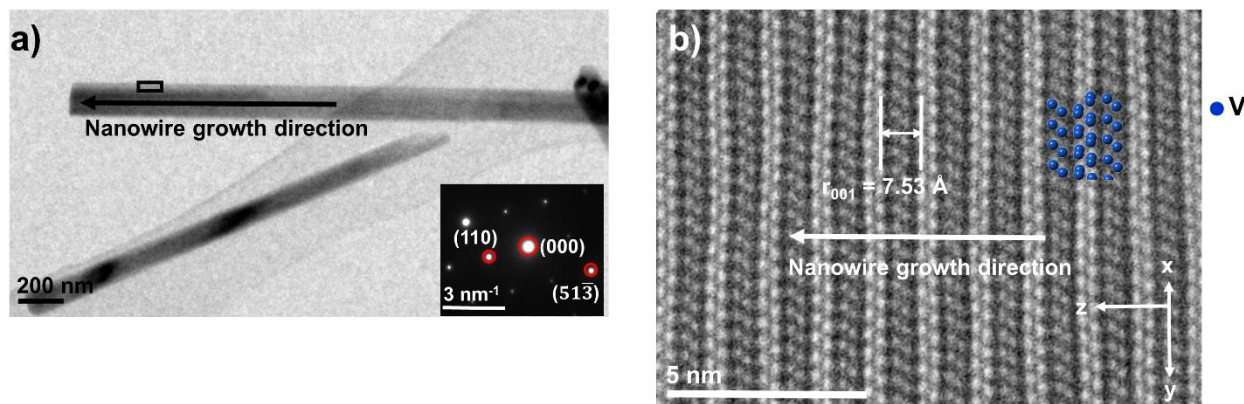


**Figure 4.13** Schematic illustration of reversible chemical intercalation of  $\text{Mg}^{2+}$  in  $\zeta\text{-V}_2\text{O}_5$  and elucidation of the structure of empty  $\zeta\text{-V}_2\text{O}_5$  framework. (a) Illustration of the approach employed to synthesize the metastable  $\zeta\text{-V}_2\text{O}_5$  phase, and reaction scheme for topochemical magnesiation and demagnesiation reactions. Relevant equations for the chemical magnesiation/demagnesiation are presented in Eq. 4.1 and Eq. 4.2. (b) High-resolution synchrotron powder diffraction data showing the empty  $\zeta\text{-V}_2\text{O}_5$  framework and a magnified region from the same.

#### 4.10 TEM/ STEM characterization of pristine $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire cathode

The distinctive tunnel structure of pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires have also been investigated by transmission electron microscopy, electron diffraction, and aberration-corrected scanning transmission electron microscopy (STEM), presented in Figure 4.14, (as also discussed in Chapter 3, Figure 3.9).

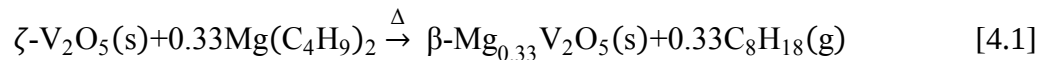
Figure 4.14(a) shows a low-magnification TEM image of  $\zeta$ -V<sub>2</sub>O<sub>5</sub>, which elucidates the nanowire morphology; the electron diffraction pattern shown as an inset to Figure 4.14 (a) verifies the single-crystalline nature of the pristine nanowires. It is important to note that in this system, as shown in Figure 4.14 (a), the growth direction of the nanowires is perpendicular to the one-dimensional tunnels. Hence, ion insertion is expected to occur radially within these  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires. The atomic-resolution high angle annular dark field (HAADF) image [Figure 4.14 (b)] confirms the structure solution of this metastable polymorph. In this HAADF image, which is sensitive to Z-contrast, the vanadium atoms can be clearly imaged and the observed motif is reproduced well by the structural model of pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> along the [110] zone which is overlaid on the experimentally acquired image. This provides a direct view of the empty tunnels and verifies the structural assignment noted before. The nanowire growth direction as well as the spacing between V atomic columns is clearly marked on the atomic-resolution HAADF image presented in Figure 4.14 (b).



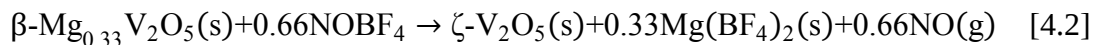
**Figure 4.14** Electron microscopy characterization data for pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub>. (a) Low magnification TEM image of  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires, thin area used for atomic-resolution imaging marked with a rectangle, inset shows electron diffraction. (b) Atomic-resolution high angle annular dark field (HAADF) image (filtered) showing tunnels perpendicular to nanowire growth. Structural model for  $\zeta$ -V<sub>2</sub>O<sub>5</sub> along the [110] zone axis showing V atoms (blue) overlaid on the experimental image.

#### 4.11 Brief summary of topochemical Mg insertion studies into $\zeta$ -V<sub>2</sub>O<sub>5</sub>

The pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> sample could be chemically magnesiated directly by reaction with di-n-butylmagnesium in heptane solution under reflux, reaction scheme presented in Eq. 4.1:



So the chemical magnesiation led to insertion of 0.33 Mg<sup>2+</sup>/V<sub>2</sub>O<sub>5</sub> unit. Following Mg insertion chemically, the  $\beta$ -Mg<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> sample can be demagnesiated (i.e. Mg ions could be chemically removed from the structure), by treatment with a strong oxidizing agent, NOBF<sub>4</sub> in dry acetonitrile solution,



These chemical magnesiation and demagnesiation reactions are schematically represented in Fig. 4.13 (a). The magnesiated samples were characterized by high-resolution synchrotron X-ray diffraction studies. Comparison with the XRD data for the pristine sample [shown in Fig. 4.13 (b)], showed shift of reflections, particularly the (001) and (100) ones, to lower  $2\theta$  values, suggesting lattice expansion upon Mg insertion into the structure. For the demagnesiated samples, return of the reflections in the XRD closer to the  $2\theta$  values as seen for the pristine material, suggested successful removal of Mg ions from the structure. Further characterization by XAS also confirmed reduction of the V valence state, as well as changes in O K fine structure, consistent with reversible Mg insertion. More details from these experiments can be found here.<sup>123</sup>

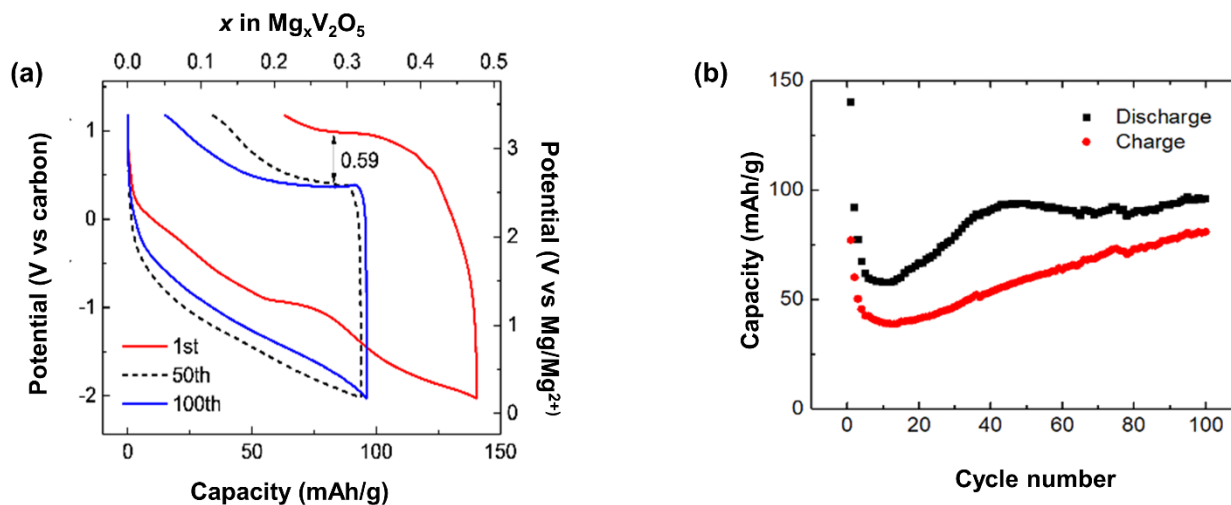
These results motivated pursuing electrochemical Mg intercalation experiments followed by multimodal characterization into this  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph.

#### 4.12 Electrochemical $\text{Mg}^{2+}$ insertion in $\zeta\text{-V}_2\text{O}_5$

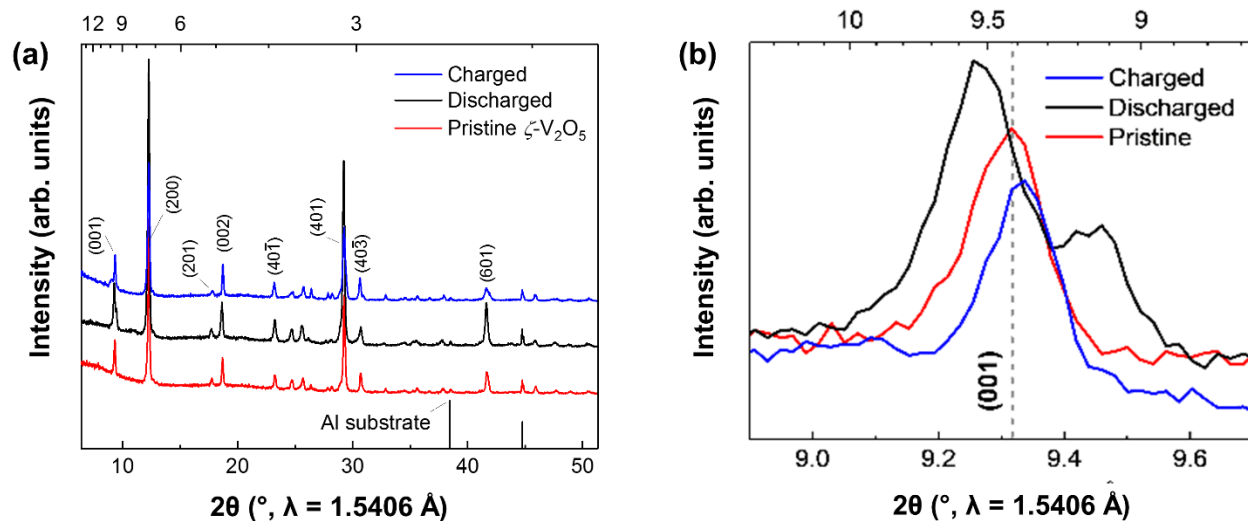
The  $\zeta\text{-V}_2\text{O}_5$  nanowires were also electrochemically cycled in a  $\text{Mg}^{2+}$  electrolyte using coin-type cells in a hybrid configuration at  $50^\circ\text{C}$  (Figure 4.15). The first discharge cycle [Figure 4.15 (a)] shows a capacity of  $140 \text{ mAh g}^{-1}$ , which corresponds to the intercalation of  $0.48 \text{ Mg}^{2+}$  per  $\text{V}_2\text{O}_5$  unit, as opposed to  $0.33 \text{ Mg}^{2+}$  observed for chemically discharged samples. This increased capacity observed for the first cycle is likely due to the decomposition of electrolyte at the cathode surface to form a solid electrolyte interphase (SEI) region and is evidenced by the poor Coulombic efficiency observed for the first cycle (55%). Despite the poor initial Coulombic efficiency, the discharge capacity is stabilized at  $90 \text{ mAh/g}$  (i.e.,  $0.31 \text{ Mg}^{2+}$ ) after 50 cycles. Although the Coulombic efficiency was limited to 55% during the first cycle, likely due to the observed sluggish intercalation kinetics, especially during demagnesiumation (charging), continued cycling reduces the polarization of charging by  $0.59 \text{ V}$  and enhances Coulombic efficiency up to 84.2% for 100<sup>th</sup> cycle, suggesting improved intercalation kinetics with increased cycling, likely due to a combination of interfacial stabilization and improved wetting of the composite electrode by the electrolyte. Such an abrupt increase in coulombic efficiency over the first several cycles is often observed as the solid-electrolyte interphase (SEI) layer is formed and then reconstituted, marking a pronounced decrease in the amount of parasitic, irreversible side reactions, which limit capacity in early cycling.<sup>124</sup> As the number of parastitic reactions decreases and SEI is stabilized, the accessible capacity stabilizes at  $90 \text{ mAh/g}$ . This exceptional cycling stability is depicted strikingly in Figure 4.15 (b) , which depicts cycling performance and a stabilization of the capacity at  $90 \text{ mA h g}^{-1}$  after 85 cycles. A magnified view of powder XRD patterns in Figure 4.16 (b) [full XRD data presented in Fig. 4.16 (a)] further evidences the reversibility of the

structural changes during electrochemical cycling (collected following the initial discharge cycle).

Upon magnesiation (discharge), the (001) reflection shifts to a lower angle  $\zeta$ -V<sub>2</sub>O<sub>5</sub>, reflecting an expansion of the lattice due to Mg<sup>2+</sup> insertion and V reduction. An additional reflection is observed at a higher angle of 9.5° and likely corresponds to stage-ordering phenomena wherein upon electrochemical insertion, specific tunnels are filled. Regardless, the insertion is entirely reversible as the reflection disappears on demagnesiation. Interestingly, upon charging, the (001) reflection returns to an angle higher than that of even pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub>, likely due to the removal of a very small amount of residual silver within the empty tunnels of the pristine material under very high potential (ca. 0.04 Ag per V<sub>2</sub>O<sub>5</sub>).



**Figure 4.15** Electrochemical cycling results of  $\zeta\text{-V}_2\text{O}_5$  cathode (a) Voltage *versus* capacity profiles acquired at different cycle numbers for the electrochemical cycling of  $\zeta\text{-V}_2\text{O}_5$ . After 50 cycles, the material exhibits a stable discharging capacity of 90 mAh/g with an exceptional average operating voltage of 1.65 V *versus* Mg/Mg<sup>2+</sup>. (b) Capacity *versus* cycle number plot (for cycles 1-85) which illustrates the exceptional stability and reversibility of the material during cycling.

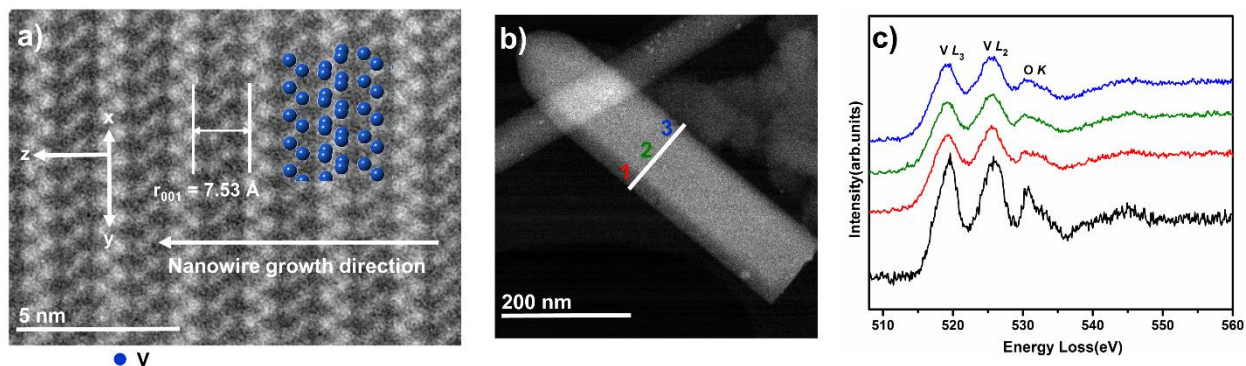


**Figure 4.16** Structural characterization results from  $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode (a) Full expanded view of the XRD pattern for pristine, discharged and subsequently charged  $\zeta$ -V<sub>2</sub>O<sub>5</sub> cathode (b) Magnified view of the evolution of the (001) reflection for pristine, discharged and charged  $\zeta$ -V<sub>2</sub>O<sub>5</sub> samples.

#### 4.13 STEM/EELS/EDX characterization of electrochemically cycled $\zeta$ -V<sub>2</sub>O<sub>5</sub>

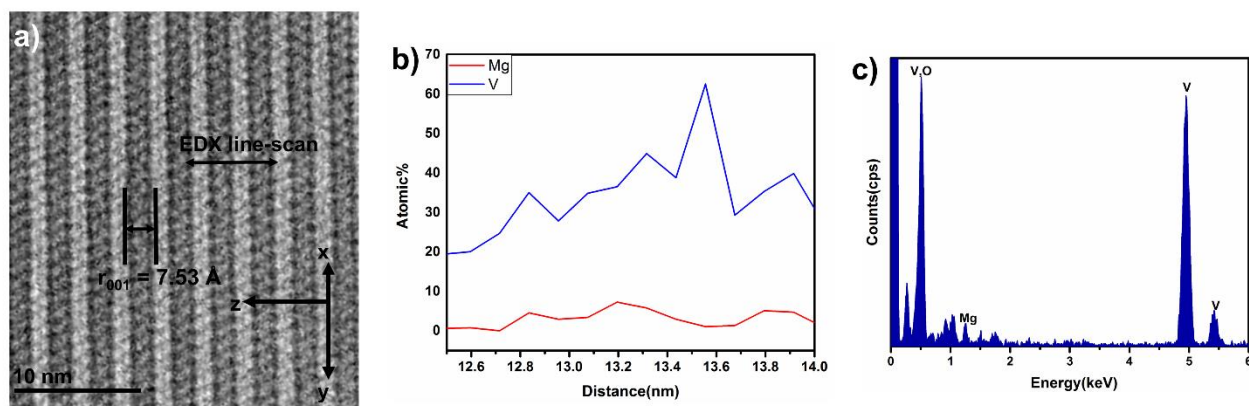
The electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires have also been investigated by transmission electron microscopy techniques, which is depicted in Figure 4.17 and Figure 4.18. (collected following the initial discharge cycle). The atomic-resolution HAADF image [Fig 4.17 (a)] for the electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires clearly identifies the V atomic framework. This image can be compared directly with the structural model of pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> overlaid on the experimental image, which similarly shows only V atoms along the [110] zone axis. This verifies that these  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires retained their tunnel structure upon Mg-ion insertion, consistent with the high structural reversibility seen in the XRD data presented in Figure 4.16(a) and (b). The electrochemically magnesiated samples were also analyzed by electron energy loss spectroscopy (EELS), presented in Figure 4.17 (b) and (c) (data collected after initial discharge cycle). A comparison of EEL spectra between pristine and electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> is provided. The EELS data for the electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> was extracted from three areas probed during a linescan, as indicated in the HAADF image in Figure 4.17 (b). The O K- pre-edge showed a sharp feature in the case of the pristine EEL spectrum, which lost intensity in case of the electrochemically magnesiated sample. Furthermore, the ratio of the two peaks at 531 and 533 eV corresponding to  $t_{2g}$  and  $e_g$ , respectively, inverts upon magnesiation, which is consistent with studies on the electronic structure of V<sub>2</sub>O<sub>5</sub> on lithiation. It has previously been reported<sup>91</sup> that the relative intensity of O K- pre-edge compared to V L<sub>III</sub>- edge increases linearly with the valence of vanadium. Hence, the decreased intensity when moving from the pristine to the electrochemically magnesiated sample indicates a reduction of the compound, consistent with a true Mg<sup>2+</sup> insertion reaction.

Further evidence of Mg-ion intercalation is provided by EDX analysis. The atomic-resolution HAADF image used for EDX line scan is presented in Figure 4.18 (a) which has also been acquired along the [110] zone axis. The EDX line scan presented in Figure 4.18 (b), performed perpendicular to the tunnels, along the z direction, shows clear evidence for Mg, indicating presence of Mg within the tunnel sites. The integrated EDX spectra collected along the same line scan is presented in Figure 4.18 (c). It shows a clear Mg signal (along with V and O, as expected), corresponding to a ca.  $4 \pm 0.4$  at% value for Mg, corresponding to a stoichiometry in the range  $\text{Mg}_{0.26}\text{V}_2\text{O}_5 - \text{Mg}_{0.32}\text{V}_2\text{O}_5$  upon electrochemical Mg-ion insertion. This value is also consistent with the extent of Mg-ion insertion levels deduced from the stabilized discharge capacity of 90 mAh/g after 50 cycles [Figure 4.15(a)].



**Figure 4.17** Electron microscopy characterization data for electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub>.

a) Atomic-resolution HAADF image of the electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires (collected following the initial discharge cycle), corresponding structural model for  $\zeta$ -V<sub>2</sub>O<sub>5</sub> along the [110] zone axis overlaid. b) HAADF image showing nanowire for EELS linescan with the probed area clearly marked. c) Comparison of EEL spectra between pristine and electrochemically magnesiated  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire showing a reduction of the V valence state in the magnesiated sample.



**Figure 4.18** EDX line scan normal to the tunnel growth direction acquired for the electrochemically cycled  $\zeta$ - $\text{V}_2\text{O}_5$  nanowires. a) Atomic-resolution HAADF image in the [110] zone axis, showing the direction of the EDX line scan perpendicular to the tunnels. Scale bar is 10 nm b) the results of the EDX line scan showing V (blue) and Mg (red) signals in units of atomic percent. c) Integrated EDX scan showing relative intensities of the V, O, and Mg. The integrated values yield a ca.  $4 \pm 0.4$  at% value for Mg, corresponding to a stoichiometry in the range  $\text{Mg}_{0.26}\text{V}_2\text{O}_5$ -  $\text{Mg}_{0.32}\text{V}_2\text{O}_5$ .

#### 4.14 Results from electrochemical cycling experiments at higher temperatures and $\zeta$ -V<sub>2</sub>O<sub>5</sub> particles

The  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires were also cycled with Mg<sup>2+</sup> at elevated temperatures, 110°C. The initial experiments [Fig. 4.15] were done at 50 °C. This was done to investigate if the sluggish intercalation kinetics show some improvement upon higher temperature cycling. Another set of experiments were done with nanoparticles synthesized in the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> phase. These  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanoparticles were similarly cycled with Mg<sup>2+</sup> at 110°C and the electrochemical performance of the nanowires vs the particles were compared to see if size effects played any significant role in the intercalation behavior.

Figure 4.19 compares the electrochemical performance for cycling the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires and particles with Mg<sup>2+</sup> at 110°C for the first few cycles. We can compare Fig. 4.19 (a) with the electrochemical performance for  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires with Mg<sup>2+</sup> at 50 °C [Fig. 4.15 (a)]. The initial discharge capacity was ~140 mAh/g as seen in Fig. 4.15 (a), in the case of higher temperature cycling, the initial discharge capacity was ~110 mAh/g. Thereafter, the capacity reduces to ~80-90 mAh/g. So it almost appears as if the electrochemical performance in this case is somewhat worse at higher temperatures. The reactions of multivalent intercalants with the oxide cathode can be quite complicated, thus it is not entirely surprising that the intercalation behavior is not quite what we expected. It indicates that the sluggish intercalation kinetics is perhaps more dependent on the anion coordination topology, which is a characteristic of the cathode material, and thus cannot be improved upon elevated temperature cycling. The electrolyte decomposition at the cathode, leading to solid electrolyte interphase (SEI) formation also likely plays a crucial role, it is possible that the SEI is less stable at higher temperatures in this case which could explain the somewhat worse electrochemistry. Unfortunately, the role of SEI in case of

multivalent intercalation, especially for Mg-ion systems is still not well understood. As is clear from these studies, future efforts in this field need to address this issue more thoroughly. In Chapter 6 of this thesis, I will present some possible pathways for designing *in situ* TEM experiments using monolayer window encapsulated liquid cells, that can elucidate the formation/evolution of the electrolyte/cathode interface (SEI) in these systems.

Fig. 4.20 present the STEM/EDX characterization done for electrochemically cycled  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires at 110 °C after the initial discharge cycle. Fig. 4.20 (a) shows the EDX map from a  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire showing homogeneous Mg distribution (along with V and O as expected). The HAADF image of the nanowire used for mapping as well as the individual elemental maps for V, O and Mg are shown.

From EDX quantification, the Mg: V atomic% ratio is found to be 1:5.7 which indicates a stoichiometry  $\sim$ Mg<sub>0.35</sub>V<sub>2</sub>O<sub>5</sub>. So it is consistent with the  $\sim$ 110 mAh/g discharge capacity as seen in Fig. 4.19 (a). Fig. 4.20 (b) presents the atomic-resolution HAADF-STEM image from the thin area of the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire as highlighted in (a). The structural model for pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> in [100] zone is overlaid on the experimental image, as can be seen they correspond well. Thus, as before, we see preservation of the V atomic framework upon Mg insertion even at higher temperatures. This is somewhat remarkable, since although the capacities are not very high in this case, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph does appear to be a very stable intercalation based host, showing preservation of the pristine atomic framework even under stress as in the deep discharged Li cycling [Fig. 3.12 (b)] or high temperature Mg cycling [Fig. 4.20 (b)].

Fig. 4.21 present the STEM/EDX characterization of the as-synthesized Ag<sub>x</sub>V<sub>2</sub>O<sub>5</sub> nano-particles. The Low-magnification HAADF-STEM image [Fig. 4.21 (a)] shows a typical nano-particle, with the thin area marked used for atomic-resolution imaging. The atomic-resolution HAADF-

STEM image acquired from the thin area is presented in Fig. 4.21 (b); wherein the structural motif corresponds well with the [110] zone of tunnel structured  $\zeta$ -V<sub>2</sub>O<sub>5</sub> as shown in Fig. 3.9 (b), Fig. 4.14 (b) and Fig. 4.17 (a). Some brighter atoms as highlighted by white arrows may represent Ag occupancy in this Z-contrast image. As explained in Chapter 2, Section 2.3, the contrast seen in this HAADF image is  $\sim Z^2$ , since  $Z_{\text{Ag}} = 47$  is more than twice that of  $Z_{\text{V}} = 23$ , the Ag atoms are expected to have a much brighter contrast compared to V atoms.

Fig. 4.21 (c) presents the integrated EDX spectra acquired from the nano-particle shows Ag, V and O signals, with Ag: V ratio 0.17, indicating a stoichiometry of  $\sim \text{Ag}_{0.34}\text{V}_2\text{O}_5$ , quite close to the expected stoichiometry of  $\sim \text{Ag}_{0.33}\text{V}_2\text{O}_5$ .

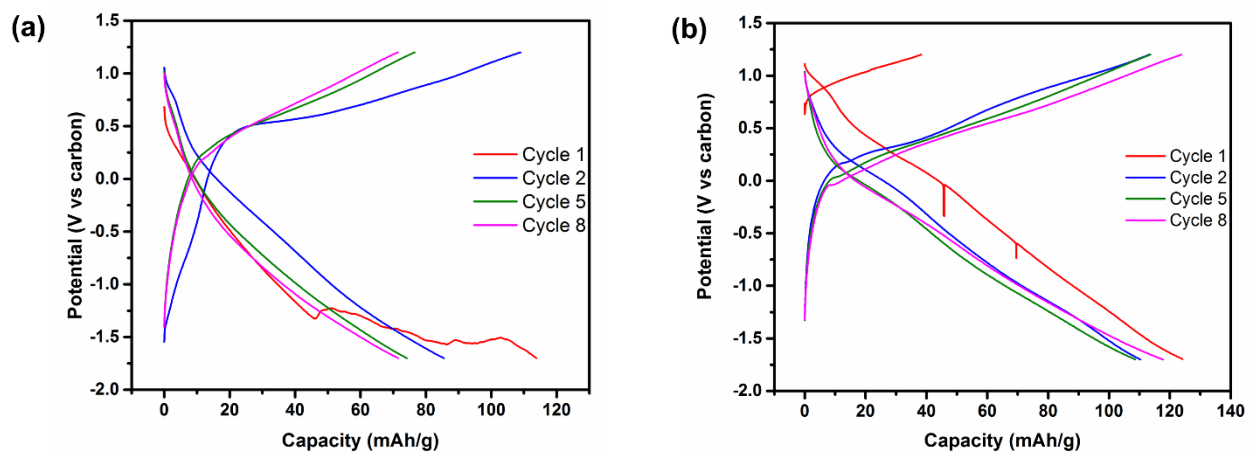
Figure 4.22 presents the STEM/EELS/EDX characterization results from Ag-leached  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nano-particles. The low-magnification HAADF-STEM image [Fig. 4.22 (a)] shows the morphology of a typical nano-particle cluster, the thin one used for higher-resolution imaging and EELS indicated. As can be seen, these nano-particles have a wide size distribution. ( $\sim 60$  nm -300 nm). For comparison, the diameter of the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire [Fig. 4.14 (a)] is  $\sim 140$  nm. The high-resolution HAADF-STEM image from the highlighted nano-particle is shown in Fig. 4.22 (b), while the atomic columns are not clearly resolved it does show the general tunnel structure as expected, showing the tunnel walls.

Fig.4.22 (c) shows the EEL spectra from the highlighted nano-particle showing the V  $L_{3,2}$  and O  $K$  edge. It is quite interesting to note that the O  $K$  fine-structure shows similar features as that of pristine  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowire [Fig. 3.14 (b)] with a clear split between the pre-edge at  $a$  and  $b$ .

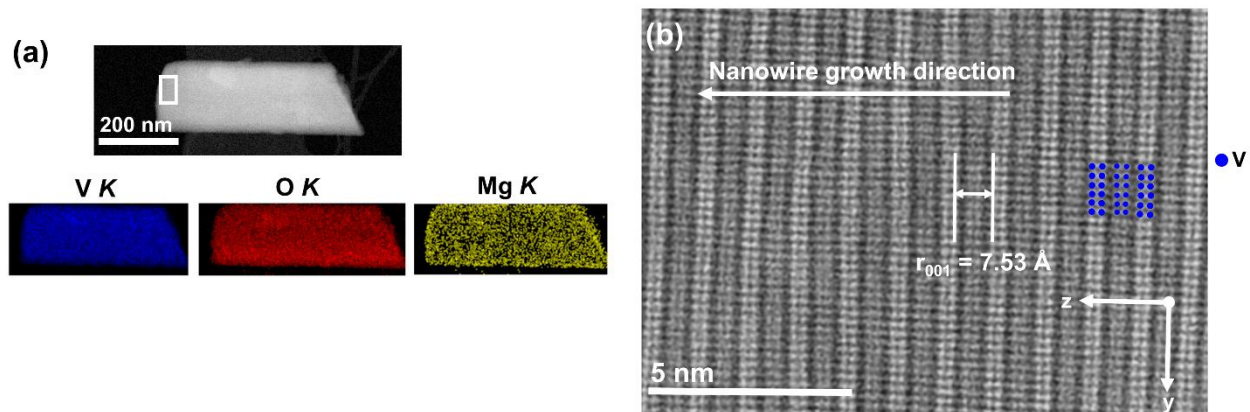
Fig. 4.22 (d) shows the integrated EDX spectra acquired from the nano-particle with V and O signals. But no Ag signal is seen indicating successful removal of Ag ions from the structure. The small Na signal is likely from the Ag-leaching step which uses  $\text{Na}_2\text{S}_2\text{O}_3$ .

These  $\zeta\text{-V}_2\text{O}_5$  nano-particles were also electrochemically cycled with  $\text{Mg}^{2+}$  at  $110^\circ\text{C}$  [Fig. 4.19 (b)]. In this case, the initial discharge capacity is a little higher,  $\sim 120$  mAh/g and it appears that the stable discharge capacity is around  $\sim 110$  mAh/g. Thus it is possible that the shorter diffusion lengths, (diffusion length can be approximated as the particle size) in case of intercalation through nano-particles may have helped in achieving somewhat higher capacities with  $\text{Mg}^{2+}$  in this case. Another advantage that these  $\zeta\text{-V}_2\text{O}_5$  nano-particles provide over the nanowires is the larger surface area, that would result in better contact with the electrolyte and might also contribute to the slightly better electrochemical performance. However, it must also be mentioned that these results are from some of the first experiments done with this system which is quite new. So for a more detailed comparison, further experiments are necessary, possibly also at lower temperatures ( $50^\circ\text{C}$ ) as was done for the  $\zeta\text{-V}_2\text{O}_5$  nanowires.

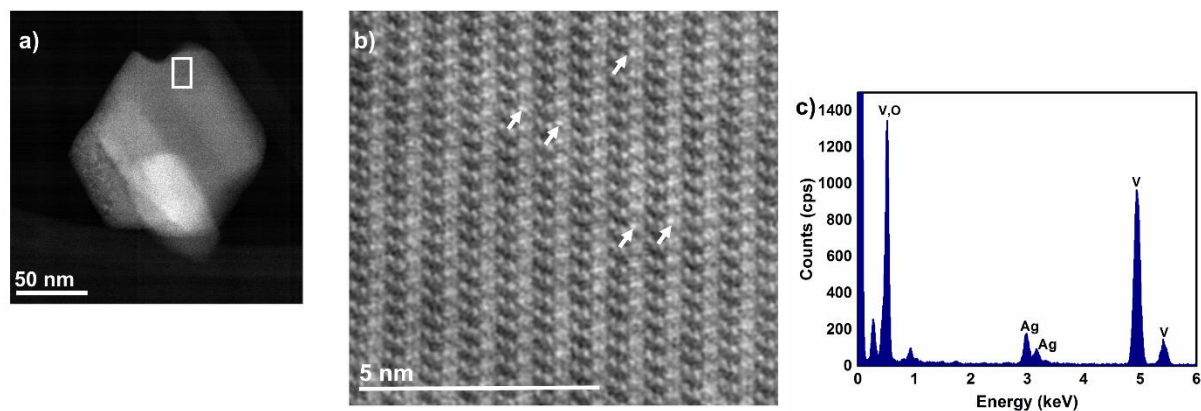
Fig. 4.23 presents the STEM-EDX characterization of electrochemically magnesiated  $\zeta\text{-V}_2\text{O}_5$  nano-particles after initial discharge cycle. The EDX mapping done on Mg cycled  $\zeta\text{-V}_2\text{O}_5$  particles does not show homogeneous Mg distribution; [Fig. 4.23 (a)] indicating limited Mg diffusion into the bulk. This could be due to the thickness of the nano-particle cluster in this case as can be seen from the HAADF-STEM image. Individual elemental maps for V, O and Mg are also shown. The integrated EDX spectra acquired exhibits V: Mg ratio of 1:5.02 which indicates a stoichiometry of  $\sim \text{Mg}_{0.4}\text{V}_2\text{O}_5$ , which is consistent with the initial discharge capacity of  $\sim 120$  mAh/g [Fig. 4.19 (b)].



**Figure 4.19** Comparison of electrochemical cycling with  $\text{Mg}^{2+}$  at  $110^\circ\text{C}$  for  $\zeta\text{-V}_2\text{O}_5$  nanowires vs particles. Capacity vs voltage curve for the (a)  $\zeta\text{-V}_2\text{O}_5$  nanowires and (b)  $\zeta\text{-V}_2\text{O}_5$  nano-particles.

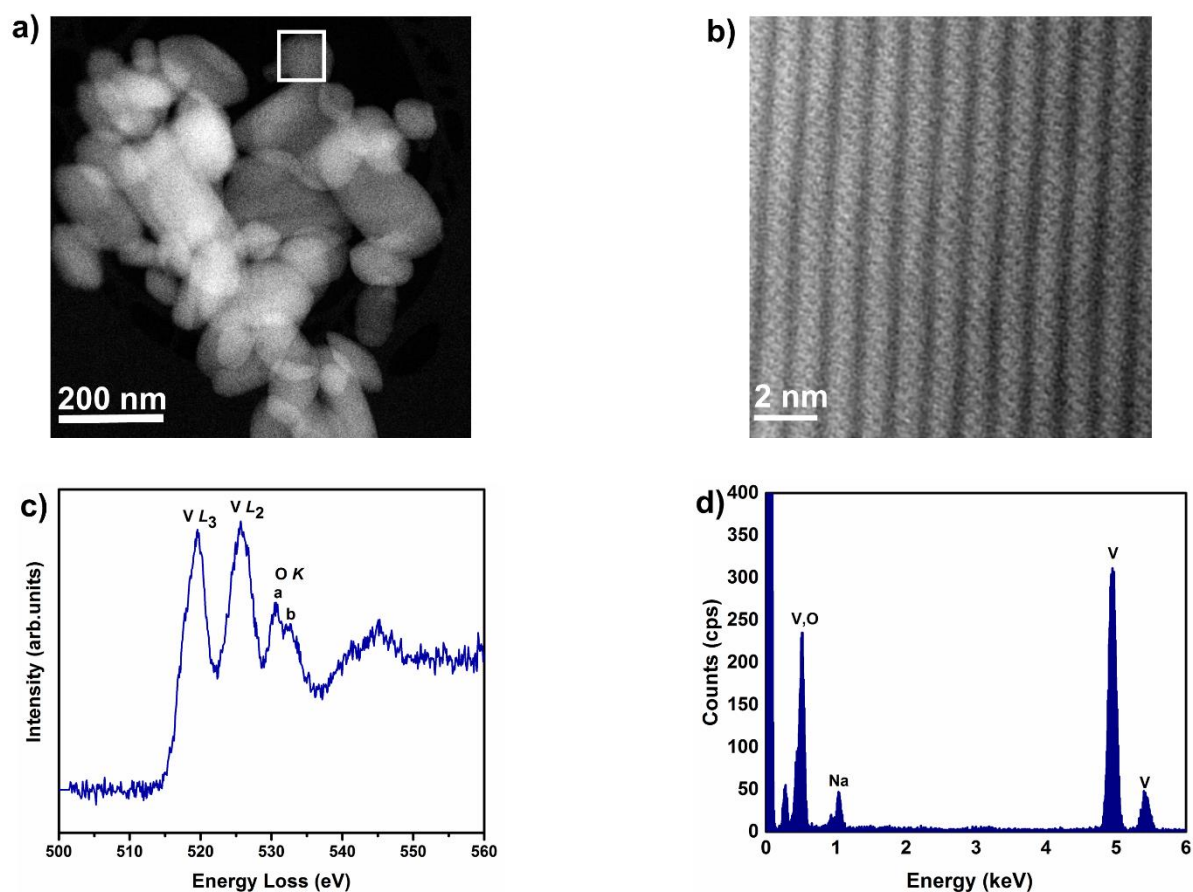


**Figure 4.20** STEM/EDX characterization for electrochemically cycled  $\zeta$ - $\text{V}_2\text{O}_5$  nanowires at  $110^\circ\text{C}$  (a) EDX map from a  $\zeta$ - $\text{V}_2\text{O}_5$  nanowire showing homogeneous Mg distribution (along with V and O as expected), with the HAADF image of the nanowire used for mapping as well as the individual elemental maps. Mg :V ratio is found to be 1:5.7 which indicates a stoichiometry  $\sim\text{Mg}_{0.35}\text{V}_2\text{O}_5$ . (b) Atomic-resolution HAADF STEM image from the thin area of the  $\zeta$ - $\text{V}_2\text{O}_5$  nanowire as highlighted in (a); structural model for pristine  $\zeta$ - $\text{V}_2\text{O}_5$  in [100] zone overlaid and spacing between V atomic columns indicated.

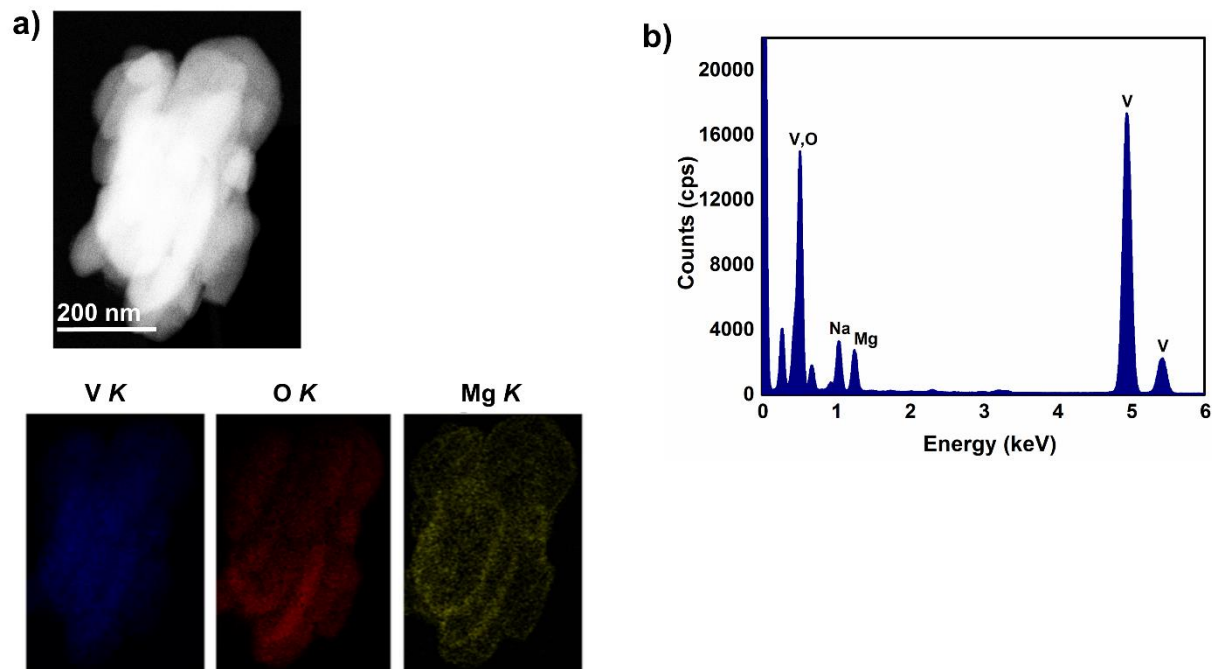


**Figure 4.21** STEM/EDX characterization of as-synthesized  $\text{Ag}_x\text{V}_2\text{O}_5$  nano-particles

(a) Low-magnification HAADF-STEM image showing a typical nano-particle, thin area marked used for atomic-resolution imaging (b) Atomic-resolution HAADF-STEM image acquired from the thin area, some brighter atoms as highlighted by white arrows may represent Ag occupancy in this Z-contrast image. (c) Integrated EDX spectra acquired from the nano-particle shows Ag, V and O signals, with Ag: V ratio 0.17, indicating a stoichiometry of  $\sim\text{Ag}_{0.34}\text{V}_2\text{O}_5$ .



**Figure 4.22** STEM/EELS/EDX characterization results from Ag-leached  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nano-particles (a) Low-magnification HAADF-STEM image showing the morphology of a typical nano-particle cluster, thin one used for higher-resolution imaging and EELS indicated (b) High-resolution HAADF-STEM image from the highlighted nano-particle (c) EEL spectra from the highlighted nano-particle showing the V  $L_{3,2}$  and O  $K$  edge (d) Integrated EDX spectra acquired from the nano-particle shows V and O signals, but no Ag signal indicating successful removal of Ag ions from the structure.



**Figure 4.23** : STEM-EDX characterization of electrochemically cycled  $\zeta$ -V<sub>2</sub>O<sub>5</sub> particles

(a) EDX mapping done on Mg cycled  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nano-particles does not show homogeneous Mg distribution; HAADF-STEM image showing the nano-particle cluster on which mapping was done as well as individual elemental maps shown (b) Integrated EDX spectra acquired with V: Mg ratio 1:5.02 which indicates a stoichiometry of  $\sim$ Mg<sub>0.4</sub>V<sub>2</sub>O<sub>5</sub>.

#### 4.15 Conclusions from Mg intercalation experiments into $\zeta$ -V<sub>2</sub>O<sub>5</sub> polymorph

From the results presented here, it can be seen that both chemical and electrochemical Mg<sup>2+</sup> intercalation into  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires leads to the formation of  $\sim$ Mg<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> phase, which is an improvement over the Mg<sub>0.17</sub>V<sub>2</sub>O<sub>5</sub> phase as observed with the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> polymorph [Section 4.5]. For the higher temperature cycling, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires showed somewhat worse electrochemical profile, possibly due to the unstable SEI at elevated temperature. On the other hand, the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> particles showed some improvement in capacity, leading to the formation of  $\sim$ Mg<sub>0.4</sub>V<sub>2</sub>O<sub>5</sub>, suggesting that the shorter diffusion paths for intercalation through particles as opposed to nanowires might help in the capacity improvement. The diffusion path lengths can be approximated as the nanowire diameter/ particle size, so it would be  $\sim$ 140 nm for the  $\zeta$ -V<sub>2</sub>O<sub>5</sub> nanowires and  $\sim$ 60 nm for the smallest  $\zeta$ -V<sub>2</sub>O<sub>5</sub> particles.

Overall, it is clear that the field of Mg-ion batteries still has a long way to go in terms of achieving the theoretically possible high energy densities that would make it a competitor for conventional Li-ion based batteries. To that end, further exploration of novel oxide based cathodes, understanding of SEI layer for both anode and cathode sides, as well as development of electrolyte systems compatible with both the Mg metal anode and oxide cathode are crucial areas that need attention. The techniques, results and discussions presented in this chapter can provide a direction for ongoing research efforts, especially highlighting the significance of multimodal characterization methods probing the intercalation phenomenon at both bulk and atomic scales to gain a comprehensive understanding.

## CHAPTER 5

### Calcium insertion into Manganese dioxide ( $\alpha$ -MnO<sub>2</sub>) cathode

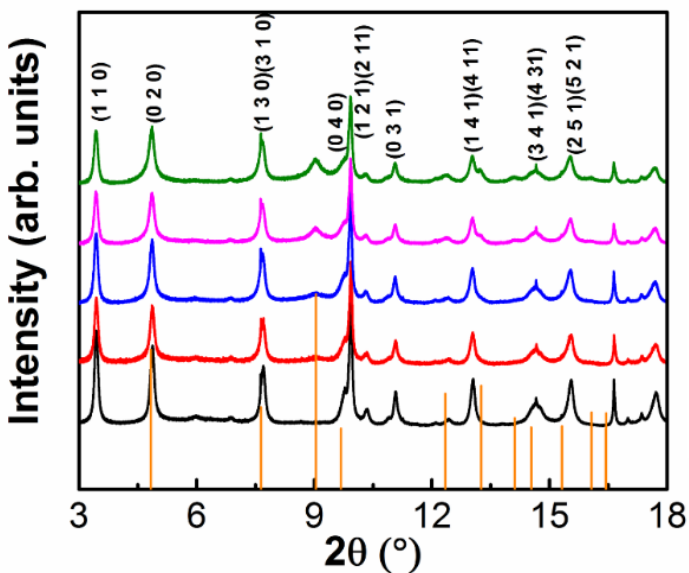
#### 5.1 Introduction

This section is partially reproduced from [P. Senguttuvan, A. Mukherjee, S. Kim, T. T. Fister, A. L. Lipson, A. K. Burell, R. F. Klie, C. S. Johnson, “Unravelling the Reaction Pathway of Calcium ion Insertion into  $\alpha$ -MnO<sub>2</sub> Host , ” (manuscript in preparation)]

$\alpha$ -MnO<sub>2</sub> was chosen as the host material for this study mainly because of its structural similarity with hollandite mineral containing larger alkali and alkaline cations in its interstitial (cubic) sites.<sup>125</sup> Its crystal structure is made of 2x2 tunnels, which are formed by interconnected MnO<sub>6</sub> octahedra, running along c-axis. This open framework was previously investigated as possible intercalation cathode material for lithium ion batteries and reversible capacities closer to 180 mAh/g were obtained.<sup>126,127</sup> Recently,  $\alpha$ -MnO<sub>2</sub> has also been evaluated as possible intercalation cathode for Mg-ion batteries, due to similar ionic radii of Mg<sup>2+</sup> and Li<sup>+</sup>.<sup>128</sup> The XRD patterns collected on discharged cathodes doesn't show any noticeable shifts albeit the peak intensities decrease, however, the corresponding X-ray absorption spectroscopy revealed a concomitant reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup>, thus raising an intriguing question on the redox mechanism. The subsequent TEM study unambiguously proved that indeed magnesiation of  $\alpha$ -MnO<sub>2</sub> proceeds through conversion reaction, forming an amorphous magnesium manganese oxide shell covered on top of unreacted  $\alpha$ -MnO<sub>2</sub> core.<sup>129</sup> Divalent calcium ion (Ca<sup>2+</sup>) is less electropositive than Mg<sup>2+</sup> ion and expected to have lesser electrostatic interactions with the host lattice, therefore it might provide an interesting alternative. So in this work, the cycling of Ca<sup>2+</sup> ion into the  $\alpha$ -MnO<sub>2</sub> cathode host was studied via a chemical method, the mixture of Ca/liq. NH<sub>3</sub> was employed as reducing reagent to chemically intercalate Ca<sup>2+</sup> into  $\alpha$ -MnO<sub>2</sub>.

## 5.2 X-ray diffraction studies of attempted calciation reaction

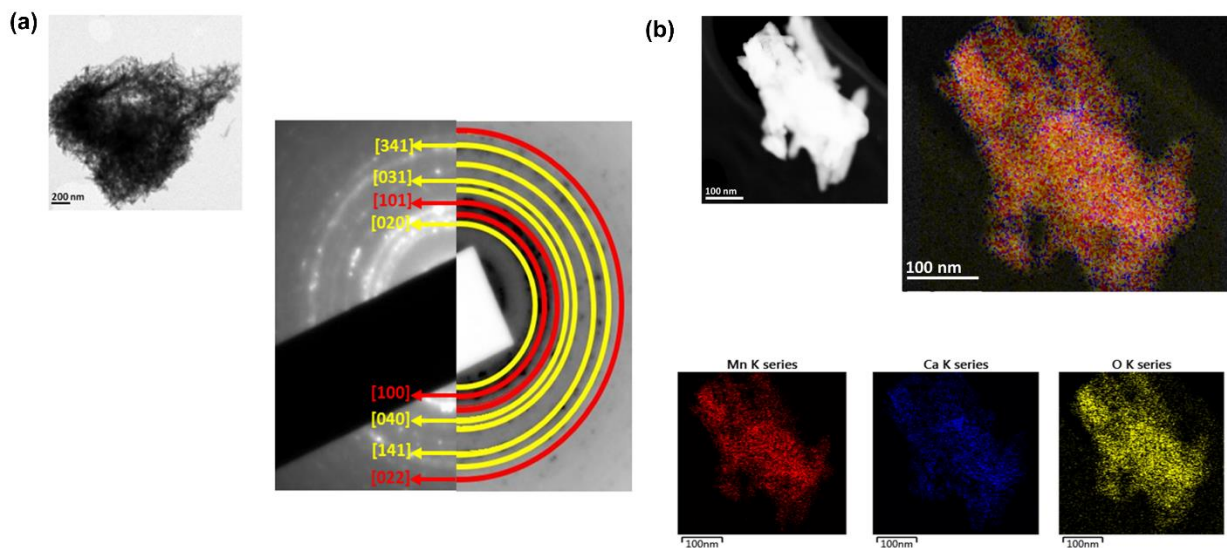
Figure 5.1 presents the XRD patterns of chemically synthesized  $\text{Ca}_x\text{MnO}_2$  ( $x = 0 - 0.4$ ) samples along with pristine  $\alpha\text{-MnO}_2$ . The XRD pattern of the pristine sample could be fully indexed with  $I4/m$  space group and the cell parameters were found to be  $a = 9.7608 \text{ \AA}$  and  $c = 2.8616(7) \text{ \AA}$  in accordance with literature values. As the amount of calcium insertion into  $\alpha\text{-MnO}_2$  was increased, the XRD patterns of the corresponding  $\text{Ca}_x\text{MnO}_2$  samples did not exhibit any peak shifts compared to that of pristine  $\alpha\text{-MnO}_2$  as expected for calcium ion intercalation, however, their intensities were diminished at the expense of a new set of reflections growing at  $2\theta = 9.03, 13.2$  and  $16.08^\circ$ , which could be indexed for the presence of secondary  $\text{Ca(OH)}_2$  phase (represented in orange line). Thus, the XRD data suggested that the calciation reaction does not follow the intercalation pathway, rather it may proceed through the conversion reaction mechanism via formation of a secondary phase as in the case of magnesiation process.



**Figure 5.1** : XRD patterns of  $\text{Ca}_x\text{MnO}_2$  samples with different amount of  $x$ ;  $x=0$  (black);  $x=0.1$  (red);  $x=0.2$  (blue);  $x=0.3$  (pink) and  $x=0.4$  (green). The peak positions of  $\text{Ca(OH)}_2$  shown in orange lines.

### 5.3 Electron diffraction and EDX analysis of attempted calcination reaction

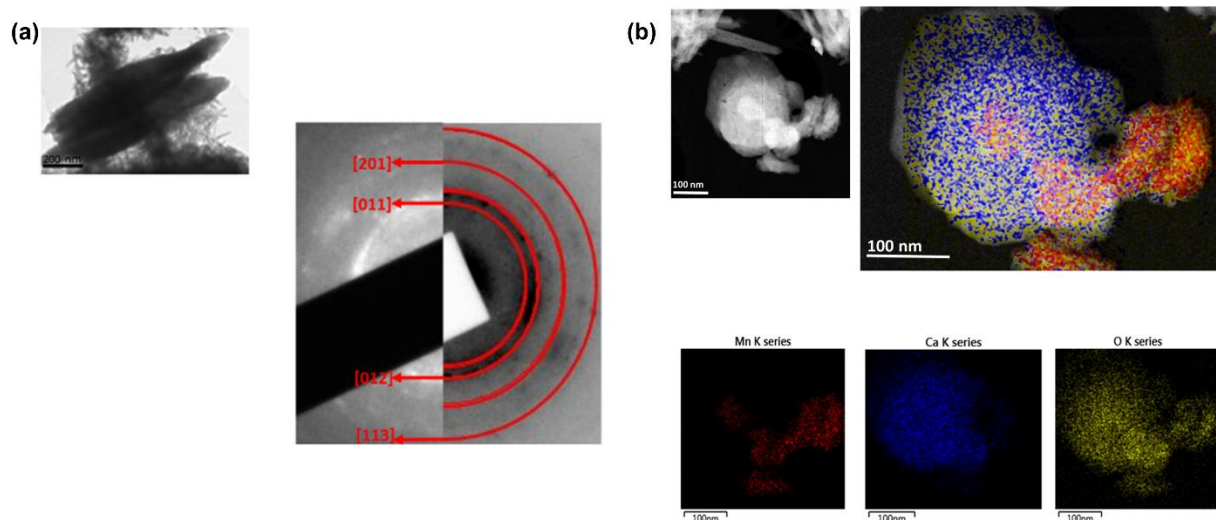
Figure 5.2 (a) and 5.2 (b) present the polycrystalline electron diffraction data and EDX map collected from the primary phase of the  $\text{Ca}_{0.4}\text{MnO}_2$  sample. In each case, the particle clusters from which the EDX mapping/ electron diffraction data were acquired from have also been shown. The polycrystalline diffraction pattern in Fig. 1.5 (a) has been indexed, with the yellow rings corresponding to the primary phase [indexed according to  $d$  spacing values extracted from XRD data presented in Fig 1.4]. The red rings can be indexed according to the  $\text{Ca}(\text{OH})_2$  phase. The H likely comes from the liquid  $\text{NH}_3$  treatment during the chemical calcination step. Thus, some reflections characteristic of the secondary  $[\text{Ca}(\text{OH})_2]$  phase are identified in the diffraction data, however the dominant phase is the primary one derived from the XRD data. Similarly, both Ca and Mn presence can be identified in both the overlaid EDX map as well as the individual elemental maps shown, exhibiting the phase distribution expected from the primary phase. In this primary phase, EDX quantification indicated Ca : Mn ratios  $\sim 1 : 2.2$ , that would yield a stoichiometry of  $\sim \text{Ca}_{0.45}\text{MnO}_2$ , very close to the expected stoichiometry of  $\text{Ca}_{0.4}\text{MnO}_2$ .



**Figure 5.2** a) Electron Diffraction from primary phase clearly indexed identifying the primary phase as dominant reflections (shown in yellow) while some secondary reflections (marked in red) also present ; BF-TEM image of particle cluster used for electron diffraction data acquisition also shown. b) EDX data collected from primary phase; ADF image of particle cluster used for EDX mapping shown along with overlaid EDX and individual elemental maps.

Figure 5.3 (a) and (b) present the electron diffraction data and EDX map collected from the secondary phase of the  $\text{Ca}_{0.4}\text{MnO}_2$  sample, also showing the particle cluster used for data acquisition in both cases. In Fig. 1.6 (a), the rings, marked in red can be systematically indexed according to the  $\text{Ca}(\text{OH})_2$  phase, thus this phase is representative of the secondary phase of the calcination reaction, as also seen from the XRD data shown in Fig. 1.4. Similarly, the EDX data in Fig. 1.6 (b) clearly represents a secondary, Ca-rich and Mn-deficient phase as evidenced by the overlaid EDX map data as well as the individual elemental maps. Essentially the calcination reaction proceeds through phase segregation into the primary and secondary phases, which is the

signature of a conversion based reaction. Once again, in this case, EDX quantification yielded Ca :O atomic% ratio of  $\sim 1 : 2.4$ , pointing to a stoichiometry of  $\text{Ca}_{0.83}(\text{OH})_2$ , close to the expected composition of the secondary phase  $\text{Ca}(\text{OH})_2$ .



**Figure 5.3** a) Electron Diffraction from secondary phase clearly indexed consistent with  $\text{Ca}(\text{OH})_2$ ; BF-TEM image of particle cluster used for electron diffraction data acquisition also shown. b) EDX data collected from secondary phase; ADF image of particle cluster used for EDX mapping shown along with overlaid EDX and individual elemental maps.

#### 5.4 Conclusions from this study

Thus, it can be seen that the attempted chemical Ca intercalation of  $\alpha\text{-MnO}_2$  leads to a clear two-phase reaction. The overlaid EDX map in Fig. 1.5 (b) indicates that the majority of Ca signal comes from the surface of the chemically treated  $\alpha\text{-MnO}_2$  cathode, which would indicate a surface-rich Ca layer and not true intercalation behavior, even in case of the primary phase. One of the possibilities for such two-phase reaction could be thermodynamic instability of the  $\text{Ca}_{0.4}\text{MnO}_2$  phase, that leads to phase transition forming the secondary,  $\text{Ca}(\text{OH})_2$  phase, similar to

observation of MgO formation for Mg cycling into  $\alpha$ -MnO<sub>2</sub>.<sup>129</sup> The thickness of the needle like primary particles and loss of crystallinity upon cycling with Ca<sup>2+</sup> ion made high-resolution characterization impossible in this case, that could have shed more light on the detailed reaction mechanism. Further, detailed experiments and analyses, possibly by *in-situ* or *in-operando* methods are necessary to more accurately pin down the extent of the conversion reaction in this case. Nevertheless, it is important to note the occurrence of conversion reaction in  $\alpha$ -MnO<sub>2</sub>, a cathode known to exhibit intercalation type reaction with Li<sup>+</sup> ions,<sup>127</sup> for cycling with divalent cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup>.<sup>129</sup> This example helps to elucidate the unique advantage provided by the V<sub>2</sub>O<sub>5</sub> polymorphs, which exhibit intercalation type behavior for both monovalent Li and divalent Mg ions.

## CHAPTER 6

### Role of *in situ* experiments in studying battery systems

#### 6.1 Possible design of a multimodal system for *in situ* studies

In this thesis, the results presented thus far have mostly relied on ex-situ/post-mortem characterization of electrochemically/chemically cycled cathode materials. However, for a more comprehensive understanding of the ion intercalation phenomenon, questions regarding nonequilibrium structural modifications, the dynamics and kinetics of the intercalation reaction as well as formation/evolution of the solid-electrolyte interphase (SEI) surface layer on anodes/cathode need to be addressed. These requirements call for an *in situ* /*in-operando* approach for studying battery systems.

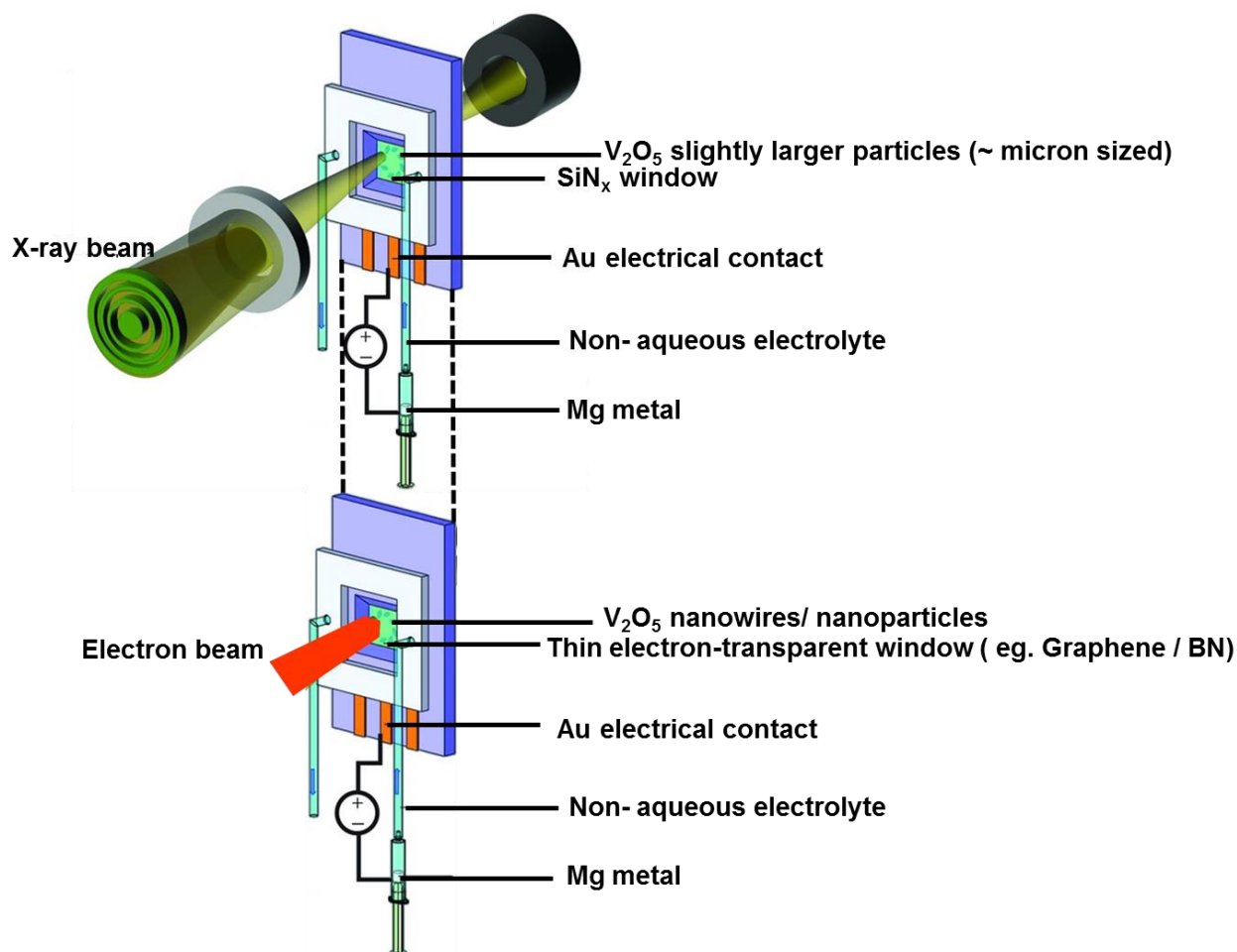
The *in situ* TEM experiments probing lithiation of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> nanowires [Chapter 3, Section 3.2-3.4] employing the open cell battery setup is one of the possible approaches to design an *in-situ* setup for studying battery systems. As discussed in detail elsewhere in this thesis [Chapter 2, Section 2.8, Part III], this open-cell battery setup allows us to directly study the structural and chemical changes occurring in the electrodes as a consequence of interaction with the working ion/electrolytes. However, one of the practical concerns with this open-cell nano-battery setup is that it is directly exposed to the high vacuum ( $\sim 10^{-5}$  Pa) TEM column, and hence can only sustain either a solid state electrolyte (such as Li<sub>2</sub>O, as shown in this thesis), or an ionic liquid electrolyte. The ionic liquid based electrolytes usually have extremely low vapor pressure ( $\sim 10^{-10}$  Pa at room temperature), and thus, are very unlikely to evaporate and contaminate the TEM column. But a lot of real battery electrolytes are organic solvent based, which are completely incompatible with this open-cell battery setup. So it cannot provide insights on crucial phenomenon such as the solid-electrolyte interphase (SEI) formation/evolution which can only occur upon electrode interactions with such real organic solvent based electrolytes. Also, in the

open cell setup, the electrode is only in point contact with the electrolyte, as opposed to being completely immersed in it (as would happen inside a real battery), thus the information we can obtain may not be fully representative of a real system. These concerns are especially significant in case of multivalent systems, which are still being developed and much remains unknown about the structure/properties of the SEI in such cases. Furthermore, unlike lithium oxide ( $\text{Li}_2\text{O}$ ), which is a relatively good ionic conductor for  $\text{Li}^+$  ions, the oxides/hydroxides of the commonly used multivalent metals, (eg. Mg, Zn, Al etc.) have poor ionic conductivity, and hence the idea of using the corresponding metal oxide as a solid state electrolyte will not work for multivalent systems, thus rendering the open-cell battery setup challenging to use.

Recently, Lim *et. al.*<sup>130</sup> introduced a platform for doing *in-operando* scanning transmission X-ray microscopy (STXM) measurements studying the lithiation of olivine  $\text{FePO}_4$  particles. In fact, a similar approach, using a microfluidic electrochemical cell enclosed by Silicon nitride ( $\text{SiN}_x$ ) windows has been implemented for in-situ TEM experiments as well, an overview of such a setup and a brief review of some interesting work done so far has been provided in Section 6.2. Ideally, future efforts in this field would greatly benefit by a combination of both in-operando X-ray and in-situ electron microscopy experiments that can provide complementary information about structural and spectroscopic changes associated with ion intercalation reactions, accessing both the bulk and nano scales. One of the disadvantages of the  $\text{SiN}_x$  windows employed in the liquid cell design for *in-situ* TEM studies is the window layer thickness and the associated liquid layer ( $\sim > 100$  nm) hinder high-resolution imaging and EEL/EDX spectroscopy. Thus, development of liquid cells enclosed by thin, electron-transparent windows such as graphene (as discussed in Chapter 2, Section 2.7) are essential. However, graphene has a strong background in the low-loss region, which make it difficult to do vibrational spectroscopy for studying phonon

signals, and recent work has also shown that graphene is an active participant in beam-specimen interactions, acting as a getter of the reactive species.<sup>131</sup> Thus, in the ideal scenario, one should be able to choose the monolayer window material based on the chemical/electrochemical reaction they wish to study, so that the window material does not obscure desired signals or actively participate in the ongoing reaction. In Section 6.3, I will present results from a liquid cell system enclosed by thin Boron nitride (BN) windows that allows us to do vibrational spectroscopy of water. So, it is possible to generalize the monolayer windows to other thin, 2D materials as well, and one can choose the window material that is best suited for the study at hand.

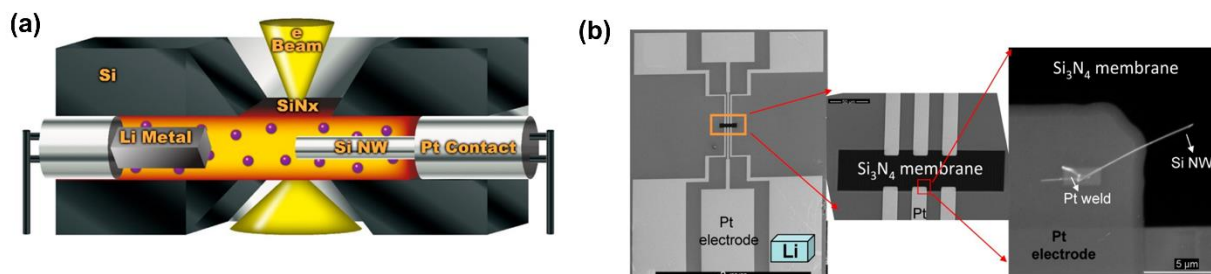
Fig. 6.1 presents a possible design scheme for a multimodal holder that can be adapted for both *in-operando* STXM and *in-situ* TEM/STEM studies, the X-ray studies could be facilitated by a liquid electrochemical cell enclosed by SiN<sub>x</sub> windows, whereas the *in-situ* TEM/STEM experiments could employ the thin window liquid cells (with graphene/BN/ any suitable 2D material) as the window.



**Figure 6.1** Possible design of a multimodal holder for *in-situ/in-operando* X-ray and TEM experiments. Modified with permission from Lim, J.; Li, Y.; Alsem, D. H.; So, H.; Lee, S. C.; Bai, P.; Cogswell, D. A.; Liu, X.; Jin, N.; Yu, Y.-s.; Salmon, N. J.; Shapiro, D. A.; Bazant, M. Z.; Tyliszczak, T.; Chueh, W. C., Origin and hysteresis of lithium compositional spatiodynamics within battery primary particles. *Science* **2016**, 353 (6299), 566-571.

## 6.2 *In situ* liquid stage experiments for studying battery systems

Gu *et. al.*<sup>132</sup> introduced a special liquid cell based approach for operando TEM studies of battery systems. In this work, they studied Silicon (Si) nanowire as a model system, with a lithium (Li) metal counter electrode. Fig. 6.2 (a) illustrates the design of the liquid stage holder, employed for such experiments.



**Figure 6.2** Design of the liquid cell for operando TEM experiments (a) Schematic showing the experimental setup for the liquid cell battery. (b) SEM image of the biasing chip, magnified image of the area marked by orange rectangle and SEM image showing the welded Si nanowire electrode onto the Pt contact. Adapted with permission from Gu, M.; Parent, L. R.; Mehdi, B. L.; Unocic, R. R.; McDowell, M. T.; Sacci, R. L.; Xu, W.; Connell, J. G.; Xu, P.; Abellan, P.; Chen, X.; Zhang, Y.; Perea, D. E.; Evans, J. E.; Lauhon, L. J.; Zhang, J.-G.; Liu, J.; Browning, N. D.; Cui, Y.; Arslan, I.; Wang, C.-M., Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy Observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes. *Nano Letters* **2013**, 13 (12), 6106-6112. Copyright (2013) American Chemical Society.

The tip of the holder can support specially designed biasing chips which is where the electrodes and electrolytes are set up. Fig. 6.2 (b) shows the Scanning electron microscopy (SEM) image of a typical biasing chip. As illustrated in Fig. 6.2 (b), the electrode geometry is implemented using SiN<sub>x</sub> membranes deposited on Si chips, a ~50 nm thin membrane seals the liquid from the TEM column vacuum. This SiN<sub>x</sub> membrane is electron transparent. The biasing chip shown in Fig. 6.2 (b) supports six platinum (Pt) electrodes which extend from the SiN<sub>x</sub> window to the edge of the chip, thereby allowing connection with the outside circuit. As also seen in Fig. 6.2 (b), single or multiple nanowire electrodes (Si nanowire in this case), can be welded to the Pt contact. These welded nanowire electrodes typically extend to the electron transparent part of the SiN<sub>x</sub> window, so as to allow direct imaging of the electrochemical reactions *in situ*. In this case, a small piece of Li metal was also loaded onto a separate Pt electrode to function as the counter electrode.

The chief advantage of using this setup was that it was possible to implement a realistic Li battery using conventional electrolytes. A droplet of the electrolyte was applied to the top surface of the SiN<sub>x</sub> membrane, so all the Pt electrodes, Li metal and Si nanowires were fully immersed in the electrolyte. Then an empty chip with a SiN<sub>x</sub> membrane facing down was used to complete the experimental cell, using a 3 O-ring seal.<sup>132</sup> Thus, this setup did not expose the electrolyte directly to the high column vacuum of the TEM, (~10<sup>-5</sup> Pa) hence addressing the main concern associated with the open cell nanobattery setup.

In recent years, *in situ* STEM experiments using this liquid stage holder have been successfully employed to probe electrolyte degradation. The electrolyte breakdown/degradation limits the electrochemical stability of the battery, determining the useful voltage range for the system. Thus, a fundamental understanding of the electrolyte breakdown mechanisms and products are key to designing more electrochemically stable systems. For these experiments, the electron beam

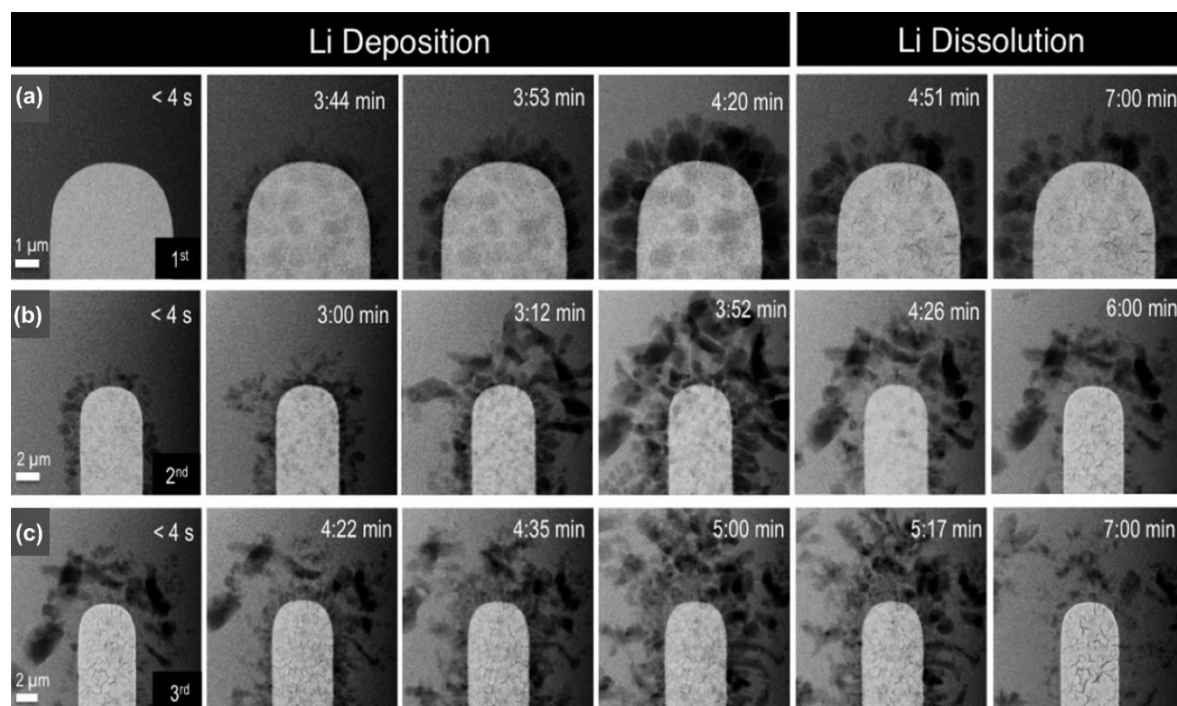
itself was used to trigger the breakdown of commonly used Li battery electrolytes, thus providing important insights into the electrochemical stability of such electrolytes as well as directly characterizing the electrode/electrolyte interfacial reactions.<sup>133</sup>

Another well-known phenomenon originating from the interaction of Li metal anode and electrolyte is the formation of Li dendrites which restrict the use of Li metal anodes in real batteries. That is because these Li dendrites can keep growing on repeated cycling and can ultimately short the electrochemical cell causing fire hazards. The initial stages of dendrite formation and their subsequent evolution was also explored using this method.<sup>134</sup>

Fig. 6.3 presents HAADF images showing Li deposition and dissolution at the interface of Pt working electrodes and the Li-salt containing electrolyte for the first three electrochemical cycles. The contrast seen around the Pt electrodes in this case represents the SEI layer. It can be seen from the first set of images [Fig. 6.3 (a)] that Li is being uniformly distributed along the Pt electrode, which represents charging. However, during the first discharge, Li dissolution, which lead to the formation of  $\text{Li}^+$  ions is found to be not perfect, some residual Li is left at the anode/electrolyte interface. The amounts of residual Li are found to increase in subsequent cycles. Also, some amount of inactive Li is found around the Pt electrodes in the final images for all 3 cycles. This is the Li that is unable to participate in any subsequent charge/discharge cycles. Interestingly, in these images, the Li being the least electron dense material (both the Pt electrode as well as the electrolyte are heavier in terms of atomic number, hence more efficient scatterers) appears dark in the Z contrast image. Thus, these observations helped provide insights into the role of SEI in the case of Li ion batteries as well as the initial stages of Li dendrite formation.

It is thus possible to employ these *in situ* liquid stage experiments to directly probe electrode/electrolyte interactions. Similar experiments could also yield valuable information in

the field of Mg-ion batteries where several complex scientific issues remain unanswered. For example, it might be worthwhile to design experiments to study the initial stages of the formation of passivation layer on the Mg metal anode and also the effect of changing amounts of water in the electrolyte. As discussed in Chapter 4, Section 4.1, previous studies often reported high capacities with Mg ion batteries, using a wet electrolyte, that is incompatible with the Mg metal anode. It might be interesting to study both dry and wet electrolytes for Mg-ion systems, and investigate their electrochemical stability, degradation mechanisms etc. Indeed, similar studies have already been conducted in case of Li-ion battery electrolytes, showing dramatically different morphologies for Li dendrite growth in the dry vs wet electrolyte, which could also be directly correlated to the higher Coulombic efficiency in case of the wet electrolyte system.<sup>135</sup>



**Figure 6.3** HAADF images showing Li deposition and dissolution at the interface between Pt working electrode and electrolyte during (a) first, (b) second and (c) third charge/discharge cycles from the operando TEM experiment. Adapted with permission from Mehdi, B. L.; Qian, J.; Nasybulin, E.; Park, C.; Welch, D. A.; Faller, R.; Mehta, H.; Henderson, W. A.; Xu, W.; Wang, C. M.; Evans, J. E.; Liu, J.; Zhang, J. G.; Mueller, K. T.; Browning, N. D., Observation and Quantification of Nanoscale Processes in Lithium Batteries by Operando Electrochemical (S)TEM. *Nano Letters* **2015**, *15* (3), 2168-2173. Copyright (2015) American Chemical Society.

### 6.3 Using monolayer window encapsulated liquid cells as chemical nano-reactors

While the *in situ* liquid stage holder can reveal the dynamics of SEI formation and evolution, identification of different chemical species requires the use of electron energy loss spectroscopy (EELS). The SiN<sub>x</sub> membrane windows used in the biasing chip of the liquid stage holder [Fig. 6.2 (a)] make it too thick to do EELS/high-resolution imaging on the enclosed liquid systems. The quality of the EELS signal as well as image resolution is degraded due to multiple scattering of the incident electrons by the SiN<sub>x</sub> membrane, yielding a poor signal to noise (s/n) ratio. As introduced in Chapter 2, [Section 2.7], the graphene liquid cell (GLC) provides a unique platform to study chemical/biological systems in their native liquid environment, while also being thin enough to allow high resolution STEM imaging and EELS analysis. In fact, the GLC approach also allows the use of EDX, which is often extremely helpful for understanding the elemental distribution in the sample. It was shown that these GLCs could also provide protection against electron beam induced damage, facilitating characterization of beam-sensitive proteins, using both high-resolution ABF imaging and EDX mapping [Chapter 2, Fig. 2.10].

Wang *et al.* introduced the concept of using the GLC as a chemical nano-reactor. This nano-reactor was designed by encapsulating deionized water (DI water) between monolayer graphene sheets. The interaction with high-energy electron beam causes radiolysis of the encapsulated water generating free radicals and ionic species such as hydroxyl, hydrogen as well as hydrated electrons, thereby altering the local liquid chemistry. Among these species, H<sub>2</sub> is the most dominant with the highest concentration in the solution, additionally its low solubility in water makes it easily detectable in the form of gas bubbles. It was shown that by carefully controlling the electron dose rate, and using the differential scanning technique, it was possible to reduce the reaction volume to  $\sim 10^3 \text{ nm}^3$  ( $\sim 10^{-21} \text{ L}$ ) and precisely modulate the generation of H<sub>2</sub> gas as a

function of position and time. Furthermore, the thin window liquid cells allowed direct identification of the generated H<sub>2</sub> gas through low-loss EELS.<sup>136</sup>

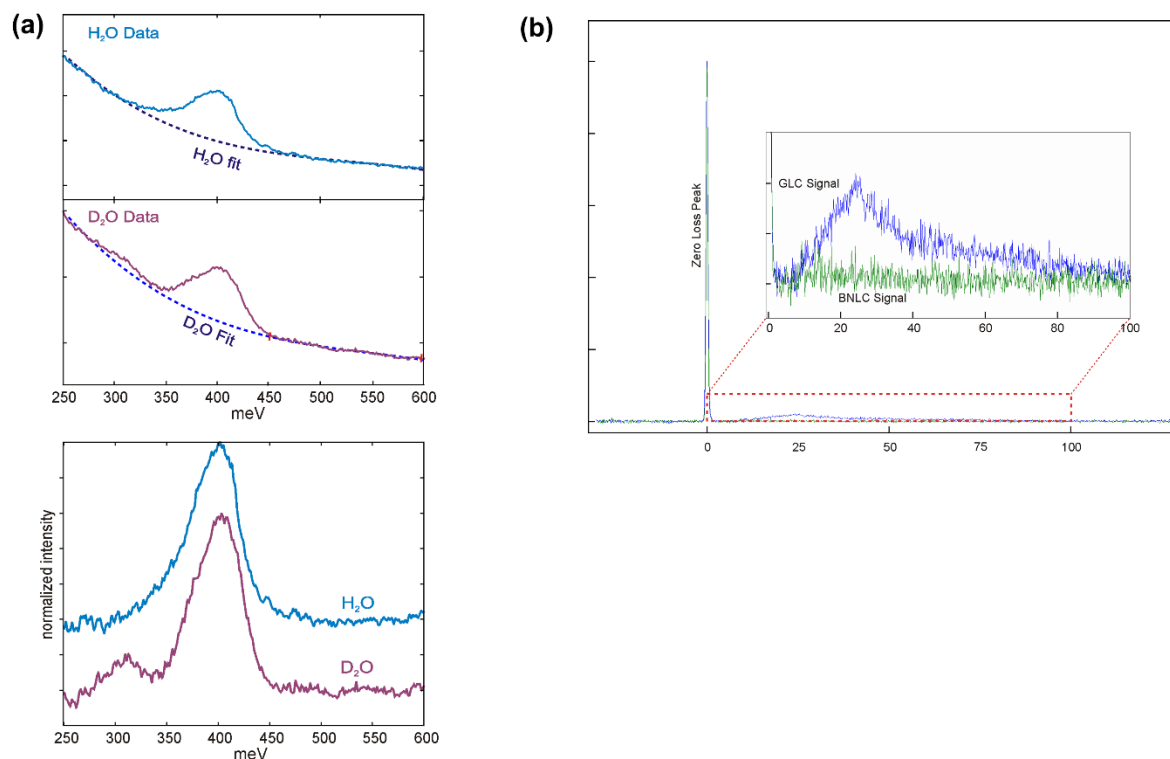
Thus, it would be indeed interesting to extend this approach for studying different electrolyte systems. In this context, it is pertinent to introduce the development of another platform for doing liquid chemistry inside the TEM : the Boron nitride liquid cell (BNLC).

[The following section is partially reproduced from, Isotope-resolved vibrational spectroscopy of water by electron microscopy, Jacob R. Jokisaari, Jordan Hachtel, Xuan Hu, Arijita Mukherjee, Ondrej Krivanek, Juan-Carlos Idrobo, and Robert F. Klie, (manuscript in preparation)]

Recent advances in EELS instrumentation have made it possible to achieve energy resolution limits of < 30 meV using monochromated EELS technique, which allows the use of vibrational spectroscopy, and can directly determine phonon modes of the encapsulated liquid.<sup>137</sup> Using this cutting-edge technology, and the extremely low-background BNLC, our most recent experiments have shown that it is indeed possible to directly measure the vibrational modes of water with nanoscale resolution using aloof, monochromated EELS in STEM mode. For aloof mode EELS, the electron beam was not directly positioned on the water sample to avoid radiolysis damage, rather the distance between the electron beam and the edge of the liquid cell was chosen to maximize the phonon signal, and many spectra were collected from the vicinity of the liquid cells and averaged to get an acceptable signal to noise ratio. Furthermore, if the H is substituted with heavier deuterium, a shift in the phonon frequency occurs and can be clearly distinguished, yielding sensitivity even to differing isotopes of hydrogen in water via this isotope-resolved EELS (IR-EELS) method.

Fig. 6.4 (a) presents the background-subtracted and averaged EEL spectra for water ( $\text{H}_2\text{O}$ ) and heavy-water ( $\text{D}_2\text{O}$ ) (averaged over 100 spectra). The  $\text{D}_2\text{O}$  peak at  $\sim 0.312$  eV is easily distinguished from the  $\text{H}_2\text{O}$  peak at  $\sim 0.4$  eV. These measurements are also in relatively good agreement with previously reported Fourier transform infra-red spectroscopy (FTIR) observations.<sup>138</sup> These peaks represent the  $-\text{OH}$  stretching mode for  $\text{H}_2\text{O}$  and the  $-\text{OD}$  stretching mode for  $\text{D}_2\text{O}$ . It is also clear from Fig. 6.4 (a) that these phonon modes correspond to extremely low energy losses, thereby elucidating the need for the use of monochromated EELS in this case. These phonon signals are very small compared to the zero loss peak, so for successful detection, they require a very sharp ZLP (as in the monochromated system) and also a very low background signal from the window material.

Fig. 6.4 (b) compares the low-loss background signals in EELS for graphene and boron nitride (BN). It can be readily seen that the BN offers a much lower background than the more commonly used graphene. Thus, use of BNLC can provide unique advantages over the GLC, especially for doing vibrational spectroscopy of encapsulated liquid solutions. Furthermore, BN is non-conductive compared to graphene and hence it could possibly be more useful for studying electrically active materials like batteries.



**Figure 6.4** Results from EELS experiments with BNLC (a) EEL spectra showing the –OH and –OD stretching modes for H<sub>2</sub>O and D<sub>2</sub>O and the fit line used for background subtraction; combined EEL spectra from a H<sub>2</sub>O/D<sub>2</sub>O mixture showing the signatures for H<sub>2</sub>O at 0.4 eV and D<sub>2</sub>O at 0.312 eV. (b) Comparison of low-loss EEL spectra from a graphene liquid cell (GLC) and a boron nitride liquid cell (BNLC), showing the extremely low background for the BNLC spectra.

## **6.4 Possible applications of monolayer window encapsulated liquid cells for in situ electrochemistry**

As established in the previous section, it is now possible to extend monolayer window encapsulated liquid cells to materials other than the often used graphene. As shown in Section 6.3, we have successfully employed Boron nitride liquid cells to study the vibrational EEL spectra of H<sub>2</sub>O vs D<sub>2</sub>O. Thus, similar experiments can also be envisioned for the different electrolyte systems. Depending on the expected chemical species of the sample and the energy range of interest, one can appropriately choose the material for making the liquid cells to ensure a low background from the window material. One of the unique advantages of these monolayer window encapsulated liquid cells is that they allow high-resolution imaging, as shown in Fig. 2.10. Perhaps more importantly in case of electrolyte studies, it is possible to do EELS for the encapsulated solution, even at extremely low energy losses, as long as the sample material does not contribute to the background in the region of interest.

As already mentioned it would be of great scientific interest to study the role of the anode/electrolyte SEI in the case of Mg-ion batteries. It is known that the Mg metal anode passivates after a few cycles, impeding further diffusion of the Mg<sup>2+</sup> cation. Thus, it would greatly benefit the community if the exact chemical composition of the SEI could be studied, possibly by employing a combination of liquid stage and GLC/BNLC type experiments. As an example, a possible experimental setup has been presented in Fig. 6.1. By using such a holder, it could be possible to study the SEI both at the Mg metal anode/electrolyte as well as the V<sub>2</sub>O<sub>5</sub> cathode/electrolyte interface by combining both X-ray and electron microscopy. Furthermore, since X-ray can probe slightly larger (~micron sized) particles and TEM will require nanoparticles to be used, such multimodal experiments could also probe size effects in ion

intercalation reactions directly. This novel approach can help answer some of the fundamental scientific challenges that still remain in order to attain the high energy densities theoretically possible for Mg-ion based batteries.

## CHAPTER 7

### Conclusion

#### 7.1 Conclusions and future outlook

In this thesis, I have presented results from state-of-the-art transmission electron microscopy experiments, probing ionic intercalation at the atomic scale. Specifically, I have studied Li and Mg ion intercalation into two different  $V_2O_5$  polymorphs, orthorhombic  $\alpha$ - $V_2O_5$  and tunnel-structured  $\zeta$ - $V_2O_5$  adopting a multimodal approach. I have compared the structural changes occurring at the bulk scale with those at the atomic scale, and correlated these to the electrochemical performance of these materials. I have presented results comparing effects of temperature and size/morphology upon Mg intercalation. I have also discussed the significance of *in situ* experiments for studying battery materials and presented results from several different types of *in situ* methodologies : the open-cell battery setup, the liquid stage holder as well as the novel GLC/BNLC approach.

The field of Mg-ion batteries is relatively new, and currently one of the major thrusts of battery research worldwide. As repeatedly pointed out in this thesis, much work needs to be done to improve the capacities, energy densities, cycling stability etc. for these Mg-ion based systems. But it is equally, if not more important, to address the fundamental science questions that limit the electrochemical performance in these systems. Questions regarding intercalation pathways, the intercalated sites at the atomic-scale, the evolution of the intercalation reaction dynamically etc. remain extremely important, and in this regard, the results presented in this thesis address some of these questions in case of Li and Mg intercalation into the  $V_2O_5$  cathodes. The results also prove the significance and usefulness to combine various experimental techniques with different spatial and energy resolutions, in order to understand the complete story. Indeed, it is

my belief that the battery community would greatly benefit from such comprehensive, multimodal studies, and these could ultimately lead to the next breakthrough.

Looking ahead, it is quite possible that the *in-situ* TEM experiments, by combining the somewhat complementary approaches of the liquid stage holder along with the graphene/BN liquid cells, [as described in Chapter 6, Section 6.1] could help answer some of the fundamental, scientific questions that still limit our understanding of multivalent intercalation. As presented in Chapter 6 of this thesis [Section 6.3], the BN liquid cells along with the cutting-edge monochromated EELS technique can open up the entirely new field of using vibrational spectroscopy for studying encapsulated nano-liquid specimens. Another aspect that could (and hopefully will) dominate battery research would be multimodality: the idea of combining techniques across different length and energy scales to probe the intercalation phenomenon. Indeed, several new liquid stage holders are currently under development where the holder tip can be changed/modified to fit into both a transmission electron microscope and X-ray beamline. This way, the same chemical/electrochemical reactions (within potentially the same specimens) can be analyzed both at the nano and meso/micro scales. This would indeed define the future for *in situ*, multimodal studies. Possible design scheme for such multimodal experiments have been discussed in Chapter 6 [Section 6.1].

Another aspect that I have also presented in this thesis is the comparison and correlation between first principles theoretical predictions with atomic scale imaging. Indeed high-throughput density functional theory (DFT) /molecular dynamics (MD) simulations can broaden the phase space for multivalent cathodes/electrolytes by discovering new, metastable phases that can potentially offer better electrochemical performance. At the same time, they can also help to down-select a few promising candidates from a large pool of known materials by evaluating and comparing

parameters such as migration barriers, thermodynamic stability, predicted voltages and capacities etc. These theoretical efforts should ideally be accompanied by thorough electrochemical experiments to test the few selected materials, followed by extensive multimodal characterization to understand the various aspects of the intercalation reaction and the associated structural evolution. Such a research paradigm, established by the Joint Center for Energy Storage Research (JCESR) collaboration, could define the future landscape of battery research and development efforts.

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## APPENDICES

### APPENDIX A (Copyright permission for Figure 1.1)



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**Author:** John B. Goodenough, Kyu-Sung Park  
**Publication:** Journal of the American Chemical Society  
**Publisher:** American Chemical Society  
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**Title:** Lithium Batteries and Cathode Materials  
**Author:** M. Stanley Whittingham  
**Publication:** Chemical Reviews  
**Publisher:** American Chemical Society  
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**Title:** Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures  
**Author:** Ziqin Rong, Rahul Malik, Pieremanuele Canepa, et al  
**Publication:** Chemistry of Materials  
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G. S. Gautam, P. Canepa, R. Malik, M. Liu, K. Persson and G.  
Ceder, *Chem. Commun.*, 2015, **51**, 13619

**DOI:** 10.1039/C5CC04947D

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**Title:** Topochemically De-Intercalated Phases of V2O5 as Cathode Materials for Multivalent Intercalation Batteries: A First-Principles Evaluation

**Author:** Abhishek Parija, Yufeng Liang, Justin L. Andrews, et al

**Publication:** Chemistry of Materials

**Publisher:** American Chemical Society

**Date:** Aug 1, 2016

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**Title:** Role of Structural H<sub>2</sub>O in Intercalation Electrodes: The Case of Mg in Nanocrystalline Xerogel-V2O<sub>5</sub>

**Author:** Gopalakrishnan Sai Gautam, Pieremanuele Canepa, William Davidson Richards, et al

**Publication:** Nano Letters

**Publisher:** American Chemical Society

**Date:** Apr 1, 2016

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**Title:** Experimental study of annular bright field (ABF) imaging using aberration-corrected scanning transmission electron microscopy (STEM)

**Author:** Eiji Okunishi, Hidetaka Sawada, Yukihito Kondo

**Publication:** Micron

**Publisher:** Elsevier

**Date:** March 2012

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**Title:** Direct Atomic-Scale Imaging of Hydrogen and Oxygen Interstitials in Pure Niobium Using Atom-Probe Tomography and Aberration-Corrected Scanning Transmission Electron Microscopy

**Author:** Yoon-Jun Kim, Runzhe Tao, Robert F. Klie, et al

**Publication:** ACS Nano

**Publisher:** American Chemical Society

**Date:** Jan 1, 2013

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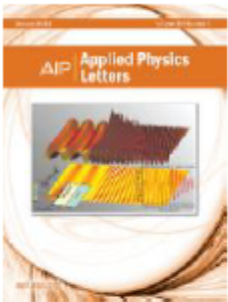
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**Author:** Arjita Mukherjee, Hasti Asayesh Ardakani, Tanghong Yi, et al

**Publication:** Applied Physics Letters

**Volume/Issue** 110/21

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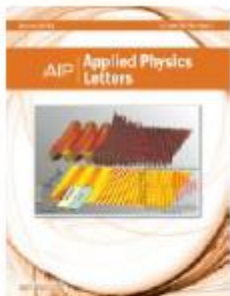
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This paper [J. Andrews, A. Mukherjee, H.D Yoo, A. Parija, P.M Marley, D.G Prendergast, J. Cabana, R.F Klie, S. Banerjee, Reversible Mg ion insertion in a metastable one dimensional polymorph of  $V_2O_5$ , *Chem*, (accepted for publication)] was accepted for publication by the journal *Chem* on December 18, 2017, and is tentatively scheduled to be published in the March 2018 issue of the journal.

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**Author:** Jongwoo Lim, Yiyang Li, Daan Hein Alsem, Hongyun So, Sang Chul Lee, Peng Bai, Daniel A. Cogswell, Xuzhao Liu, Norman Jin, Young-sang Yu, Norman J. Salmon, David A. Shapiro, Martin Z. Bazant, Tolek Tyliczszak, William C. Chueh

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 Apt 2R  
 CHICAGO, IL 60607  
 United States  
 Attn: Mrs. Arjita Mukherjee  
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**Title:** Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy Observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes

**Author:** Meng Gu, Lucas R. Parent, B. Layla Mehdi, et al

**Publication:** Nano Letters

**Publisher:** American Chemical Society

**Date:** Dec 1, 2013

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 **Title:** Observation and Quantification of Nanoscale Processes in Lithium Batteries by Operando Electrochemical (S)TEM  
**Author:** B. L. Mehdi, J. Qian, E. Nasybulin, et al  
**Publication:** Nano Letters  
**Publisher:** American Chemical Society  
**Date:** Mar 1, 2015  
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## **VITA**

### **Arijita Mukherjee**

1420 West Taylor Street, Apt 2R

Chicago, Illinois 60607

[www.linkedin.com/in/arjita-mukherjee/](http://www.linkedin.com/in/arjita-mukherjee/)

[mukherjeearijita@gmail.com](mailto:mukherjeearijita@gmail.com)

## **EDUCATION**

PhD (Physics), University of Illinois at Chicago (2017) (expected) [CGPA: 3.62/4]

Master of Science (M.Sc. Physics), Indian Institute Of Technology Madras (IIT Madras) (2012)

Bachelor of Science (B.Sc. Physics Honors), University Of Calcutta (2010)

## **RESEARCH EXPERIENCE**

### **Graduate Research Assistant, Nanoscale Physics Group, UIC**

Area of research: Materials science/ electrochemistry/ transmission electron microscopy

Summer 2014 – present

Advisor: Professor Robert F. Klie

PhD thesis project involves application of analytical transmission electron microscopy (TEM) techniques to investigate cathodes for battery systems, focusing on both lithium ion batteries, as well as “beyond Li” magnesium ion based batteries. Specifically, the goal is to study and directly prove ion intercalation in vanadium pentoxide polymorphs. The techniques being employed include *in situ* TEM experiments with the open cell battery setup; high-resolution TEM (HRTEM), electron diffraction, aberration-corrected scanning transmission electron microscopy (STEM) imaging, electron energy loss spectroscopy (EELS), energy dispersive X ray spectroscopy (EDX), as well as STEM image simulations. In addition, graphene liquid cells are developed for *in situ* imaging/spectroscopy of nano-bio interfaces, as well as studying chemical reactions dynamically. This project is a part of Joint Center for Energy Storage Research (JCESR) collaboration and involves working closely with electrochemists and first-principle computational physicists at various universities and national labs.

### **Masters Thesis Project, IIT Madras**

Area of research: Experimental High-energy physics/ Data analysis using C++ and ROOT  
August 2011- May 2012

Data from a prototype RPC detector was analyzed using C++ and ROOT to study the response of the RPC to cosmic muon hits. Muon tracks inside the detector were reconstructed using linear fitting and the efficiency of the RPC was calculated.

### **Summer Project, University of Calcutta**

Area of research: Statistical mechanics/C programming  
May 2011-July 2011

Analyzed simple one dimensional classical spin systems using the transfer matrix technique, simulated Pareto's law using kinetic theory assumptions following the econophysics formulation.

### **TEACHING EXPERIENCE**

Taught labs and led discussion sections for undergraduate classical mechanics courses with extremely positive student feedback.

TA coordinator of Physics 106 (undergraduate classical mechanics course) [Fall 2013; Spring 2014]; responsibilities included planning the course syllabus; supervising other TA's; and final grading.

### **AWARDS AND HONOURS**

LAS PhD Student Travel Award (January 2016 and 2017)

Next Generation Electrochemistry (NgenE) workshop (June 2016)

Scholarship for attending Winter School on High Resolution Electron Microscopy and Post School Course on Aberration corrected Electron Microscopy (January 2015)

Best All Rounder Student award from Lady Brabourne College, Kolkata (June 2010)

INSPIRE scholarship by Department of Science and Technology, Government of India (August 2009)

## **PUBLICATIONS**

A. Mukherjee, N. Sa, P. J. Phillips, A. Burrell, J. Vaughey and R. F. Klie, Direct investigation of Mg intercalation into orthorhombic  $V_2O_5$  cathode using atomic resolution transmission electron microscopy, *Chem. Mater.* **2017**, 29, 2218-2226. \*

A. Mukherjee, H. A. Ardakani, T. Yi, J. Cabana, R.S. Yassar, R. F. Klie, Direct characterization of the Li intercalation mechanism into  $\alpha$ - $V_2O_5$  nanowires using *in-situ* Transmission Electron Microscopy, *Appl. Phys. Lett.* **2017**, 110, 213903 \*

A. Mukherjee, H. D. Yoo, G. Nolis, J. Andrews, S. Banerjee, J. Cabana and R. F. Klie, Multimodal investigation of electrochemical lithium intercalation in tunnel structure  $\zeta$ - $V_2O_5$  nanowire cathode [*in preparation*]

A.R Riberio, A. Mukherjee, X. Hu, S. Shafiee, R. Ghodsi, K. He, S. Gemini-Piperni, C. Wang, R.F Klie, T. Shokhufar, R. S Yassar, R. Borojevic, L. A Rocha, Jose M. Granjerio, Bio-camouflage of anatase nanoparticles explored by in situ high-resolution electron microscopy, *Nanoscale*, **2017**, 10.1039/c7nr02239e

J. Andrews, A. Mukherjee, H.D Yoo, A. Parija, P.M Marley, D.G Prendergast, J. Cabana, R.F Klie, S.Banerjee, Reversible Mg ion insertion in a metastable one dimensional polymorph of  $V_2O_5$ , *Chem*, [accepted for publication]

Jacob R. Jokisaari, Jordan Hachtel, Xuan Hu, Arijita Mukherjee, Ondrej Krivanek, Juan-Carlos Idrobo, and Robert F. Klie, Isotope-resolved vibrational spectroscopy of water by electron microscopy (manuscript in preparation)]

\* Featured as research highlight on JCESR website: <https://www.jcesr.org/investigation-of-mg-intercalation-into-%ce%b1-v2o5-using-atomic-resolution-transmission-electron-microscopy>

\* Featured as research highlight on JCESR website: <https://www.jcesr.org/study-of-liintercalation-into-%ce%b1-v2o5nanowires-using-in-situ-transmission-electron-microscopy/>

## **CONFERENCE PRESENTATIONS**

A. Mukherjee, H.D. Yoo, G. Nolis, J. Andrews, S. Banerjee, J. Cabana, R.F. Klie, Systematic Transmission Electron Microscopy Study Investigating Lithium and Magnesium Intercalation in Vanadium oxide polymorphs, Oral Presentation, Microscopy and Microanalysis Conference, August 6-August 10, 2017, St. Louis, MO, USA

A. Mukherjee, G. Nolis, H.D. Yoo, J. Andrews, S. Banerjee, J. Cabana, R. F. Klie, Systematic Electron Microscopy Study Investigating Mg Intercalation of Tunnel Structured  $\zeta$ - $V_2O_5$  Polymorph, Oral Presentation, MRS Meeting, April 17- April 21, 2017, Phoenix, AZ, USA

A. Mukherjee, H.D. Yoo, G. Nolis, J. Andrews, S. Banerjee, J. Cabana, R.F. Klie, Transmission electron microscopy study investigating Li intercalation in tunnel structured  $\zeta$ - $V_2O_5$  nanowire, Oral Presentation, APS March Meeting, March 13- March 17, 2017, New Orleans, LA, USA

A. Mukherjee, N. Sa, P. J Phillips, J. Andrews, S. Banerjee, A.K. Burrell, R.F. Klie, Aberration corrected STEM and High Resolution EELS study Investigating Magnesium Intercalation in Vanadium Pentoxide Cathode, Oral Presentation, Microscopy and Microanalysis Conference, July 24-July 28, 2016, Columbus, OH, USA

A. Mukherjee, J. Andrews, S. Banerjee, R.F. Klie, Investigation of Novel Tunnel Structured  $\zeta$ - $V_2O_5$  nanowire As a Potential Cathode for Li and Mg Ion Intercalation Using in Situ TEM and Aberration Corrected STEM, Poster Presentation, International Meeting on lithium batteries, June 19-June 24, 2016, Chicago, IL, USA

A. Mukherjee, H.A. Ardakani, T. Yi, C. J. Kim, J. Andrews, S. Banerjee, J. Cabana, R.S. Yassar, R.F. Klie, Transmission Electron Microscopy and First Principle Studies Investigating Intercalation Phenomenon Of Vanadium Pentoxide ( $V_2O_5$ ) nanowire cathode, Oral Presentation, APS March Meeting, March 14-March 18, 2016, Baltimore, MD, USA

A. Mukherjee, N. Sa, H.A. Ardakani, T. Yi, P.J. Phillips, J. Cabana, A. Burrell, R.S. Yassar, R.F. Klie, Investigation of Li ion and Multivalent battery systems using In situ TEM and High Resolution EELS, Poster Presentation, Microscopy and Microanalysis Conference, August 2-August 6, 2015, Portland, OR, USA

A. Mukherjee, H.A. Ardakani, T. Yi, J. Cabana, R.S. Yassar, R.F. Klie, In situ Transmission Electron Microscopy Investigations into Intercalation of different cations into  $V_2O_5$  nanowire cathode, Oral Presentation, ECS Meeting, May 24- May 28, 2015, Chicago, IL, USA

### **OUTREACH ACTIVITIES**

Organized and volunteered at UIC Physics table at APS March Meeting Graduate School fair (March 2017 and March 2016)

Conducted lab tours for prospective physics graduate students at various times

Science Fair judge, Poe classical elementary school (December 2012)