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Structural and Electrochemical Characterization of Sodium-Ion Insertion Electrodes

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials Science and Engineering

by

Jesse Sun-Woo Ko

2016
ABSTRACT OF THE DISSERTATION

Structural and Electrochemical Characterization of Na-Ion Insertion Electrodes

by

Jesse Sun-Woo Ko

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2016

Professor Bruce S. Dunn, Chair

With the alarming rate of fossil fuel consumption in the world, electrochemical energy storage technologies that are low in cost and high in performance will need to be developed. Na-ion batteries are now being considered an ideal alternative to lithium-ion batteries given that their intercalation properties are similar, the cost of sodium is low, and there are infinite reserves of sodium. However, since sodium is heavier and less electropositive than lithium, there is a gravimetric energy density penalty. Nonetheless, the work presented in this dissertation offers the prospect of safer, greener, and low cost rechargeable batteries. The first system we studied was sodium titanate (Na$_2$Ti$_3$O$_7$), where we modified the nanomorphologies of this compound, first into nanosheets and nanotubes, then optimized its electrochemical properties in the form of nanoplatelets for use as a negative electrode. It is noteworthy that a combination of nanoplatelets
and nanosheets offered the best combination of high energy and high power densities. The next class of materials we studied were phosphates, as these materials exhibit higher operating voltages due to the inductive effect of the phosphate anion. However, slow kinetics plague phosphate-based compounds so nanostructuring and conductive coatings are required. For the second system, NaTi$_2$(PO$_4$)$_3$, size-reduction and the use of reduced graphene oxide was investigated to solve this problem of slow kinetics. Similarly, for the third system, Na$_2$FePO$_4$F, we utilized a novel (polyol) synthesis to prepare nanoparticles and also used reduced graphene oxide to promote high rate-capability of this material. The last part of the dissertation involves a pseudocapacitive energy storage system. This energy storage mechanism leads to both high energy and high power densities by suitably modifying the physical properties of the material of interest. For this work, we supported pseudocapacitive charge-storage of MoS$_2$ nanoparticles using in-situ X-ray diffraction.
The dissertation of Jesse Sun-Woo Ko is approved.

Sarah H. Tolbert
Yongjie Hu
Bruce S. Dunn, Committee Chair

University of California, Los Angeles
2016
To my Parents, Chang Young Ko and Bok Soon Park, my brother and sister-in-law Richard Ko
and Elizabeth Ko, and my nephews Warren Ko and Isaac Ko
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Being born and raised in southeast Los Angeles, it was a dream of mine since childhood to attend the University of California, Los Angeles (UCLA). Now, towards the end of pursuing a Ph.D at this institution, I cannot express my gratitude enough for all the people who have supported me throughout this journey.

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Members of the Dunn lab reflect the great mentorship of Dr. Dunn, who continues to select students who not only are capable researchers but also have great personalities. I would like to think of the Dunn lab as a tight-knit group of individuals that continuously support each other, especially when the strength of one’s spirit is constantly being tested during graduate school. During the first couple years, Dr. Veronica Augustyn, Dr. Emilie Perre, Dr. Jongwoung (Jason) Kim, and Dr. Enrico Della Gaspera, who were the senior members at the time, taught me the basics of synthesis and electrochemical characterization for Li-ion pseudocapacitance. As I began to mature as a researcher, my knowledge and experience expanded dramatically by working with Dr. Guillaume Muller, Dr. Xavier Petrissans, Dr. Hyung-seok (Jimmy) Kim, Dr. Vicky Doan-Nguyen, and Dr. John B. Cook. They showed great passion for their research, and together, we were able to iron out the difficulties of Na-ion electrochemistry in addition to identifying novel materials that dual-intercalate Li and Na-ions coupled with fast charge-storage
rates. For the sake of brevity, for the members not mentioned, know that I am thankful for not only the research companionship, but also the friendships that were made during our time together. I know that we will all continue to keep in touch, as we always have, and I sincerely thank everyone for all the love and support. I wish you all the best in your future endeavors.

Another crucial element to the progression of my research career has been to work with Dr. Jeffrey Long, Dr. Chris Chervin, and Dr. Debra Rolison at the Naval Research Laboratory (NRL) in Washington, D.C. Throughout the summers, I would spend 10 weeks at NRL to widen my understanding of materials synthesis and characterization. I’m thankful for the researchers here at NRL and I would also like to mention the funding support from the Office of Naval Research. As a part of the Navy Undersea Research Program, I would also like to express my thankfulness for the advisory board, in particular, Dr. Robert Nowak, Rear Admiral Millard Firebaugh, and Mrs. Maria Medeiros. I look forward to returning as a Postdoctoral researcher for the Naval Research Laboratory. The work on VFe$_2$O$_x$ aerogels in Appendix E was a work in collaboration with Dr. Chris Chervin under the mentorship of Dr. Jeffrey Long.

I would also like to thank my committee members Dr. Sarah Tolbert, Dr. Yu Huang, and Dr. Yongjie Hu for their constructive criticisms, advices, and comments about my projects. Dr. Sarah Tolbert has also played a role in being a mentor and that is reflected by the many co-publications we share.

Lastly, I cannot thank enough the support from my family and friends. Although growing up in southeast Los Angeles may not be the most ideal for raising children, my parents have worked extremely hard to provide a quality education. My brother Richard Ko has also been a father figure to me throughout my youth and has always supported my dreams, no matter how ridiculous they may have sounded and changed throughout the years.
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Publications and Presentations


3. H.-S. Kim, X. Petrissans, J. S. Ko, G. A. Muller, J. B. Cook, “Synthesis of Na$_{1.5}$VPO$_4$F$_{0.7}$ Nanoparticles for High Rate, High Voltage Sodium Ion Batteries” In preparation


8. J. B. Cook, H.-S. Kim, Y. Yan, J. Ko, B. Dunn, S. H. Tolbert, “Nanoporous MoS$_2$ as an electrode material exhibiting high levels of pseudocapacitive charge storage with both Li and Na-ions” ECS meeting, Jul 2015, Glasgow, Scotland (Poster Presentation)


Chapter 1. Introduction and Background

Chapter 1.1. The Electric Grid

The word “grid” is commonly used to describe a framework. In terms of energy, the electric grid is a network for transferring generated energy to consumers. The generated energy is converted into electricity which is purchased and used by consumers\(^1\). This network’s key component is the distribution of energy through interconnected power lines since the sources of energy need to be delivered to where energy is in demand. The electric grid is composed of power plants where energy is generated, transmission lines through which electrical energy is transported, and transformers to reduce the voltages of the electrical energy for consumer use\(^3\). Typically, power plants generate energy from non-renewable sources such as coal, gas, fossil fuels, and a small percent from renewables (10%)\(^4\). They are usually located far from industrial, commercial, and residential areas due to concerns in pollution, taking up large amounts of land, and not being aesthetically pleasing. Since electrical energy often needs to be transported over long distances over transmission lines, such as across states or across countries, a distribution center is used to lower the voltage of electrical energy suitable for distribution and this voltage is further lowered as it arrives to the consumer. In the United States, electrical energy is lowered to 120 V and 60 Hz before it can be used by the consumers\(^5\).\(^6\).

One of the largest barriers for the electric grid is to meet specific energy demands of customers efficiently and reliably\(^7\). Energy demands vary according to time of day, date, time of year, temperature, holidays, etc. Power plants supplying the grid cannot always match consumer’s energy needs fast enough, thus causing power surges, sags, and spikes, which can cause electronic devices and generators to shut down, thus causing blackouts to occur (Fig. 1.1). For instance, a drop of 2 Hz from the standard 60 Hz will destroy generators due to the rapid
buildup of heat. Current solutions include using peaker plants; these plants are reserved for times when the demand for energy is greater than the energy that is produced. These peaker plants generate additional pollution and are costly to operate. Since the demand for energy changes drastically depending on many variables in time and day, the price of energy could cost much higher. When there is a surplus in energy being produced, the price of energy may even be negative, meaning that energy is free or that one can even earn money when using energy.

Recently, research on electrochemical energy storage (EES) in the form of batteries, as an added dimension to the electric grid, have commenced. The development of low-cost EES systems for the electric grid is particularly attractive because of the prospect of handling peak demand without the need to build additional generating capacity. Secondary batteries possess a number of desirable features for EES systems including scalability, pollution-free operation, high round-trip efficiency and flexible power and energy characteristics to meet different grid functions. In order for batteries to have success for the electric grid, a two-fold approach needs to be taken: design a system that exhibits high-performance (high energy density, high power density, superior cycle life) and low cost.
Chapter 1.2. Electrical Energy Storage Based on Na-ion Batteries

Among the various battery technologies, Li-ion batteries (LIBs) have emerged as the most attractive one for grid storage since this technology outperforms competing battery technologies by a substantial margin\(^9\). The high energy density, safety and reliability demonstrated by LIBs for mobile applications are also beneficial for stationary energy storage and a number of grid demonstration projects are underway\(^3\). There is, however, a growing concern that the demand for lithium will impact the existing world reserves and its abundance will inevitably become an economic concern. For this reason, there is renewed interest in Na-ion batteries (NIBs) as there are ample reserves of sodium and its intercalation chemistry is similar to that of lithium\(^{10-13}\). Some fundamental differences impede the immediate implementation of NIBs such as the larger ionic radius of Na\(^+\) (1.02 Å) compared to Li\(^+\) (0.76 Å), its mass (23 g mol\(^{-1}\)) is three times heavier than Li\(^+\) (6.9 g mol\(^{-1}\)), and the standard reduction potential (-2.71 V vs. S.H.E.) is slightly more positive compared to Li\(^+\) (-3.04 V vs. S.H.E.)\(^{10}\); these differences inevitably lead to lower energy densities and possibly lower power densities. Nonetheless, there

![Figure 1.1. Power generated and electricity demand with and without energy storage across time of day\(^3\).](image)
have been several reports indicating that Na-ion insertion compounds can exhibit capacities of up to 150 mAh g^{-1} for use as positive electrodes\textsuperscript{10,13,14}. It should be noted that the number of positive electrode materials that have been studied far outweigh the number of negative electrode materials\textsuperscript{14,15}.

![Elemental abundance in the Earth’s crust](image)

**Figure 1.2.** Elemental abundance in the Earth’s crust\textsuperscript{15}.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Li\textsuperscript{+}</th>
<th>Na\textsuperscript{+}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atomic Mass / g mol\textsuperscript{-1}</strong></td>
<td>6.94</td>
<td>23.00</td>
</tr>
<tr>
<td><strong>Shannon’s Ionic Radii / Å</strong></td>
<td>0.76</td>
<td>1.02</td>
</tr>
<tr>
<td><strong>E\textdegree vs. SHE / V</strong></td>
<td>-3.04</td>
<td>-2.71</td>
</tr>
<tr>
<td><strong>Theoretical Capacity of Metal / mAh g\textsuperscript{-1}</strong></td>
<td>3861</td>
<td>1166</td>
</tr>
<tr>
<td><strong>Material Abundance / ppm</strong></td>
<td>20</td>
<td>23600</td>
</tr>
</tbody>
</table>

Table 1.1. Comparison of properties between lithium and sodium

The two basic reversible approaches which have been developed for LIB negative electrodes, namely the use of alloying and intercalation reactions, have been extended to NIBs. Group 14 and 15 elements (metals and metalloids) are known to alloy with Na\textsuperscript{+}, and sodium...
alloys with P, Sb and Sn lead to capacities in excess of 500 mAh/g, much greater than what can be achieved with commercial lithium negative electrodes based on graphite. However, the high volume expansion which occurs on alloying lithium, also plagues sodium-based alloys making these materials difficult to utilize for energy storage as the high volume expansion limits long-term cycling. Upon continuous charge-discharge cycles, alloying materials suffer from mechanical stress caused by volume expansion and repeated passivation of the electrolyte\textsuperscript{15}. Although intercalation compounds are not capable of storing as much capacity compared to that of alloying compounds, their limited volume expansion and overall stability upon repeated cycling make this a promising class of materials for negative electrodes.

**Chapter 1.3. Overview**

In our quest to identify a novel negative electrode, we chose sodium titanate (Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}) as the first system to study. In this research, we wanted to exemplify how nanomorphologies affect electrochemical properties, so we derived three different types of morphologies: nanosheets, nanotubes, and nanoplatelets. These were prepared using highly efficient synthetic routes and subsequently prepared as an electrode material to assess its electrochemical properties.

After identifying a negative electrode, we went on to study a high-rate positive electrode material, sodium iron fluorophosphates (Na\textsubscript{2}FePO\textsubscript{4}F). Nanoparticles of this material were prepared using a polyl medium for solution-phase synthesis. This material was then prepared as a carbon-composite electrode utilizing both high surface area amorphous carbon coupled with reduced graphene oxide. Fundamental electrochemical properties were then utilized to evaluate this material’s electrochemical properties.
Lastly, we investigated the pseudocapacitive properties of metal dichalcogenides, in particular, molybdenum disulphide (MoS$_2$). This material’s crystal structure contains empty Van der Waals gaps for Na-ion intercalation. When prepared as a nanoparticle, this material does not undergo a phase transition, and this leads to extremely fast charge-storage capability. Operando X-ray diffraction was used to further support the fast electrochemical charge-storage behaviour due to phase suppression during Na-ion intercalation.
Chapter 2. Modulation of Titanate Morphologies in Graphene Composites for High-Performance Lithium and Sodium-Ion Insertion

Chapter 2.1. Introduction and Background

Electrochemical energy storage (EES) is now dominating the landscape for widespread applications ranging from portable electronics to electric vehicles and is now currently being applied as stationary storage for storing electricity from renewables\(^1\),\(^2\),\(^3\). From a fundamental materials perspective, in order to develop proficient EES systems, novel materials are required to meet stringent performance requirements in terms of high energy and high power densities; these materials must undergo fast redox chemistries while also being able to store high amounts of charge. One method of modulating physical and chemical properties of materials has been to derive these same materials of specific nanomorphologies\(^17\). It is commonly understood now that electrochemical properties of certain electrode materials can be significantly enhanced when prepared in the form of a specific nanomorphology\(^17\). For example, nanosheets and nanotubes have demonstrated significant improvements in electrochemical properties due to high surface areas and larger pore volume\(^18\),\(^19\).

Nanosheets have attracted tremendous attention since the discovery of graphene (2D) where Geim and Novoselov demonstrated higher electron and hole mobilities when compared to its 3D derivative, graphite\(^20\). Moreover, graphene’s dimensionality leads to a high theoretical surface area (~2600 m\(^2\).g\(^{-1}\)) which is considered to be crucial for enhancing particular applications that require surface reactivity\(^21\). The study on graphene served as a platform for exposing 3D metal oxides into nanosheets and several reports have revealed improved catalytic and electrochemical properties of 2D metal oxides\(^22\). In order to obtain nanosheets of metal oxides, exfoliation is considered to be an efficient method for yielding highly stable colloidal
suspensions of nanosheets\textsuperscript{9,10,11,12}. One requirement for exfoliation is based on the premise that the starting compound is a layered metal oxide phase\textsuperscript{22,23}. For instance, sodium titanate (Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}) has previously been exfoliated into 2D Ti\textsubscript{3}O\textsubscript{7} nanosheets\textsuperscript{26}. With a stable suspension of these nanosheets, a pre-deposited propylammonium-exchanged PA/Ti\textsubscript{3}O\textsubscript{7} film was prepared. Subsequently, this titanate film was then ion-exchanged with a much larger cyanine dye to demonstrate the successful fabrication of a supramolecular composite film\textsuperscript{26}. However, there has been no report yet of electrochemical studies of Li and Na-ion intercalation with PA/Ti\textsubscript{3}O\textsubscript{7} nanosheets.

Another class of nanomaterials that have been highly considered are nanotubes. The advent of nanotube research began with the discovery of carbon nanotubes (both single-walled and multi-walled nanotubes; SWNT and MWNT)\textsuperscript{27,28}. Apart from the enhancement of chemical and physical properties, the high theoretical surface areas (50 – 1315 m\textsuperscript{2}.g\textsuperscript{-1}; MWNTs – SWNTs) have made nanotubes a promising morphology for EES which have also been successfully demonstrated\textsuperscript{16,17,18}. The nanotube morphology has now been extended to metal oxides, in particular hydrogen titanate nanotubes. The synthetic approach to obtaining high-yields of nanotubes are well-established for H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} and is mainly based on the direct rolling of sodium titanate (Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}) sheets into tubes based on an imbalance of Na\textsuperscript{+}/H\textsuperscript{+} charges when shifting towards more acidic environments\textsuperscript{19,20,21,22,23,24}. These H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} nanotubes have shown promising electrochemical properties for pseudocapacitive Li-ion storage, however, there is yet to be any report on its interaction with Na-ions\textsuperscript{25,26,27}.

The investigations of nanosheets and nanotubes have piqued intense interest in exploiting specific nanomorphologies for EES\textsuperscript{4,5,6}. Furthermore, alkali ion-intercalation studies, namely Li\textsuperscript{+} and Na\textsuperscript{+} are increasingly becoming important since intercalation chemistry is the hallmark for
the charge-storage mechanism of Li-ion batteries (LIBs) and now, Na-ion batteries (NIBs)\textsuperscript{41}. We report in this study the difference in Li and Na-ion charge storage properties for the same building block material Ti$_3$O$_7^{2-}$ in the form of nanosheets and nanotubes. Although there have been reports on the catalytic activity of Ti$_3$O$_7$ nanosheets and nanotubes, no one has studied the intercalation chemistry of both Li and Na-ions\textsuperscript{32,33}. We correlate the effect of nanostructuring Ti$_3$O$_7^{2-}$ building blocks to electrochemical properties based on the surface area and porosity of each nanomorphology. Lastly, reduced graphene oxide was utilized as a conductive agent to improve charge storage kinetics of the nanosheets and nanotubes. The titanate-graphene composites in the form of both nanosheets and nanotubes show promise as viable electrode materials for both LIBs and NIBs.

Chapter 2.2. Methods

Chapter 2.2.1. Synthesis

A three step liquid-phase exfoliation process adapted from N. Miyamoto \textit{et al.} was used to separate slabs of Ti$_3$O$_7^{2-}$ sheets from the parent layered compound Na$_2$Ti$_3$O$_7$\textsuperscript{26}. First, bulk Na$_2$Ti$_3$O$_7$ was synthesized by reacting stoichiometric amounts of anatase TiO$_2$ (Sigma-Aldrich, 99.9\%) and Na$_2$CO$_3$ (Sigma-Aldrich, 99.9\%) at 800°C for 40 hours. Proton exchange of the sodium ions in Na$_2$Ti$_3$O$_7$ was then carried out by dissolving roughly 0.5 g of Na$_2$Ti$_3$O$_7$ in 50 mL of 1M hydrochloric acid and stirring for three days. This proton exchanged product H$_x$Na$_{2-x}$Ti$_3$O$_7$ was then reacted with methylamine (Sigma-Aldrich, 40 wt.\% in H$_2$O) for six days at 60°C to expand the spacing between sheets to form a compound that consists of methylammonium ions charge balancing the negatively charged Ti$_3$O$_7^{2-}$ sheets methylammonium/Ti$_3$O$_7$. This compound was then further reacted with propylamine (Alfa-Aesar, 98\%) for an additional 6 days at 60°C to further expand the spacing between sheets to form a propylammonium (PA)/Ti$_3$O$_7$ compound.
This PA/Ti$_3$O$_7$ compound was then ultrasonicated for 5 minutes and then centrifuged at 5000 rpm for 20 minutes to separate out the sedimented non-exfoliated particles with the nanosheets suspended in the supernatant. This supernatant was then collected as a stable colloidal suspension containing PA/Ti$_3$O$_7$ nanosheets (NS) in water (~2 g L$^{-1}$).

Several reports have previously been published on the synthesis of H$_2$Ti$_3$O$_7$ nanotubes and nanobelts with detailed studies on their shape formation mechanism$^{32,33,37,42}$. First, 0.1 g of TiO$_2$ (Degussa P25) was dispersed in 30 mL of 10 M aqueous NaOH (Sigma-Aldrich, 97%) and stirred and ultrasonicated for a couple hours. This suspension was then transferred into a teflon-lined stainless steel autoclave (45 mL capacity) and the temperature was kept at 120ºC for 48 hours and then cooled to room temperature. This hydrothermal reaction resulted in the formation of long Na$_2$Ti$_3$O$_7$ nanosheets. The resultant nanosheets were then subjected to a proton exchange reaction with 0.5 M hydrochloric acid until a pH value of 1 – 2 was reached. During this step, the proton exchange reaction initiated the scrolling of the nanosheets to nanotubes due to a local concentration imbalance of Na$^+$ or H$^+$ ions on opposite sides of the sheet, thus giving rise to excess surface energy, which results in bending$^{42}$. The pH of this solution was then adjusted to a value of 4 – 5 using de-ionized H$_2$O and stirred overnight. Afterwards, the nanotubes were washed a couple times with ethanol and a final suspension containing a stable colloidal suspension of H$_2$Ti$_3$O$_7$ nanotubes (NT) in ethanol (~2 g L$^{-1}$) was obtained.

For all reduced graphene oxide (RGO) composite solutions, graphene oxide (GO) was first prepared using a modified Hummers Method and a stable colloidal suspension of GO in H$_2$O was obtained (~3.9 g L$^{-1}$)$^{43}$. To prepare a composite suspension of NS and RGO (NSG), GO was reduced under hydrothermal conditions. An overall ratio of 90% NS and 10% GO was first prepared as a solution and then sonicated for an hour to obtain a well-dispersed mixture. This
solution was then transferred to a teflon-lined autoclave and kept at a temperature of 120ºC for 1 hour. Composites of NT and RGO (NTG) were prepared using the same procedure as the NT hydrothermal synthesis. An initial solution containing 90 mg of TiO₂ and 10 mg of GO was dispersed in 30 mL of 10 M NaOH. This mixture was then subjected to the same synthesis conditions and procedures as described for obtaining NT.

**Chapter 2.2.2. Characterization**

The size distribution of the nanosheets and nanotubes was determined by transmission electron microscopy (TEM) using an FEI Technai T12 TEM (120 keV). Vacuum-dried powder samples were characterized by X-ray diffraction (XRD) using a Rigaku Miniflex II diffractometer equipped with a Cu-Kα (λ=1.54 Å) radiation source. Raman spectra were obtained using a Renishaw InVia micro-Raman spectrometer equipped with an 1800 lines mm⁻¹ grating and the excitation source used to acquire the spectra was a 514 nm line from an argon ion laser (25 mW). Brunauer-Emmett-Teller (BET) surface areas were measured from the linear portion of the N₂-sorption isotherms at 77K (Micromeritics ASAP 2010 gas adsorption analyzer).

Electrochemical measurements were carried out in 3-electrode flooded cells using a BioLogic VMP-3 Potentiostat in an argon-filled glovebox with moisture and oxygen levels < 1 ppm. The working electrode was prepared by drop-casting a 2 g L⁻¹ solution of nanosheets and nanotubes onto an O₂ plasma cleaned stainless steel current collector. Average mass loadings for thin-film electrodes were on the order of 20 – 30 μg. For lithium cycling, 1M LiClO₄ in propylene carbonate was used as the electrolyte (Sigma-Aldrich, 99.7%, anhydrous) and lithium metal foils were used as both the auxiliary and reference electrodes. Sodium cycling was conducted using 1M NaClO₄ in propylene carbonate (Sigma-Aldrich, 99.7%, anhydrous) with
sodium metal foils serving as the auxiliary and reference electrodes. Cyclic voltammetry and galvanostatic cycling were performed using cutoff voltages of 3 and 1 V vs. Li/Li⁺ and 2.7 and 0.7 V vs. Na/Na⁺. For galvanostatic cycling, C-rates were taken based on a battery capacity of 100 mAh g⁻¹.

Chapter 2.3. Results and Discussion

The synthetic approaches used in this report yield high-quality Ti₃O₇ NS and NT as shown by TEM in Fig. 2.1(a) and 2.1(b), respectively. The dimensions of the NS vary in lengths and widths ranging between 300 μm to 1 μm and 100 nm to 200 nm, respectively. The thickness of the nanosheets are on the order of 0.98 nm. In contrast, the dimensions of the NT are much higher in aspect ratio with overall widths of a tube on the order of 15 – 20 nm with lengths ranging from 100 to 300 nm. The wall thicknesses of the tubes are roughly 4 nm with an inner tube diameter of 10 nm. In addition, TEM images of the graphene composites, NSG and NTG (Fig. 2.1(c) and 2.1(d), respectively), reveal that individual particles of NS and NT are adhered onto the surface layer of graphene. Based on porosimetry measurements, BET surfaces areas of the NS and NT were identified to be 27 and 285 m² g⁻¹, respectively. The average pore volume and pore sizes for the NS and NT were found to be approximately 0.7 and 3.0 cm³ g⁻¹, and 9 nm and 30 nm, respectively. The BJH desorption plots can be found in Fig. A.1.
Phase identification of the nanosheets and nanotubes was carried out using XRD. As shown in Fig. 2.2(a), the NS phase has a corresponding shift of the \((h00)\) peaks to lower \(2\theta\), signifying an expansion of the \(d\)-spacing from 0.8 to 1.1 nm as calculated using Bragg’s Law \((n\lambda=2d\sin\theta)\) in which case \(n\) is an integer (1 f or 1\textsuperscript{st}-order diffraction), \(\lambda\) is the x-ray wavelength (1.54 Å), \(d\) is the spacing between layers of atoms, and \(\theta\) is the Bragg angle. The \(d\)-spacing expansion is caused by the presence of the larger positively charged cation PA\(^+\) compared to the
initial presence of Na\(^+\) found in Na\(_2\)Ti\(_3\)O\(_7\). In addition, only the (h00) peaks are apparent since the NS are preferentially aligned in this direction upon re-stacking. On the other hand, the NT phase corresponds well to H\(_2\)Ti\(_3\)O\(_7\) given that the negatively charged Ti\(_3\)O\(_7^{2-}\) sheets are re-protonated during the acid-wash step. The \(d\)-spacings for H\(_2\)Ti\(_3\)O\(_7\) is measured to be 0.76 nm, however, a slight shift in \(2\theta\) for the NT is observed due to water retention in the powdered samples where the \(d\)-spacings is measured to be 0.9 nm. This has been consistently reported in previous papers\(^{32,38,45}\). With the incorporation of graphene, both NS and NTG show consistency of their respective phases.

Raman spectroscopy was used to correlate the structural similarity of the Ti\(_3\)O\(_7^{2-}\) building block between the nanosheets and nanotubes. During the process of replacing Na\(^+\) with PA\(^+\) cations or smaller protons, either to exfoliate or to scroll, respectively, the main Na-O-Ti modes (304 and 345 cm\(^{-1}\)) were non-existent in both the NS and NT (Fig. 2.2(b))\(^{46}\). Verification of the structural similarity between the nanosheets and nanotubes are displayed in Fig. 2.2(b) where the Raman spectra of both NS and NT show similar band intensities. The bands between 600 and 800 cm\(^{-1}\) are attributed to Ti-O stretching vibrations in edge and corner-shared TiO\(_6\) octahedra and the bands at higher frequencies ranging between 800 and 950 cm\(^{-1}\) are assigned to short Ti-O bonds of low coordination\(^{47}\). The correspondence between the two NS and NT Raman spectra specifies that both morphologies being studied have the same Ti\(_3\)O\(_7^{2-}\) building block.

The graphene-derived nanosheets and nanotubes were identified using Raman spectroscopy (Fig. A.2). The quality of graphene\(^{44}\) can also be determined by analyzing the ratio of the G and D peaks for a given Raman spectrum scanned between 1200 to 1800 cm\(^{-1}\). For GO (before hydrothermal treatment of GO to RGO), the I\(_D\)/I\(_G\) ratio is roughly 1.02. After hydrothermal treatment of NS-GO at 120ºC for 1 hour, the I\(_D\)/I\(_G\) ratio decreases to 0.98 thus
suggesting that the hydrothermal reaction is able to recover the aromatic structure by repairing defects (Fig. 2.2(c))\textsuperscript{44}. Similarly, the $I_D/I_G$ ratio for NTG heated at 120ºC for 2 days was identified to be 0.90 verifying the reduction of GO to RGO.

Figure 2.2. (a) X-ray diffraction patterns of nanosheets, nanotubes, and reduced graphene oxide composites of nanosheets and nanotubes (Green: JCPDS 72-0148 Na$_2$Ti$_3$O$_7$/Orange: JCPDS 47-0681 H$_2$Ti$_3$O$_7$). (b) Raman spectra of nanosheets and nanotubes (Green: Si reference peak, 520 cm$^{-1}$) and reduced graphene oxide composites of (c) nanosheets and nanotubes.

Cyclic voltammetry results for NSG and NTG swept at 1 mV·s$^{-1}$ in both Li and Na-ion configurations are shown in Fig. 2.3(a) and 2.3(c), respectively. The overall performance in terms of capacity and rate capability were higher for the graphene composites; individual cyclic voltammograms (CVs) of NS and NT and their corresponding electrochemical performance can be found in Fig. A.3. By cycling in a Li-ion environment, there is a broader voltammetric response of NTG compared to that of the NSG. At a sweep rate of 1 mV·s$^{-1}$ (33 minute charging time), NTG stores a Li-ion capacity of 160 mAh·g$^{-1}$ whereas NSG stores 110 mAh·g$^{-1}$. At faster rates, NTG is able to store a capacity of 140 mAh·g$^{-1}$ at a sweep rate of 10 mV·s$^{-1}$ (3.3 minute charging time) which is significantly higher compared to NSG which stores only 70 mAh·g$^{-1}$. In
a Na-ion environment, NTG shows an extremely broad CV response which is indicative of a surface capacitive process. On the other hand, NSG portrays a slightly sharper nature of the redox peaks for the NS. The NTG and NSG are able to store are 75 and 20 mAh g\(^{-1}\) at a sweep rate of 1 mV s\(^{-1}\), respectively. Consistently, the performance of NTG in a Na-ion system is significantly better compared to NSG.

Figure 2.3. Cyclic voltammograms of Ti\(_3\)O\(_7\) reduced graphene oxide composites of nanosheets and nanotubes swept at 1 mV s\(^{-1}\) in a (a) Li and (c) Na-ion environment. Capacity vs. charge time
for reduced graphene oxide composites of nanosheets and nanotubes samples cycled in a (b) Li and (d) Na-ion environment.

In order to gain a fundamental understanding of the charge-storage mechanism of NTG and NSG, cyclic voltammetry was performed within a select voltage window for either Li-ion (1.0 – 3.0 V vs. Li/Li+) or Na-ion (0.7 – 2.7 V vs. Na/Na+) studies where each material was cycled from 1 – 200 mV s⁻¹. By sweeping these materials from slow to fast sweep rates, a kinetic analysis (b-value analysis - dependence of current on the sweep rate) can be used to determine whether or not the charge-storage mechanism is limited by solid-state diffusion of ions or fast capacitor-like processes. Plots of log(i) versus log(ν) from 1 to 200 mV s⁻¹ of the cathodic peak for both Li and Na-ion testing are presented in Fig. 2.4(a) and 2.4(d); the cathodic sweep is the process responsible for ion-insertion. By assuming that the current (i) obeys a power-law relationship with the sweep rate (ν)

\[ i = a \nu^b \]  

(1)

where a and b are adjustable values, the rate-limiting mechanism can be identified by obtaining the b-value at a given redox potential. A b-value of 0.5 would indicate charge-storage that is controlled by semi-infinite linear diffusion, whereas a value of 1 would indicate processes that are capacitive. The b-value for NTG in both Li and Na-ion systems was determined to be 0.9 whereas the b-value for NSG is 0.7. Based on this kinetic analysis, charge-storage of ions is not limited by solid-state diffusion for NTG which is indicative of fast capacitive processes. Slight diffusion-limitations are observed for NSG and this directly leads to inherently slower charge-storage properties.
A more detailed analysis of the $b$-value characterization can be applied using a slightly different version of the power-law relationship:

$$i(V) = k_1 v + k_2 v^{1/2}$$  \hspace{1cm} (2)

where $k_1$ and $k_2$ are constants at a specific potential. The constants $k_1$ and $k_2$ are determined from a plot of $i(V)/v^{1/2}$ versus $v^{1/2}$ and thus the capacitive and diffusion contributions to the overall ion-storage capacities can be determined. This analysis can be used to quantitatively measure the extent to which charge-storage results from fast capacitor-like processes. At a sweep rate of 10 mV s$^{-1}$, the overall capacitive contribution amounts to 90% from fast capacitive processes (Fig. 2.4(b)), indicating that diffusion is not the key mechanism for charge-storage. Another characteristic feature of the NTG is the broad CV response which is representative of pseudocapacitive properties where charge-storage is not severely limited by long-range ion diffusion. The surface area-normalized capacitance is 82 μF/cm$^2$; a surface area-normalized capacitance of approximately 100 μF/cm$^2$ indicates pseudocapacitance$^{49,50}$. Based on the premise that charge-storage is pseudocapacitive, nearly 100 mAh g$^{-1}$ is stored at a charging time of 20 seconds. The fast rate capability of this material is mainly attributed to circumventing diffusion-limitations with by preparing a composite of high-surface area nanotubes with reduced graphene oxide$^{23}$.  

When NTG is cycled in a Na-ion system, the overall capacitive contribution is nearly 90% at 1 mV s$^{-1}$, as shown in Fig. 2.4(d), demonstrating that the overall charge storage contribution is also arising from capacitive processes. Similarly, the CV of NTG cycled in a Na-ion system shows a very broad response and there are no distinct redox peaks, as shown in Fig. 2.3(c). The majority of the charge storage contribution is associated with the adsorption of Na-ions onto the surface of the nanotubes. This correspondingly highly capacitive contribution is
due to the high surface area of NTG and a porous network (3.0 cm$^3$ g$^{-1}$) that provides for ion accessibility. For the case of the NTG where Na-ions are much larger than Li-ions, the overall capacities are lower when cycled in a Na-ion due to its larger size.

The CV response of NSG cycled in a Li-ion environment is shown in Fig. 2.3(a). The overall capacitive contribution is 70% as shown in Fig. 2.4(c). NSG shows a much stronger dependence of ion diffusion limitations. The re-stacking of the Ti$_3$O$_7$ nanosheets does not provide a high-surface area for appreciable electrolyte penetration. Thus the access of Li-ions is heavily limited due to low porosity (0.7 cm$^3$ g$^{-1}$). Due to this low porosity, it is expected that graphene would not drastically improve overall Li-ion capacities since coupled with a small surface area, Li-ion accessibility from the electrolyte is heavily limited. As suggested from the $b$-value analysis, NSG is limited by solid-state ion diffusion and the overall charge-storage kinetics lag behind that of NTG.

When cycled in a Na-ion system, the overall contribution to charge storage of NSG is also heavily limited by Na-ion diffusion. The capacitive contribution is 70% as shown in Fig. 2.4(f). In addition, a Na-ion capacity of approximately 20 mAh g$^{-1}$ is stored at a sweep rate of 1 mV s$^{-1}$. The reason for this low capacity can be explained by the arrangement of the TiO$_6$ octahedra that network together to form the Ti$_3$O$_7^{2-}$ slabs. As illustrated in Fig. 2.5, the TiO$_6$ are arranged in edge and corner-sharing positions and at the positions where the octahedra are corner-shared, an empty octahedral site opens up within the Ti$_3$O$_7^{2-}$ slabs. This empty octahedral site is indeed a possible occupation site for Na-ions as described in detail by Rousse, et al.$^{51}$ If all the empty octahedral sites are to be occupied by Na-ions, the maximum capacity contributed from these sites would be 45 mAh g$^{-1}$. To elucidate further on the diffusion limitation of this empty octahedral site, Pan et al. used DFT calculations to study the transport properties of Na-
ions through various pathways through the layers of the Ti$_3$O$_7$ slabs$^{52}$. It turns out that the pathway for Na-ion diffusion through this empty octahedral site has an overly high activation energy of 1750 meV, accompanied by a very low diffusion coefficient of $9.39 \times 10^{-34}$ cm$^2$ s$^{-1}$, which signifies the difficulty of Na-ion diffusion$^{52}$. For this reason, NSG is limited by Na-ion diffusion in addition to having inherently lower capacities.

Figure 2.4. $b$-value analysis of reduced graphene oxide composites of nanotubes and nanosheets in a (a) Li-ion and (d) Na-ion system. $k_1/k_2$-analysis showing capacitive contribution of charge storage of reduced graphene oxide composite of nanotubes in a (b) Li-ion and (e) Na-ion system and reduced graphene oxide composite of nanosheets in a (c) Li-ion and (f) Na-ion system.
Figure 2.5. Crystal structure of Na$_2$Ti$_3$O$_7$. Illustration also shows empty octahedral sites for Na- ion intercalation.

In an attempt to more accurately assess the electrochemical performance of NTG and NSG, galvanostatic cycling (constant current measurements) was performed in both Li and Na- ion systems (individual galvanostatic discharge curves for each nanoscale morphology can be found in Fig. A.4 (Li-ion) and Fig. A.6 (Na-ion)). The electrochemical performance of NTG and NSG cycled in both Li and Na-ion systems is illustrated in Fig. 2.6(a). At a C-rate of 20C, NTG (160 mAh g$^{-1}$) stores nearly double the capacity of NSG (80 mAh g$^{-1}$). Similarly, when cycled in a Na-ion environment, NTG stores a capacity of 70 mAh g$^{-1}$ compared to 10 mAh g$^{-1}$ for NSG. Slow galvanostatic charge-discharge curves for both NTG and NSG cycled at 5C in a Li and Na-ion system are shown Fig. 2.6(b) and 2.6(d), respectively. The decrease in capacity when cycled in a Na-ion environment stems from the larger Na-ion size. However, NTG cycled in a Na-ion system shows faster kinetics compared to NSG cycled in a Li-ion system. At C-rates of 50C and 100C, both NTG and NSG store the same capacity (50 mAh·g$^{-1}$), regardless of ion size. The high performance of NTG cycled in both Li and Na-ion systems stems from its pseudocapacitive nature, as explained above, where most of the capacity being stored is a result of fast capacitative processes. This parallel study indicating pseudocapacitance for NTG is consistently evident.
using both cyclic voltammetry and galvanostatic cycling. Another feature of pseudocapacitance is a sloping voltage profile for Voltage vs. Capacity. Fig. 2.6(c) and 2.6(e) show the sloping voltage profiles of NTG when cycled in either a Li or Na-ion system. In addition, the rate capability is also a key signature of NTG’s pseudocapacitive behavior since at an order of magnitude capacity (10C (charging time 6 minutes) vs. 100C (charging time of 36 seconds)), 70% of the capacity at the slower rate is retained.

Figure 2.6. (a) Capacity vs. cycle number for reduced graphene oxide composites of nanotubes and nanosheets cycled in both Li and Na-ion systems. Charge-discharge profile of reduced graphene oxide composites of nanotubes and nanosheets in a (b) Li-ion and (d) Na-ion system. Charge-discharge profiles cycled at 5C–100C of reduced graphene oxide composite of nanotubes in a (c) Li-ion and (e) Na-ion system.
Chapter 2.4. Conclusion

Ti$_3$O$_7$-derived NS and NT coupled with conductive RGO (NSG, NTG, respectively) were successfully synthesized and electrochemically characterized in both Li and Na-ion configurations. The particle morphology and assembly as an electrode material dramatically affected the electrochemical performance due to surface area and porosity for ion-accessibility; NT exhibited much higher surface areas and porosity compared to re-stacked NS. In constant current measurements, we observed the highest specific capacity (170 mAh g$^{-1}$) from NTG in a Li-ion containing electrolyte. For NTG, the charge-storage mechanism inherently eliminates diffusion-controlled limitations and the electrochemical performance is dramatically improved. In a Na-ion containing electrolyte, a specific capacity of 80 mAh g$^{-1}$ is obtainable. NTG cycled in either a Li or Na-ion system exhibits broad voltammetric CVs coupled with sloping voltage profiles, which is highly indicative of pseudocapacitance.
Chapter 3. Na$_2$Ti$_3$O$_7$ Nanoplatelets and Nanosheets Derived from a Modified Exfoliation Process for Use as a High Capacity Sodium-Ion Negative Electrode

Chapter 3.1. Introduction and Background

The ubiquitous nature of electrochemical energy storage (EES) has led to improvements in areas ranging from grid reliability to vehicle electrification and portable electronics. The development of low-cost EES systems for the electric grid is particularly attractive because of the prospect of handling peak demand without the need to build additional generating capacity$^{3,9}$. Secondary batteries possess a number of desirable features for EES systems including scalability, pollution-free operation, high round-trip efficiency and flexible power and energy characteristics to meet different grid functions. Among the various battery technologies, Li-ion batteries (LIBs) have emerged as the most attractive one for grid storage since this technology outperforms competing battery technologies by a substantial margin$^9$. The high energy density, safety and reliability demonstrated by LIBs for mobile applications are also beneficial for stationary energy storage and a number of grid demonstration projects are underway$^3$.

There is, however, a growing concern that the demand for lithium will impact the existing world reserves and its abundance will become an economic concern. For this reason, there is renewed interest in Na-ion batteries (NIBs) as there are ample reserves of sodium and its intercalation chemistry is similar to that of lithium$^{10-13}$. Some fundamental differences impede the immediate implementation of NIBs such as the larger ionic radius of Na$^+$ (1.02 Å) compared to Li$^+$ (0.76 Å), its mass (23 g mol$^{-1}$) is three times heavier than Li$^+$ (6.9 g mol$^{-1}$), and the standard reduction potential (-2.71 V vs. S.H.E.) is slightly more positive compared to Li$^+$ (-3.04 V vs. S.H.E.$^{10}$; these differences inevitably lead to lower energy densities and possibly lower power densities. Nonetheless, there have been several reports indicating that Na-ion insertion
compounds can exhibit capacities of up to 150 mAh g\(^{-1}\) for use as positive electrodes\(^{10,13,14}\). It should be noted that the number of positive electrode materials that have been studied far outweighs the number of studies of negative electrode materials\(^{14,15}\).

The two basic reversible approaches that have been developed for LIB negative electrodes, namely the use of alloying and intercalation reactions, have been extended to NIBs. Group 14 and 15 elements (metals and metalloids) are known to alloy with Na\(^{+}\), and sodium alloys with P, Sb, and Sn lead to capacities in excess of 500 mAh g\(^{-1}\), much greater than what can be achieved with commercial lithium negative electrodes based on graphite\(^{54}\). However, the high volume expansion that occurs on alloying lithium also plagues sodium-based alloys, making these materials difficult to utilize for energy storage as the high volume expansion limits long-term cycling. Upon continuous charge-discharge cycles, alloy materials suffer from mechanical stress caused by volume expansion and repeated passivation of the electrolyte\(^{15}\). Although intercalation compounds are not capable of storing as much capacity compared to that of alloying compounds, their limited volume expansion and overall stability upon repeated cycling make this a promising class of materials for negative electrodes.

Intercalation compounds based on metal oxides, in particular sodium titanates, are currently being studied as negative electrode materials for NIBs. These sodium titanates include a variety of metastable and stable compounds (i.e. Na\(_2\)Ti\(_3\)O\(_7\), Na\(_2\)Ti\(_6\)O\(_{13}\), NaTi\(_3\)O\(_6\)(OH)\(_2\)H\(_2\)O, and lepidocrocite structures) that have low operating voltages\(^{47,55–58}\) vs. Na/Na\(^+\). With Na\(_2\)Ti\(_3\)O\(_7\), the subject of this paper, Senguttuvan et al. first demonstrated that layered Na\(_2\)Ti\(_3\)O\(_7\) can reach capacities of 200 mAh g\(^{-1}\) at relatively low potentials (0.3 \textit{vs.} Na/Na\(^+\)), albeit at a slow charging rate (C/25)\(^{57}\). After this initial report, Rudola \textit{et al.} and Pan \textit{et al.} investigated several process-related parameters such as smaller particle size and ball-milling. This approach led to high
capacities of approximately 190 mAh g\(^{-1}\) at slightly faster rates\(^{52,58}\). However, one of the biggest limitations for this material is its long-term cycling performance where a capacity of 190 mAh g\(^{-1}\) decreases about 60% after 100 cycles\(^{58}\). Moreover, there has yet to be any report where Na\(_2\)Ti\(_3\)O\(_7\) exhibits rapid charge storage and retains high capacity.

The problem of capacity fade and slow kinetics can be traced to the bulk material properties of Na\(_2\)Ti\(_3\)O\(_7\). First, micron-sized particles inherently face longer diffusion times throughout the structure due to longer diffusion path lengths. In addition, bulk Na\(_2\)Ti\(_3\)O\(_7\) is predicted to undergo a moderate amount of volume expansion of 6% from Density Functional Theory (DFT) calculations\(^{51}\). The repeated expansion and contraction of the structure may be an important factor that contributes to poor long-term cycling. For these reasons, we became interested in the question of whether these limitations can be overcome by changing the dimensionality of Na\(_2\)Ti\(_3\)O\(_7\) from 3D to 2D, with the latter being in the form of nanoplatelets and nanosheets.

The extraordinary properties of graphene have led to renewed interest in a wide range of two-dimensional (2D) materials\(^{20}\). When prepared as nanosheets, various transition metal oxides and chalcogenides can exhibit interesting modulation of their chemical and physical properties\(^{22-25}\). Several synthesis strategies have been carried out to obtain 2D nanosheets such as liquid-phase exfoliation, mechanical exfoliation, thermal decomposition, direct chemical synthesis, and chemical vapor deposition\(^{24,25,59-61}\). Among the various techniques, liquid-phase exfoliation offers a scalable process which has the potential to provide large quantities of dispersed nanosheets that can be processed using existing industrial techniques such as reel-to-reel manufacturing\(^{24}\).
In the research reported here, we developed a liquid-phase exfoliation method that enabled us to obtain both 2D nanoplatelets and nanosheets. The motivation for evaluating nanoplatelets was based on the premise that few layers of sheets can provide for facile Na-ion intercalation compared to bulk materials. Furthermore, it is not clear whether a single layer nanosheet can store high levels of charge since there are a limited number of intercalation sites for Na-ions. By establishing a good understanding of the exfoliation process, we were able to control synthesis conditions and obtain both nanosheets and nanoplatelets. To achieve charge storage levels greater than 100 mAh g\(^{-1}\), we show that a combination of both 2D nanoplatelets and nanosheets provides an optimized condition that offers rapid kinetics, high capacities for Na-ion charge storage, and a wider electrochemical voltage window.

Chapter 3.2. Methods

Chapter 3.2.1. Synthesis of Na\(_2\)Ti\(_3\)O\(_7\) Nanoplatelets and PA/Ti\(_3\)O\(_7\) Nanosheets

Bulk Na\(_2\)Ti\(_3\)O\(_7\) (2 mmol) was prepared by mixing stoichiometric amounts of anatase titanium(IV) oxide (Sigma-Aldrich, 99.9\%) and sodium carbonate (Sigma-Aldrich, 99.9\%) and subsequently heating in air at 800 °C for 40 h with intermediate re-grinding. The first step in the exfoliation process involved proton exchange for Na-ions present in the layered compound Na\(_2\)Ti\(_3\)O\(_7\). This process was carried out by completely dissolving ~0.3 g of Na\(_2\)Ti\(_3\)O\(_7\) powder in 25 mL of 1M hydrochloric acid and stirring at 1000 rpm for 24 h. The partially protonated form [H\(_x\)Na\(_{2-x}\)]Ti\(_3\)O\(_7\) was then centrifuged at 5000 rpm. The remaining hydrochloric acid was then decanted and the resultant [H\(_x\)Na\(_{2-x}\)]Ti\(_3\)O\(_7\) powder was re-suspended in 11 mL of methylamine (80 mol methylamine per mol of [Ti\(_3\)O\(_7\)]\(^2-\)) solution (Sigma-Aldrich, 40 wt.% in H\(_2\)O) and stirred at 1000 rpm for 6 days at 60 °C. Next, the methylamine-reacted mixture [MA\(_y\)H\(_x\)-y]Na\(_{2-x}\)]Ti\(_3\)O\(_7\) was centrifuged at 5000 rpm and re-suspended with 8 mL of propylamine (80 mol propylamine...
per mol of $[\text{Ti}_3\text{O}_7]^{2-}$) solution (Sigma-Aldrich, ≥99.9%) after decanting the reacted methylamine solution. This propylamine mixture $[\text{PA}_y\text{H}_{x-y}\text{Na}_{2-x}]\text{Ti}_3\text{O}_7$ was then stirred at 1000 rpm for 6 days at 60 °C. It was important to tightly seal the container with Teflon tape due to the high volatility of this solvent. This 8 mL solution containing $[\text{PA}_y\text{H}_{x-y}\text{Na}_{2-x}]\text{Ti}_3\text{O}_7$ was then washed with de-ionized water and centrifuged at 5000 rpm. The supernatant was decanted and the sediments particles were re-suspended with de-ionized water and subjected to ultrasonication for 5 minutes to exfoliate $[\text{PA}_y\text{H}_{x-y}\text{Na}_{2-x}]\text{Ti}_3\text{O}_7$. After sonication, by adjusting centrifuge conditions, we were able to obtain solutions comprised solely of nanoplatelets (Na$_2$Ti$_3$O$_7$ NP) and nanosheets (PA/Ti$_3$O$_7$ NS) or mixtures of both (Na$_2$Ti$_3$O$_7$ NP-NS).

**Chapter 3.2.2. Characterization**

Transmission electron microscopy (TEM) images were taken with an FEI Technai T12 TEM (120 keV) using a carbon-coated copper grid as a substrate. Vacuum-dried powder samples were characterized by X-ray diffraction (XRD) by using a Rigaku Miniflex II diffractometer. X-ray pair distribution function analysis was performed at the Advanced Photon Source 11-ID-B at Argonne National Laboratory. Total scattering experiments were performed using a $\lambda = 0.2112$ Å ($\approx 58$ keV ) x-ray source with a Perkin-Elmer amorphous Si-based 2D detector, which allows for rapid acquisition$^{62}$ To calibrate the experimental geometry of the measurements, a N.I.S.T.-traceable CeO$_2$ (Standard Reference Material® 674b) standard powder was used. The sample-to-detector distance for synchrotron XRD was calibrated to 952.276 mm. Azimuthal angle analysis was performed with NIKA$^{63}$. The sample-to-detector distance for PDF experiments were calibrated to 181.574 mm. The 2D data were integrated using Fit2D$^{64}$. Pair distribution functions (PDFs), $G(r)$, were calculated from the sine Fourier transform of the product $q(S(q)-1)$ in which $S(q)$ is the structure factor. PDFs were generated with a $q_{\text{max}} = 24$ Å$^{-1}$ using PDFgetX2$^{65}$. X-ray
Photoelectron Spectroscopy (XPS) measurements were collected using an AXIS Ultra DLD instrument (Kratos Analytical Inc., Chestnut Ridge, NY). All measurements were conducted under ultrahigh vacuum ($10^{-9}$ torr) using a monochromatic Al Kα X-ray source (20 mA, 14 kV) with a 200 μm circular spot size. XPS spectra for all samples were acquired at 300 W (20 mA, 15 kV), with a pass energy of 160 eV for collecting atomic compositions (survey scans can be found in Fig. B.10) and a pass energy of 20 eV for collecting high-resolution spectra. Each scan had a dwell time of 200 ms where each element was swept 20 times. Samples for XPS were prepared by drop-casting a 2 g L$^{-1}$ solution of Na$_2$Ti$_3$O$_7$ NP onto an O$_2$ plasma cleaned 1cm × 1cm stainless steel current collector. Atomic force microscopy was performed in tapping mode using a Bruker Dimension Icon system.

Cyclic voltammetry (CV) experiments were carried out in a 3-electrode flooded cell using a BioLogic VMP-3 Potentiostat. All experiments were conducted in an argon-filled glovebox with moisture and oxygen levels <1 ppm. The electrolyte solution used was 1M sodium perchlorate (NaClO$_4$, Alfa-Aesar, 99.8% anhydrous) in propylene carbonate:fluoroethylene carbonate (PC:FEC, 95/5:v/v, Alfa-Aesar, 98%) and sodium metal foils were used as both the counter and reference electrodes. The working electrode was prepared by drop-casting a 2 g/L solution of either PA/Ti$_3$O$_7$NS, Na$_2$Ti$_3$O$_7$ NP or the mixed nanoplatelet-nanosheet system (Na$_2$Ti$_3$O$_7$ NP-NS) onto an O$_2$ plasma cleaned stainless steel current collector (1cm x 1cm). These thin-film electrodes contained neither binder nor carbon as this arrangement enables one to determine the fundamental electrochemical properties of the electrode material$^{66}$. After drop-casting, the electrodes were heated at 120°C under vacuum overnight to remove excess solvent and also to provide sufficient binding to the current collector. The amount of active material on the electrodes, on the order of 30-40 μg cm$^{-2}$ was confirmed using a Cahn C-
31 microbalance. Cyclic voltammetry and galvanostatic cycling were performed using cutoff voltages of 2.5 and 0.1 V vs. Na+/Na. The sweep rates for the former were between 1 mV s\(^{-1}\) and 100 mV s\(^{-1}\). The currents used for galvanostatic cycling were normalized to a capacity of 100 mAh g\(^{-1}\); the specific currents ranged from 100 mA g\(^{-1}\) (1C) to 1000 mA g\(^{-1}\) (10C).

**Chapter 3.3. Results and Discussion**

Several reports have shown that liquid-phase exfoliation of layered metal oxides is an efficient method for obtaining 2D nanosheets\(^{22,24,25}\). In our study, two different nanoscale morphologies of interest in this project, titanate nanosheets (PA/Ti\(_3\)O\(_7\) NS) and sodium titanate nanoplatelets (Na\(_2\)Ti\(_3\)O\(_7\) NP), were obtained by modifying a liquid-phase exfoliation process reported by Miyamoto *et al*\(^{26}\). The synthesis is based on intercalating large cations between slabs of [Ti\(_3\)O\(_7\)]\(^2-\) sheets from the parent layered compound, Na\(_2\)Ti\(_3\)O\(_7\), and then separating by ultrasonication. The key steps that enable us to obtain both PA/Ti\(_3\)O\(_7\) NS and Na\(_2\)Ti\(_3\)O\(_7\) NP are through partial proton exchange of the Na-ions in Na\(_2\)Ti\(_3\)O\(_7\) and varying the centrifugation speed. Energy dispersive spectroscopy measurements tracking the amount of sodium based on duration of proton exchange are shown in Fig. B.1 and the corresponding XRD patterns in Fig. B.2. Upon proton exchange, the organic base methylamine is intercalated into the interlayer region of the [Ti\(_3\)O\(_7\)]\(^2-\) sheets. The protonated sheets then work as a Br\öнстed acid and react with methylamine\(^{67}\), forming an intercalation compound with now positively charged methylammonium (MA/Ti\(_3\)O\(_7\)). The methylammonium intercalation compound is then ion-exchanged with positively charged propylamine to form a propylammonium (PA\(^+\)) intercalated compound (PA/Ti\(_3\)O\(_7\))\(^{26,68}\). Upon sonication, only those layers that were inserted with the larger PA\(^+\) ions are exfoliated as single layer nanosheets due to weak sheet-to-sheet interaction. The remaining compound is in the form of nanoplatelets. As illustrated in Fig. 3.1, this solution is
then centrifuged at 5000 rpm to isolate pure PA/Ti$_3$O$_7$ NS in the supernatant. The amount of PA$^+$ ions in PA/Ti$_3$O$_7$ was previously reported to be 0.56 mol per 1 mol of [Ti$_3$O$_7$]$^{2-}$ with the remainder of the negatively charged sheets compensated by protons$^{26}$. With a slower centrifugation speed of 2000 rpm, a mixture of nanoplatelets and nanosheets (Na$_2$Ti$_3$O$_7$ NP-NS) are obtained where the concentration of nanoplatelets is $\sim$35%.

We used differential centrifugation, a technique commonly applied with biological systems to isolate cellular components, to control the relative concentrations of nanoplatelets and nanosheets in the Na$_2$Ti$_3$O$_7$ NP-NS solution$^{69}$. This preparation method is described in detail in Appendix B and an illustration of this process is shown in Fig. B.4. More importantly, centrifuging the solution of Na$_2$Ti$_3$O$_7$ NP-NS at 1000 rpm resulted in the isolation of Na$_2$Ti$_3$O$_7$ NP. That is, by adjusting centrifuge conditions, we were able to obtain solutions comprised solely of PA/Ti$_3$O$_7$ NS or nearly entirely of Na$_2$Ti$_3$O$_7$ NP. These isolated systems enable us to obtain control samples for the electrochemical experiments (vide infra). The X-ray diffraction (XRD) patterns (Fig. B.5(a)) and electrochemical characteristics (Fig. B.5(b)–(d)) of these controls are detailed in Appendix B. The best electrochemical results were achieved with a combination of nanoplatelets and nanosheets; Thus, the focus of this report is on the Na$_2$Ti$_3$O$_7$ NP-NS materials.
Figure 3.1. Exfoliation flowchart for obtaining propylammonium Ti$_3$O$_7$ nanosheets (PA/Ti$_3$O$_7$ NS) and mixed nanoplatelets and nanosheets of Na$_2$Ti$_3$O$_7$ (Na$_2$Ti$_3$O$_7$ NP-NS) by altering centrifugation and ion exchange conditions.

Transmission electron microscopy (TEM) images of bulk Na$_2$Ti$_3$O$_7$, PA/Ti$_3$O$_7$ NS, and Na$_2$Ti$_3$O$_7$ NP-NS are presented in Fig. 3.2. The bulk particles appear darker and more opaque compared to nanosheets and nanoplatelets since the larger non-exfoliated particles are thicker. On the other hand, PA/Ti$_3$O$_7$ NS appear nearly transparent given that the sheet thickness is on the order of 1.2 nm, as confirmed by atomic force microscopy (Fig. B.7); this thickness resembles the depth of a single slab of a [Ti$_3$O$_7$]$^2^-$ building block (0.98 nm)$^{26}$. In Fig. 3.2(c), Na$_2$Ti$_3$O$_7$ NP within a bed of transparent PA/Ti$_3$O$_7$ NS can be seen. The widths of both the
nanosheets and nanoplatelets range from 100 to 200 nm and their lengths extend from several hundred nanometers to microns.

Figure 3.2. Transmission electron microscopy images of (a) bulk Na$_2$Ti$_3$O$_7$ (b) PA/Ti$_3$O$_7$ nanosheets, (c) mixed nanoplatelets and nanosheets of Na$_2$Ti$_3$O$_7$.

A series of X-ray studies were performed to characterize the structural and chemical properties of the nanoscale morphologies. First, XRD was used to verify the phase of bulk Na$_2$Ti$_3$O$_7$, PA/Ti$_3$O$_7$ NS, and Na$_2$Ti$_3$O$_7$ NP-NS (Fig. 3.3(a)). These materials were compared to the bulk (P2$_1$/m) structure in which $a = 8.565$ Å, $b = 3.802$ Å, 9.128 Å, and $\beta = 101.5890^\circ$ (JCPDS 72-0148). Bulk Na$_2$Ti$_3$O$_7$ synthesized via solid state reaction agrees with referenced indices$^{70}$. After exfoliation, PA/Ti$_3$O$_7$ NS exists as a purely isolated morphology while Na$_2$Ti$_3$O$_7$ NP-NS exists as two separate morphologies, as shown in Fig. 3.3(a). PA/Ti$_3$O$_7$ NS and Na$_2$Ti$_3$O$_7$ NP-NS both exhibit preferential orientation in the ($h00$) plane since the re-stacking of the sheets leads to alignment in this direction. For pure PA/Ti$_3$O$_7$ NS, the ($100$) reflection shifts to lower 2\(\theta\) from 10.5\(^\circ\) to 8.0\(^\circ\) (20), which corresponds to an increased $d$-spacing from 0.8 to 1.1 nm. The increased $d$-spacing is consistent with previous exfoliation results reported by Zhang et al.$^{71}$ and Miyamoto et al.$^{26}$ where both reports consistently found that [Ti$_3$O$_7$]$^{2-}$ sheets reassemble and are
separated by the larger positively charged PA$^+$ cation that acts as a counter charge to the negatively charged sheets$^{26}$. The $(100)$ reflection is then accompanied by a weaker $(200)$ reflection with $d(200)$ being 0.54 nm. For Na$_2$Ti$_3$O$_7$ NP-NS, the same $(100)$ as that observed for PA/Ti$_3$O$_7$ NS is evident as is the $(100)$ reflection for bulk Na$_2$Ti$_3$O$_7$. As a result of partial ion exchange, Na$^+$ remains between the stacked layers and a characteristic peak for nanoplatelets at $10.5^\circ$ $(2\theta)$ is observed. The ratio of the concentration of nanoplatelets to nanosheets in Na$_2$Ti$_3$O$_7$ NP-NS was estimated to be 9:16 by taking the ratio of the integrated intensities of the two most intense XRD reflections, one at $10.5^\circ$ $(2\theta)$ for the nanoplatelets, and the other at $8.0^\circ$ $(2\theta)$ for the nanosheets. The estimated number of layers and crystallite thicknesses for all samples using X-ray diffraction are tabulated in Table B.1$^{72}$.

Synchrotron X-ray scattering and pair distribution functions (PDFs) of bulk and Na$_2$Ti$_3$O$_7$ NP-NS were also studied to compare their morphologies. The X-ray scattering image of Na$_2$Ti$_3$O$_7$ NP-NS is shown in the graphic in Fig. 3.3(b). The PA$^+$ interspersed layers can be seen in the decrease in $q$ for the $(100)$ planes at $0.59$ Å$^{-1}$ ($d$-spacing = 10.7 Å) as consistently evidenced from benchtop XRD ($\lambda = 1.54$Å). With increased $q$ resolution, we observed additional $(h00)$ peaks at $q = 1.16, 1.72, 2.51, 3.04$ Å for $h = 2, 3, 4, 5$, respectively. These correspond to $d$-spacings of 5.46 Å, 3.67, 2.51, 2.06 Å (Fig. B.8). For bulk Na$_2$Ti$_3$O$_7$, the $(100)$ peak is maintained at $q = 0.75$ Å$^{-1}$ ($d$-spacing = 8.38 Å) in agreement with the calculated XRD pattern. The diffraction pattern captures the morphological anisotropy of the 2D nanoplatelets shown in the azimuthal scans (Fig. B.9). The bulk PDF matches that of the calculated PDF of the monoclinic structure in Fig. 3.3(b). Moreover, the signal from Na$_2$Ti$_3$O$_7$ NP-NS PDF is quickly damped by $r \approx 10$ Å due to smaller particle size$^{73}$. The results attained from synchrotron X-ray
scattering and PDFs show that the nanostructure correlation length agrees with the interlayer spacing of the nanosheets as confirmed by X-ray diffraction.

X-ray photo electron spectroscopy (XPS) was used to determine the chemistry of the interlayers before and after the exfoliation process. XPS spectra for bulk Na$_2$Ti$_3$O$_7$, PA/Ti$_3$O$_7$ NS and Na$_2$Ti$_3$O$_7$ NP-NS are shown in Fig. 3.3(c)–(d). The Na 1s and N 1s characteristic peaks provide both quantitative and qualitative information about the amount of Na$^+$ and –C-NH$_3^+$. In addition, each Na 1s and N 1s spectrum was high-resolution fitted to obtain a more accurate measure of the amount of Na$^+$ and –C-NH$_3^+$ present; the high-resolution XPS spectra are shown in Fig. B.11 and Fig. B.12 for N 1s and Na 1s, respectively. The corresponding chemical environment based on the fittings is also listed in the corresponding figures and are consistent with what is reported in literature for both the N 1s and Na 1s binding energies$^{74-77}$. As expected, the N 1s spectrum of bulk Na$_2$Ti$_3$O$_7$ shows no indication of –C-NH$_3^+$ (~401 eV) whereas a peak is clearly evident for the PA/Ti$_3$O$_7$ NS due to the existence of PA$^+$ ions in between the [Ti$_3$O$_7$]$^{2-}$ sheets. As for the Na 1s spectrum, the intense Na 1s peak for bulk Na$_2$Ti$_3$O$_7$ (1071 eV) decreases significantly for PA/Ti$_3$O$_7$ NS. For Na$_2$Ti$_3$O$_7$ NP-NS, a strong Na 1s peak is present due to the remaining Na-ions in between the layers from the partial exfoliation process. Taken together, the combination of both the N 1s and Na 1s XPS spectra shows that the concentration of Na$^+$ and –C-NH$_3^+$ differs dramatically depending on whether we have NS or NP. Using the results from the scans in Fig. B.10–B.12, we obtained atomic percentages of Na 1s and N 1s for bulk Na$_2$Ti$_3$O$_7$, PA/Ti$_3$O$_7$ NS, Na$_2$Ti$_3$O$_7$ NP-NS, and Na$_2$Ti$_3$O$_7$ NP-NS after cycling in 1M NaClO$_4$ in PC:FEC (Table B.2). To summarize, before exfoliation, the ratio of the atomic percentage of Na$^+$ to –C-NH$_3^+$ is 1:0 (bulk Na$_2$Ti$_3$O$_7$). After exfoliation, the ratio of the atomic percentage of Na$^+$ to
–C-NH₃⁺ for PA/Ti₃O₇ NS was measured to be 1:60. For the material containing both NS and NP, the ratio of the atomic percentage of Na⁺ to –C-NH₃⁺ is 1:6.6.

Figure 3.3. Na₂Ti₃O₇, PA/Ti₃O₇ nanosheets, and mixed nanoplatelets and nanosheets of Na₂Ti₃O₇. (a) X-ray diffraction patterns obtained from the modified exfoliation process. (b) Total X-ray scattering where evidence of preferential orientation for the (h00) reflection is shown. X-ray photoelectron spectra from the (c) N 1s and (d) Na 1s core-levels.
Cyclic voltammetry measurements are able to effectively identify the electrochemical behavior of Na$_2$Ti$_3$O$_7$ NP-NS in comparison to the control samples of pure PA/Ti$_3$O$_7$ NS and Na$_2$Ti$_3$O$_7$ NP. The redox peaks for the nanoplatelets and nanosheets occur at decidedly different potentials. Individual CVs of pure PA/Ti$_3$O$_7$ NS and isolated Na$_2$Ti$_3$O$_7$ NP as control samples are shown in Fig. B.5. For pure Na$_2$Ti$_3$O$_7$ NP, only low potential redox peaks in the cyclic voltammograms (CVs) between 0.1 and 0.5 V $\text{vs.}$ Na/Na$^+$ appear; this behavior resembles the electrochemical properties of bulk Na$_2$Ti$_3$O$_7$, as shown in Fig. B.5(b)$^{52,57,58}$. In comparison, PA/Ti$_3$O$_7$ NS (inset in Fig. 3.4(a)) exhibit energy storage at higher voltages between 0.5 and 2.5 V ($\text{vs.}$ Na/Na$^+$). Thus, specific redox peaks associated with Na$_2$Ti$_3$O$_7$ NP occur at 0.18 and 0.26 V $\text{vs.}$ Na/Na$^+$ for the cathodic and anodic peaks, respectively, whereas the cathodic and anodic peaks occur, respectively, at 1.1 and 1.2 V $\text{vs.}$ Na/Na$^+$ for PA/Ti$_3$O$_7$ NS.

Combining the energy storage properties of NP and NS offers the opportunity to achieve energy storage by facile Na-ion diffusion with an expanded electrochemical window ranging from 0.1 to 2.5 V $\text{vs.}$ Na/Na$^+$. As illustrated in Fig. 3.4(a), the electrochemical signature for Na$_2$Ti$_3$O$_7$ NP-NS consists of two coupled redox peaks, one from the nanoplatelet morphology and the other from the nanosheets. Cyclic voltammograms swept from 1 to 20 mV s$^{-1}$ are shown in Fig. B.13(a). In addition to a widened electrochemical window, a key feature that distinguishes Na$_2$Ti$_3$O$_7$ NP-NS as a prospective anode material for NIBs is its fast charge-storage properties and high capacity for sodium$^{52,57,58,78}$. The rate capability and capacity of Na$_2$Ti$_3$O$_7$ NP-NS compared to pure PA/Ti$_3$O$_7$ NS are shown by the sweep rate experiments in Fig. 3.4(b). For Na$_2$Ti$_3$O$_7$ NP-NS, a capacity of 155 mAh g$^{-1}$ is achieved at a rate of 1 mV s$^{-1}$ and 70% of that capacity (110 mAh g$^{-1}$) is retained at an order of magnitude faster rate (10 mV s$^{-1}$). In contrast, PA/Ti$_3$O$_7$ NS reach a maximum capacity of approximately 20 mAh g$^{-1}$ at 1 mV s$^{-1}$.
Figure 3.4. Cyclic voltammograms of mixed nanoplatelets and nanosheets of Na$_2$Ti$_3$O$_7$ and PA/Ti$_3$O$_7$ nanosheets cycled at 5 mV s$^{-1}$ from 0.1 to 2.5 V vs. Na/Na$^+$ and (b) corresponding rate capability (capacity vs. sweep rate).

Constant current measurements were also used to assess the charge storage properties of Na$_2$Ti$_3$O$_7$ NP-NS. On the first cycle, there is irreversible sodium loss from the formation of a solid electrolyte interphase (SEI) layer (Fig. B.14). Thereafter the galvanostatic charge-discharge curves stabilize as shown in Fig. 3.5(a). A significant feature of the discharge curves is that there are no distinct horizontal plateaus; the sloping voltage transients indicate single phase behavior. When cycled at 1C (100 mA g$^{-1}$), the Na$_2$Ti$_3$O$_7$ NP-NS material stores 150 mAh g$^{-1}$. As the charge-discharge rates are increased further, Na$_2$Ti$_3$O$_7$ NP-NS retains much of this high capacity and at a rate of 10C (1000 mA g$^{-1}$), this material stores 110 mAh g$^{-1}$. In addition to the high capacities, coulombic efficiencies higher than 95% were achieved. As shown in Fig. 3.5(c), the material exhibits excellent cycling stability, maintaining a capacity of 110 mAh g$^{-1}$ for some 300 cycles at 5C. Both the high rate capability and the stable cycling behavior far exceed results reported for bulk Na$_2$Ti$_3$O$_7$.$^{32,57,58,79}$ Although nanoscale materials have demonstrated enhanced
properties for a number of systems, an important factor here for the improved electrochemical properties may be related to the single phase behavior\textsuperscript{53,80}.

Figure 3.5. (a) 5\textsuperscript{th} cycle galvanostatic charge/discharge curves of mixed nanoplatelets and nanosheets of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} cycled at c-rates of 1C, 2C, 5C, 10C, and 20C. (b) Capacity and coulombic efficiency measured from galvanostatic cycling at c-rates of 1C, 2C, 5C, 10C, and 20C. (c) Long-term cycling at 5C of mixed nanoplatelets and nanosheets of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} for 300 cycles.

The charge-storage mechanisms for the two nanoscale morphologies, nanoplatelets and nanosheets, were analyzed for the different potential regimes. In this analysis, the peak current
in the cyclic voltammetry experiment is determined as a function of sweep rate. The peak current \( i \) follows a power law relationship

\[
i = a v^b,
\]

where \( a \) is a constant and \( v \) is the sweep rate\(^{81}\). The \( b \)-value can change from 0.5, which is indicative of semi-infinite diffusion to a value of 1, indicating a capacitor-like process. This \( b \)-value is obtained by determining the slope of \( \log(i) \) vs. \( \log(v) \) as shown for \( \text{Na}_2\text{Ti}_3\text{O}_7 \) NP and \( \text{PA/Ti}_3\text{O}_7 \) NS in Fig. 3.6(a). At sweep rates ranging from 1 to 20 mV s\(^{-1}\), the \( b \)-values for the cathodic peaks associated with the nanoplatelets (0.18 V vs. Na/Na\(^+\)) and nanosheets at (1.1 V vs. Na/Na\(^+\)) are calculated to be 0.7 and 1, respectively. The \( b \)-values for the anodic peaks associated with nanoplatelets and nanosheets are shown in Fig. B.13(b) and B.13(c), respectively. A value of \( b=0.7 \) for the peak at 0.18 V suggests that there is a significant diffusion contribution to the current, which is expected because these peaks are associated with Na\(^+\) insertion in \( \text{Na}_2\text{Ti}_3\text{O}_7 \) and the accompanying redox reactions. At 1.1 V, the \( b=1 \) value is representative of a surface capacitive process, as expected for a nanosheet. These results establish that there are two different modes of charge storage for these different nanoscale morphologies.

The \( b \)-value analysis can be extended further to determine the relative contribution for each of the charge storage processes in \( \text{Na}_2\text{Ti}_3\text{O}_7 \) NP-NS materials. In this analysis, the current at a given potential has contributions from both capacitive and diffusion-controlled processes and is written as\(^{48}\):

\[
i(V) = k_1 v^{1/2} + k_2 v
\]

Solving for the values of \( k_1 \) and \( k_2 \) at a given potential enables one to distinguish between currents which are related to semi-infinite diffusion and those which have capacitor-like kinetics.
Fig. 3.6(b) shows the capacitive contribution to the overall charge storage mechanism. The results are consistent with the b-values described above. Most of the diffusion contributions occur at potentials less than 0.5 V \textit{(vs. Na/Na\textsuperscript{+})} where it is expected that Na\textsuperscript{+} will be inserted into the layers of the Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} NP, while capacitor-like behavior occurs at potentials above 0.9 V \textit{(vs. Na/Na\textsuperscript{+})} where the nanosheets are found to have their contribution.

Figure 3.6. (a) Determination of the $b$-value using the peak current relationship to sweep rate. (b) Cyclic voltammogram of mixed nanoplatelets and nanosheets of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} showing 84\% capacitive contribution when cycled at 10 mV s\textsuperscript{-1}.

An interesting feature noticed for the Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} NP-NS materials is the increase in capacity with continued cycling. This capacity increase is shown in Fig. 3.7(a) for cyclic voltammetry experiments when the potential is cycled between 0.1 and 2.5 V \textit{vs. Na/Na\textsuperscript{+}}. After several cycles, a pair of cathodic and anodic peaks appear at 0.18 and 0.26 V, respectively, with a concomitant appearance of an additional pair of cathodic and anodic peaks appearing at 1.1 V and 1.2 V. As discussed above, the low potential peaks mirror the behavior of bulk Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} and are attributed to the Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} NP while the peaks at higher potential are attributed to the
PA/Ti₃O₇ NS. The development of these peaks produces a corresponding capacity increase from 95 to 125 mAh g⁻¹ which stabilizes after 10 cycles (Fig. B.15). The reason for this capacity increase arises from ion-exchange between Na⁺ in the electrolyte and PA⁺ ions still present in Na₂Ti₃O₇ NP-NS. This ion-exchange mechanism during electrochemical cycling is quite typical of nanosheets where bulkier positively charged cations are exchanged for smaller-sized cations with a parallel increase in capacity. The first cycle does not show redox peaks at low potentials (<0.5 V) since the PA⁺ needs to be exchanged for Na⁺ before the Na⁺ can be fully intercalated. For the experiments carried out with nearly pure Na₂Ti₃O₇ NP (low concentration of nanosheets), redox peaks at low potentials are barely detectable at the first cycle (Fig. B.16(a)). By the second cycle, the redox peaks for Na-ion insertion into the nanoplatelets are observed for both Na₂Ti₃O₇ NP-NS and Na₂Ti₃O₇ NP (Fig. B.16(b)). The intensity of these peaks continues to increase with cycling.

*Ex-situ* XPS was used to investigate the ion-exchange process occurring in the Na₂Ti₃O₇ NP-NS by determining the ratio between the Na 1s and N 1s peaks before and after electrochemical cycling. Before cycling, there is an intense N 1s signal and a weaker Na 1s signal as shown in Fig. 3.7(b) and 3.7(c), respectively. After several cycles, a strong Na 1s signal now appears and although the signal-to-noise ratio is high, there still exists a slight N 1s peak, indicating that a small amount of PA⁺ is retained after cycling. As indicated in Table B.2, the Na⁺ content after cycling increases from 0.5% to 6.1% and the –C-NH₃⁺ content decreases from 3.3% to 0.6%. Also, there is a slight shift (+0.6 eV) of the Na 1s peak from 1071 to 1071.6 eV. This change in binding energy for Na was observed previously and was proposed to be associated with SEI formation. 
Figure 3.7. (a) Cyclic voltammogram of 1\textsuperscript{st} and 20\textsuperscript{th} cycle for mixed nanoplatelets and nanosheets of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} cycled at 5 mV s\textsuperscript{-1}. X-ray photoelectron spectra of mixed nanoplatelets and nanosheets of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} from the (b) N 1s and (c) Na 1s core-levels before and after electrochemical cycling.

Chapter 3.4. Conclusions

The Na-ion charge storage properties of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}, a promising negative electrode for sodium-ion batteries are compromised by the slow kinetics and poor cycling behavior of the bulk material. In this study, we considered whether exfoliated Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} could overcome these limitations as charge storage would occur on the surface or within a few layers. The liquid phase exfoliation method developed here produced both nanosheets and nanoplatelets that undergo redox reactions upon Na-ion insertion. The electrochemical properties benefitted from the ion exchange processes which occurred during the initial electrochemical cycling. The charge storage kinetics for the nanosheets is capacitor-like in nature while that of the nanoplatelets is diffusion-controlled and resembles that of bulk Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}. Materials that combined both nanosheets and nanoplatelets exhibited far better charge storage properties (110 mAh g\textsuperscript{-1} at 10C) and stable cycling behavior than that of the corresponding bulk materials, underscoring the importance of the 2D nanoscale morphology.
Chapter 4. Na$_2$FePO$_4$F Nanoparticles for High-Rate Sodium-Ion Cathodes

Chapter 4.1. Introduction and Background

There is a growing concern that the demand for lithium will impact the existing world reserves and its abundance will inevitably become an economic issue$^{14}$. Na-ion technology is considered to be an ideal alternative to lithium due to the abundance and low cost of sodium$^{10-13,15}$. One of the main advantages for developing Na-ion batteries (NIBs) is that the intercalation chemistry roughly mirrors that of lithium. The disadvantages of NIBs stem from the heavier mass of sodium, it is less electropositive than lithium, and as a result, there is a gravimetric energy density penalty. However, this is not considered to be as critical of an issue for stationary applications. Nonetheless, it is evident that in order for Na-ion technology to advance, a new generation of cathode materials (positive electrodes) is required$^{10,13,15}$. The most commonly studied materials are composed of layered oxides such as O3 and P2 type compounds where O and P represent octahedral or trigonal prismatic coordination of Na-ions and 3 or 2 represent the number of distinguishable sodium layers$^{84}$. Among these two compounds, P2 type compounds are known to exhibit higher performance and cycle life compared to O3 type compounds$^{84,85}$. However, a new class of materials, in the form of phosphates and fluorophosphates, is emerging and represents a promising direction for NIBs due to enhanced performance over layered oxides$^{86}$.

The thermal stability and higher operating voltages of phosphate-based compounds make these materials among the best candidates for positive electrodes in SIBs$^{86}$. An increased operating voltage arises from the inductive effect of the phosphate/fluorophosphates polyanion$^{86,87}$. The main obstacle for using phosphate-based compounds is their highly insulating nature; conductive coatings and nanostructured morphologies are essential for improving their
electrochemical performance, especially their high rate capability. Whereas most electrode materials networked through the phosphate polyanion develop into tunneled structures (i.e. olivine NaFePO₄), sodium iron fluorophosphates (Na₂FePO₄F) is one of the rare layered phosphate compounds. Based on a one electron process, 1 mol of Na⁺ can be intercalated from Na₂FePO₄F utilizing the Fe²⁺/Fe³⁺ couple. This leads to a theoretical capacity of 124 mAh g⁻¹.

In addition, the unit cell of the oxidized compound is only 3.7% smaller than the fully reduced compound. This makes the material attractive as a low-strain material with potential advantages for long-term cycling.

The first report on the electrochemical properties of Na₂FePO₄F was by Ellis et al., however, this report only demonstrated Li-ion transport. Liquid-phase synthesis such as sol-gel and hydrothermal reactions were used to synthesize Na₂FePO₄F in two separate reports by Ellis et al. Particle-sizes typically ranged anywhere from 75 to 100 nm. Recham et al. prepared 25 nm Na₂FePO₄F nanoparticles using an ionothermal synthesis and nanostructuring this material showed better cycling stability, however, at the expense of using costly ionic liquids. Over the next few years, several new studies were published on Na₂FePO₄F where the electrochemical properties for both Li- and Na-ion intercalation were optimized using a combination of carbon coating and high energy ball milling. Moreover, there have been several reports on the structural phase transitions, magnetic properties, and diffusion properties Na₂FePO₄F.

In the research reported here, we used a polyol medium to synthesize Na₂FePO₄F nanoparticles with sizes around 10 – 15 nm. as this synthetic route has been commonly used to successfully prepare LiFePO₄ nanoparticles. The polyol route is a versatile synthetic method for preparing a range of nanoparticles (metals, metal oxides, metal chalcogenides) of small size. The polyol route has several advantageous features such as: (i) water-comparable
solubility of metal-salt precursors; (ii) high boiling points (up to 320°C); (iii) reducing properties\textsuperscript{104}. Furthermore, composites comprised of Na\textsubscript{2}FePO\textsubscript{4}F and reduced graphene oxide (rGO) were fabricated as this conductive carbon additive helps promote high rate capability\textsuperscript{44}. Several electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic cycling were employed to characterize the high-rate electrochemical properties of Na\textsubscript{2}FePO\textsubscript{4}F nanoparticles.

**Chapter 4.2. Methods**

**Chapter 4.2.1. Synthesis**

Iron acetate (Fe(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2}, Sigma-Aldrich, ≥99.99%), ammonium dihydrogen phosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, Sigma-Aldrich, 99.999%), sodium acetate (CH\textsubscript{3}COONa, Sigma-Aldrich, ≥99.0%), and sodium fluoride (NaF, Alfa Aesar, 99.99%) were first suspended in 50 mL of tetraethylene glycol (HO(CH\textsubscript{2}CH\textsubscript{2}O\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}OH, Sigma-Aldrich, 99%) in a stoichiometric molar ratio (1:1:1:1, 2 mmol product). After stirring for several minutes, this solution was heated at 335°C for 16 hours in a 100 mL round bottom flask attached to a reflux condenser. The resultant solution was then subjected to a series of washing and centrifuging steps using acetone to remove the tetraethylene glycol and partial organic compounds. The NFPF-P nanoparticles were then dried under vacuum at 120°C for 24 hours to remove residual moisture. NFPF-P nanoparticles were then heat-treated at 450°C under argon for 5 minutes to burn off nearly all the partial organics and carburize a remaining 1 – 2% as a carbon-coating (NFPF-450CAr)

For comparison, bulk (>100 nm particle size) Na\textsubscript{2}FePO\textsubscript{4}F was prepared via solid-state reaction (NFPF-SSR) of stoichiometric molar amounts of sodium bicarbonate (NaHCO\textsubscript{3}, Sigma-Aldrich, ≥99.5%), iron oxalate dihydrate (FeC\textsubscript{2}O\textsubscript{4}2H\textsubscript{2}O, Sigma-Aldrich, ≥99.99%), ammonium
phosphate dibasic \((\text{NH}_4)_2\text{HPO}_4\), Sigma-Aldrich, ≥98%), and sodium fluoride (NaF, Alfa Aesar, 99.99%). These precursors were first ground with mortar and pestle and subsequently heated at 200°C for 2 hours and then ramped directly up to 400°C at a rate of 10°C min\(^{-1}\) for another 4 hours all under forming gas (N\(_2\)/H\(_2\); 95:5, v:v). After this initial heat-treatment, the powders were re-ground to ensure intimate contact and then sealed in a quartz ampule under argon and heated at 500°C for 6 hours.

Composites of NFPF-450CAr with reduced graphene oxide (NFPF-rGO) were prepared by mixing 80% NFPF-450CAr powder with graphene oxide (80/20 by weight). The graphene oxide solution was prepared using a modified hummers method \((3.9 \text{ g L}^{-1})\)\(^{43}\). The mixture of NFPF-450CAr and graphene oxide was ultrasonicated for an hour and then dried on a hot-plate at 120°C while stirring. This powdered mixture was subsequently reduced under argon at 350°C for 2 hours to convert graphene oxide to rGO\(^{44}\). The reduction of graphene was necessary to recover the conjugated network of graphene in order to promote electrical conductivity.

**Chapter 4.2.2. Characterization**

Transmission electron microscopy (TEM) images were taken with an FEI Technai T12 TEM (120 keV) using a carbon-coated copper grid as a substrate. Vacuum-dried powder samples were characterized by x-ray diffraction (XRD) by using a Rigaku Miniflex II diffractometer. XRD using a synchrotron x-ray source \((\lambda = 0.2112\text{Å})\) with a Perkin-Elmer amorphous Si-based 2D detector for rapid acquisition was performed at the Advanced Photon Source 11-ID-B at Argonne National Laboratory\(^{62}\). NIST-traceable CeO\(_2\) standard powder was used to calibrate experimental geometry of the measurements. The sample-to-detector distance for synchrotron XRD was calibrated to 952.276 mm. Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) was performed using the SDT Q600 from TA Instruments to measure
the amount of organics and to characterize the thermal properties. The samples were heated to 900°C at a rate of 10°C min⁻¹ in air (flow rate: 100 mL·min⁻¹). For argon heat-treatments, the samples were heated to 450°C at a rate of 5°C·min⁻¹ at a flow rate of 200 mL·min⁻¹.

Electrochemical measurements were carried out in a two-electrode Swagelok cell using a BioLogic VMP-3 Potentiostat. Experiments conducted in a glovebox with an inert atmosphere (oxygen and moisture levels < 1ppm). Sodium metal foil was used as the counter electrode and the electrolyte solution used was 1M sodium perchlorate (NaClO₄, Alfa-Aesar, 99.8% anhydrous) in propylene carbonate:fluoroethylene carbonate (PC:FEC, 95:5, v:v, Alfa-Aesar, 98%). The working electrodes were prepared by making carbon slurry in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99.5% anhydrous) consisting of 70% active material, 20% Super P carbon black and 10% polyvinylidene fluoride binder (PVDF, Kynar HSV 900). After grinding this mixture with an agate mortar and pestle, the slurry was doctor-bladed onto 3/8” diameter stainless steel foils (10 μm thick film) and air-dried overnight, followed by vacuum drying at 120°C overnight. The material loading on the electrode varied from 0.7 to 1.4 mg·cm⁻². Cyclic voltammetry and galvanostatic cycling were performed using cutoff voltages of 4.0 and 2.0 V vs. Na⁺/Na. The sweep rates for the former were between 0.1 mV·s⁻¹ and 100 mV·s⁻¹. The C-rates used in galvanostatic cycling ranged from C/10 to 20C where current rates were normalized by the theoretical capacity of Na₂FePO₄F. Electrochemical impedance spectroscopy (EIS) was taken after every pre-cycle with an AC amplitude of 10 mV scanned within a frequency range of 100 mHz to 900 kHz.
Chapter 4.3. Results and Discussion

This is the first report for the use of polyols to synthesize Na$_2$FePO$_4$F nanoparticles (NFPF-P). The lower synthesis temperature coupled with mild reducing conditions make this approach advantageous compared to traditional solid-state routes that require high-temperature heat treatment under reducing atmospheres$^{104}$. Details of the polyol synthesis of NFPF-P and bulk NFPF prepared via solid-state reaction (NFPF-SSR) are described in the Appendix C. Briefly, NFPF-P is prepared by heating stoichiometric amounts of Na, Fe, PO$_4$, and F in the form of metal salt precursors in a solution of tetraethylene glycol at 300°C under reflux for 16 hours. TEM analysis revealed sizes ranging between 10-15 nm (Fig. 4.1(a)). The NFPF-SSR samples (Fig. C.1) are comprised of large agglomerates (up to 400 nm) that are composed of smaller particles ranging from 50 to 100 nm. After synthesis and subsequent wash cycles with acetone, a residual amount of organic compounds of up to 10% still remain, as determined from TGA analysis (Fig. 4.1(b)). DSC shows a sharp endothermic peak situated around 200°C related to the volatilization of the organic compounds and moisture. In addition, an exothermic peak corresponding to the oxidation of Fe(II) to Fe(III) at 700°C is shown with continuous oxidation upon ramping to higher temperatures.

Phase purity and crystallization was verified using XRD for both NFPF-P and NFPF-SSR. As a result of lower synthesis temperature (335°C), NFPF-P exhibits phase purity in accordance with broader XRD peaks, as shown in Fig. 4.1(c); the crystal structure of Na$_2$FePO$_4$F is shown as an inset in Fig. 4.1(c). For comparison, NFPF-SSR also exhibits phase purity albeit much sharper XRD peaks as a result of larger particle sizes. By using Scherrer’s analysis, the average crystallite sizes of NFPF-P and NFPF-SSR were calculated to be roughly 10 and 45 nm, respectively, which is in good agreement with TEM analysis. For NFPF-P, we utilized a
synchrotron light source of wavelength = 0.2112 Å to obtain higher resolution diffraction spectra. In addition, Rietveld refinement was performed to further verify the purity of both NFPF-P and NFPF-SSR (Fig 4.1(d)). The corresponding lattice parameters for both materials are as follows: NFPF-P (a = 5.10(2), b = 13.35(5), c = 11.61(9)) and NFPF-SSR (a = 5.10(7), b = 13.51(1), c = 11.48(6)).

Figure 4.1. (a) Transmission electron microscopy image of NFPF-P. (b) TGA/DSC of NFPF-P. X-ray diffraction patterns of NFPF-SSR and NFPF-P using x-ray source of (c) 1.54 Å and (d) 0.2112 Å.
Nanostructuring has commonly been applied to phosphate and fluorophosphate compounds to alleviate solid-state ion diffusion limitations because these materials tend to be highly insulating. For these compounds, the capacity can be improved dramatically by coating the surface of the particles with carbon\textsuperscript{88}. Using LiFePO\textsubscript{4} as an example, carbothermal reduction at high temperatures lead to the formation of conductive iron phosphocarbides or phosphides, and in tiny quantities (1 – 3%), can facilitate surface electron transport when combined with carbon\textsuperscript{105}. Similarly, Na\textsubscript{2}FePO\textsubscript{4}F was synthesized via hydrothermal reaction with the addition of sucrose or ascorbic acid directly added to the hydrothermal reactor. Upon hydrothermal reaction, the organic species decompose and leave a carbonaceous coating on the surface, which is then later carburized at higher temperature (2% carbon coating)\textsuperscript{90}. In this report, NFPF-P was carbon coated by carburizing the organics under a neutral atmosphere (argon). This was carried out by heat-treating NFPF-P at 450°C under an argon atmosphere to remove a majority of the partial organic compounds and promote a carbon coating. As confirmed by TGA (Fig. C.2), this heat-treatment step removed roughly 7 – 8% of the organic compounds while carburizing the rest into a carbon coating (2% carbon coating); this material will now be denoted as NFPF-450CAr. The XRD pattern of NFPF-450CAr shown in Fig. 4.2(a) does not show any oxidized iron species (i.e. Fe\textsubscript{2}O\textsubscript{3}) whereas at higher temperatures or longer dwell times, carbothermal decomposition of Na\textsubscript{2}FePO\textsubscript{4}F occurs where the presence of oxidized Fe\textsubscript{2}O\textsubscript{3} and elemental Fe are detected (Fig. C.3). Furthermore, an additional step was taken to promote higher rate-capability of NFPF by combining NFPF-450CAr with reduced graphene oxide (rGO) to form a composite\textsuperscript{44}. The resulting composite NFPF-rGO, still shows phase purity albeit with a slightly higher background noise in the range of 15 - 25° due to additional carbon content, as shown in Fig. 4.2(a).

The electrochemical Na-ion insertion process is described by the following equation:
\[ \text{Na}_2\text{FePO}_4\text{F} \leftrightarrow \text{NaFePO}_4\text{F} + x\text{Na}^+ + xe^- \]

The electrochemical properties of Na$_2$FePO$_4$F samples were studied using cyclic voltammetry as this technique provides information on the rate capability and electrochemical reversibility of the material of interest. Fig. 4.2(b) shows the cyclic voltammograms (CVs) of NFPP-P, NFPP-450CAr, and NFPP-rGO. The electrochemical signature of all NFPP samples consists of two coupled redox peaks, one at 2.8 V vs. Na/Na$^+$ (denoted as A1-C1) and another at 3.0 V vs. Na/Na$^+$ (denoted as A2-C2). Based on these coupled redox peaks, the rate capability and electrochemical reversibility can be studied by measuring the extent of storage capacity as the sweep rate increases. As shown in Fig. 4.2(c), NFPP-P has a capacity of nearly 90 mAh g$^{-1}$ at 0.1 mV s$^{-1}$ (charging time of 5.5 hours) whereas NFPP-450CAr and NFPP-rGO stores near theoretical capacities of 110 mAh g$^{-1}$ at the same rate. For both NFPP-P and NFPP-450CAr, there is a dramatic drop off of capacity at rates faster than 2 mV s$^{-1}$ whereas NFPP-rGO stores 70 mAh g$^{-1}$ at 10 mV s$^{-1}$ (charging time of 3.3 minutes). A clear trend can be seen where carbon-coating (NFPP-450CAr) improves the rate capability of NFPP-P and forming a composite with rGO further improves this material to achieve the highest rate capability.
Figure 4.2. Effect of post-heat treatment at 450°C and rGO composite (a) illustrated in X-ray diffraction patterns (phase purity), (b) cyclic voltammograms cycled between 2.0 – 4.0 V vs. Na/Na$^+$ at 0.1 mV s$^{-1}$, and (c) rate capability cycled from 0.1 - 10 mV s$^{-1}$.

Another material property that can be measured with cyclic voltammetry is the electrochemical reversibility of a material. This is done by calculating the peak voltage separation of a coupled redox reaction ($\Delta V (V_{p,\text{Anodic}} - V_{p,\text{Cathodic}})$) and this reversibility directly correlates to a material’s rate capability$^{66}$. Table 4.1 summarizes $\Delta V$ for both coupled redox peaks A1-C1 and A2-C2 for NFPF-P, NFPF-450CAr, and NFPF-rGO. It is noteworthy that the $\Delta V$ consistently decreases with the incorporation of a carbon coating and subsequently, rGO incorporation. NFPF-rGO shows the smallest $\Delta V$ ($V_{p,A1} - V_{p,C1}$): 0.21 and $\Delta V$ ($V_{p,A2} - V_{p,C2}$): 0.17) for both coupled redox peaks and this further supports the high-rate capability of this material.
Table 4.1. Summary of peak voltage separation ($\Delta V (V_{p,A} - V_{p,C})$) for NFPF-SSR, NFPF-P, NFPF-450CAr, and NFPF-rGO for both pairs of anodic-cathodic peaks (A1-C1 and A2-C2).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta V (V_{p,A1} - V_{p,C1})$</th>
<th>$\Delta V (V_{p,A2} - V_{p,C2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFPF-P</td>
<td>0.35</td>
<td>0.20</td>
</tr>
<tr>
<td>NFPF-450CAr</td>
<td>0.26</td>
<td>0.19</td>
</tr>
<tr>
<td>NFPF-rGO</td>
<td>0.21</td>
<td>0.17</td>
</tr>
</tbody>
</table>

To provide more insight about the charge storage mechanism of NFPF-rGO, a series of kinetic analyses using cyclic voltammetry was used to investigate its charge-storage properties. By sweeping these materials from slow to fast sweep rates, a kinetic analysis ($b$-value analysis - dependence of current on the sweep rate) can be used to determine the dominating charge-storage mechanism. The following equation can be used by assuming that the current ($i$) obeys a power-law relationship with the sweep rate ($\nu$):

$$i = a \nu^b$$

where $a$ and $b$ are constants. The dominating charge-storage mechanism can be identified by extracting the $b$-value for a given redox potential from plots of log($i$) versus log($\nu$). A $b$-value of 0.5 would indicate charge-storage that is controlled by solid-state diffusion of ions whereas a value of 1 would indicate a capacitor-like process\(^\text{48}\). Although nanoparticles often circumvent solid-state diffusion limitations, the dominating charge-storage mechanism for NFPF-P and NFPF-450CAr is diffusion where $b$-values were calculated to be approximately 0.6 for both pairs of redox peaks (Fig. C.4 and Fig. C.5). With the incorporation of conductive rGO, NFPF-rGO shows an improvement in diffusion limitations where the $b$-value increases to 0.75 and 0.81 for A1-C1 coupled redox peaks and 0.78 and 0.74 for A2-C2 coupled redox peaks, as shown in Fig. 4.3. This increase in $b$-value is a clear indication that the charge-storage mechanism is now
deemed a more capacitive process as opposed to one consistent with semi-infinite diffusion, as was the case for NFPF-P and NFPF-450CAr.

![Graph showing b-value of NFPF-rGO](image)

Figure 4.3. $b$-value of NFPF-rGO extracted from peak current measurements cycled between 0.1 and 5 mV s$^{-1}$.

A related analysis based on the $b$-value characterization can be applied using a more detailed version of the current power-law relationship:

$$i(V) = k_1v + k_2v^{1/2} \quad (2)$$

where $k_1$ and $k_2$ are constants at a specific potential. The constants $k_1$ and $k_2$ are determined from a plot of $i(V)v^{-1/2}$ versus $v^{1/2}$ and thus the capacitive and diffusion contributions to the overall capacities can be determined. This analysis can be used to quantitatively measure the extent to which charge-storage results from capacitive processes. NFPF-P exhibits charge-storage that is predominately diffusion-controlled (Fig. 4.4(a)) where the capacitive contribution amounts to
only 44%. There is an upward trend in the capacitive contribution where after carbon-coating (NFPF-450CAr), the capacitive contribution increases to 84% (Fig. 4.4(b)). Lastly, Fig. 4.4(c) shows a CV of NFPF-rGO swept at 1 mV s⁻¹ where the overall capacitive contribution amounts to 90%, indicating that the predominant charge-storage mechanism is capacitive. This improvement in charge-storage kinetics is mainly attributed to the improvement in electrical conductivity by incorporating rGO to the NFPF electrode. For comparison, NFPF-SSR shows only a 20% capacitive contribution at 1 mV s⁻¹, indicating charge-storage being nearly entirely dependent on solid-state diffusion of ions (Fig. C.6).

Figure 4.4. Capacitive contribution determination of (a) NFPF-P, (b) NFPF-450CAr, and (c) NFPF-rGO cycled at 1 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) was also implemented as this technique allows us to study the effect of carbon coating and the composite with rGO on fundamental impedance properties. EIS was performed at open-circuit voltage for NFPF-P, NFPF-450CAr, and NFPF-rGO samples. The obtained experimental results (Fig. 4.5) were fitted using the equivalent circuit model shown in the inset of Fig. 4.5¹⁰⁶–¹⁰⁸. This circuit model is composed of $R_s$ at high frequencies, a charge-transfer resistance $R_{CT}$, along with a constant phase element (CPE), a Warburg impedance $Z_w$, and an infinite capacitance $C_{int}$. While the intercept at the $Z_{ie}$
axis in the high frequency range ($R_s$) corresponds to the electrolyte resistance, the high frequency semicircle ($R_{CT}$) refers to the charge transfer resistance for electrons and Na-ions across the electrode-electrolyte interface, carbon-particle interface and particle-particle contact$^{106–108}$. The inclined slope observed in the low frequency range is attributed to the Warburg impedance, $Z_w$, which corresponds to Na-ion diffusion in the bulk of the electrode. Table 4.2 summarizes the fitted values of $R_{CT}$ for all samples. The smaller $R_{CT}$ value for NFPF-rGO means that faster charge transfer is occurring at the interface.

EIS can also be applied as a reliable method to calculate the Na$^+$ chemical diffusion coefficient ($D_{Na}$) of the intercalated compound$^{98,109,110}$. The $D_{Na}$ ($\text{cm}^2\cdot\text{s}^{-1}$) of all NFPF samples can be calculated using the following equation$^{111}$:

$$D_{Na} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$  \hspace{1cm} (3)

where $R$ is the ideal gas constant (8.314 J mol$^{-1}$K$^{-1}$), $T$ is the ambient temperature (298.15 K), $A$ is the surface area of the electrode (0.713 cm$^2$), $n$ is the number of electrons per molecule during intercalation, $F$ is the Faraday constant (96485 C mol$^{-1}$), $C$ is the concentration of Na$^+$ ($3.80 \times 10^{-3}$ mol cm$^{-1}$)$^{98}$, and $\sigma$ is the Warburg coefficient ($\Omega\cdot\text{s}^{-1/2}$). The properties of NFPF ($\sigma$ and $D_{Na}$) are summarized in Table 4.2. A direct correlation is observed where with lower $R_{CT}$, the $D_{Na}$ increases. NFPF-rGO exhibits much higher $D_{Na}$ due to smaller charge transfer resistance and this property supports this material’s high rate capability.
Figure 4.5. Nyquist plots of NFPF-P, NFPF-450CAr, and NFPF-rGO fitted by the circuit model shown in the inset.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>$R_{CT}$, Ω</th>
<th>$\sigma$, $\Omega \cdot s^{-1}$</th>
<th>$D_{Na}$, $\text{cm}^2 \cdot s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFPF-P</td>
<td>130</td>
<td>361</td>
<td>$3.70 \times 10^{-14}$</td>
</tr>
<tr>
<td>NFPF-450CAr</td>
<td>113</td>
<td>280</td>
<td>$6.16 \times 10^{-14}$</td>
</tr>
<tr>
<td>NFPF-rGO</td>
<td>92</td>
<td>166</td>
<td>$1.74 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Table 4.2. Impedance parameters obtained from an equivalent circuit model.

To assess more accurately the electrochemical performance of the NFPF-rGO samples, galvanostatic cycling was performed within a voltage range of 2.0 – 4.0 V vs. Na/Na$^+$; galvanostatic discharge curves and corresponding capacities for NFPF-P and NFPF-450CAr can be found in Fig. C.7 and Fig. C.8, respectively. The electrochemical performance of NFPF-rGO was determined by cycling this material at different C-rates (C/10 – 20C). Corresponding charge-
discharge curves are shown in Fig. 4.6(a). This material exhibits two voltage plateaus situated at around 2.8 and 3.0 V vs. Na/Na\(^+\), consistent with the coupled redox peaks shown in the CVs earlier. A high capacity of 110 mAh g\(^{-1}\) is obtained at a discharge rate of C/10, close to theoretical capacity (124 mAh g\(^{-1}\)). At rates of C/10, 1C, and 10C, NFPF-rGO is able to store 115, 90, and 50 mAh g\(^{-1}\), respectively, as shown in Fig. 4.6(b). In addition to high capacities, coulombic efficiencies greater than 95\% were achieved. Moreover, long-term stability is displayed in Fig. 4.6(c) where nearly 70\% of the capacity is still retained after 5000 cycles when cycled 10C. The high rate capability of NFPF-rGO compared to current literature reports on NFPF are summarized in Table 4.3. One particular trait of NFPF-rGO that stands out is its capacity of 50 mAh g\(^{-1}\) at fast rate (10C). When compared to other rate studies of NFPF, the highest capacity attainable is 25 mAh g\(^{-1}\) at 9C\(^98\). NFPF-rGO cycled in a Na-ion system also shows higher fast rate capacity compared to NFPF cycled in a Li-ion system (20 mAh g\(^{-1}\) at 10C\(^96\)).
Figure 4.6. (a) Galvanostatic charge-discharge curves with C-rates imposed from C/10 – 20C and (b) corresponding capacities and coulombic efficiencies of NFPF-rGO. (c) Corresponding long-term cycling of NFPF-rGO at 10C over 5000 cycles.
<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Ion-System</th>
<th>Slow Rate C-rate, mAh g⁻¹</th>
<th>Fast Rate C-rate, mAh g⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFPF-rGO</td>
<td>Na⁺</td>
<td>C/10, 110</td>
<td>10C, 50</td>
<td>This work</td>
</tr>
<tr>
<td>Nanostructured NFPF</td>
<td>Na⁺</td>
<td>C/10, 116</td>
<td>10C, 21</td>
<td>[98]</td>
</tr>
<tr>
<td>Carbon-coated NFPF⁺</td>
<td>Na⁺</td>
<td>C/10, 105</td>
<td>8C, 15</td>
<td>[93]</td>
</tr>
<tr>
<td>Carbon-coated hollow NFPF⁺</td>
<td>Na⁺</td>
<td>C/10, 80</td>
<td>9C, 25</td>
<td>[95]</td>
</tr>
<tr>
<td>Carbon-coated NFPF</td>
<td>Li⁺</td>
<td>C/10, 119</td>
<td>10C, 20</td>
<td>[96]</td>
</tr>
</tbody>
</table>

Table 4.3. Gravimetric capacity of NFPF. *Capacity estimated from plot.

Chapter 4.4. Conclusion

In this present work, we utilized a polyol medium to synthesize 10-15 nm NFPF particles. These nanoparticles were then heat-treated to ensure a 1 – 2% carbon coating in addition to fabricating a composite structure with rGO to improve the overall electrical conductivity and particle-to-particle connectivity of NFPF. A series of kinetic analyses using cyclic voltammetry were performed to demonstrate that although diffusion-limitations are inherent for NFPF-P, with the subsequent steps for improving electrical conductivity, the charge-storage mechanism displays a more capacitor-like system. EIS was also performed to complement the kinetic analyses. Overall, the $R_{CT}$ decreased with the NFPF-rGO composite and $D_{Na}$ increased by an order of magnitude compared to NFPF-P. The electrochemical performance in terms of capacity and long-term stability were measured using galvanostatic cycling. NFPF-rGO stored a capacity of 110 mAh g⁻¹ at C/10 and exhibited high-rate capability where 50 mAh g⁻¹ was retained even at
10C. At fast rates (10C), NFPF-rGO also displayed stable cycling up to 5000 cycles. The electrochemical properties of NFPF-rGO make this a promising material for use as a positive electrode for NIBs.
Chapter 5. Crossover from Slow Sodium-Ion Storage in MoS$_2$ to Ultrafast Intercalation Pseudocapacitance in MoS$_2$ Nanoparticles by Phase Transition Suppression

Chapter 5.1. Introduction and Background

Pseudocapacitance is a form of electrochemical energy storage that combines the high energy density characteristics of a battery and the high rates associated with capacitors. Similar to capacitance, pseudocapacitance ($C$) can be understood according to Equation 5.1, in which a potential change ($\Delta E$) scales linearly with the charge ($q$) withdrawn or added to the electrochemical system. The charge-discharge processes in a pseudocapacitor are Faradaic, hence the higher energy densities, but the kinetic response more closely resembles that of a capacitor than that of a galvanic cell$^{112,113}$.

$$q = C \Delta E$$

Equation 1

Three Faradaic processes that result in pseudocapacitive electrochemical features are: (1) adsorption pseudocapacitance, e.g. faradaic deposition and desorption of H on metal surfaces, (2) redox pseudocapacitance, e.g. near surface reactions in hydrous RuO$_2$, and (3) intercalation pseudocapacitance.$^{4,5,6}$ The kinetics of adsorption and redox pseudocapacitance are intrinsically fast because that charge storage occurs on a surface and is not impeded by solid state diffusion. Intercalation pseudocapacitance maintains the high rates associated with those surface processes even though the charge storage occurs in the bulk of a nanostructured material.

Intercalation pseudocapacitance is rarely observed, however, because intercalation of ions in most solid-state energy storage materials are accompanied by distinct phase transitions that occur between the intercalated and non-intercalated states$^{7,8,9,10,11,12,13,14,15}$. Phase transitions can dominate the kinetics of the intercalation reactions, even in systems with short
solid-state diffusion lengths. Therefore, materials that store charge primarily through intercalation pseudocapacitance do not undergo a first order phase transition because those transitions limit the ion migration kinetics. One method to suppress these first-order phase transitions is to reduce the size of the primary particles, as has been shown in TiS$_2$, MoO$_2$, and LiFePO$_4$.

Although lithium-ion systems (namely Nb$_2$O$_5$ and MoO$_3$) have demonstrated high levels of intercalation pseudocapacitance, the analogue sodium-ion pseudocapacitive material has yet to perform as well as lithium-ion systems due to the difference in size between lithium- and sodium-ions; those properties are summarized in Table 1.1. The size and molar mass of sodium-ions are larger than lithium-ions, which leads to slower diffusion kinetics and shorter cycle lifetimes in most solid storage hosts (Table 1).

MoS$_2$ is especially amenable to fast sodium-ion intercalation reactions because of its large interatomic spacings, which can accommodate larger sodium-ions. These large van der Waals (vdW) gaps are 6.2 Å in large crystals, and are expanded up to 6.9 Å in small nanocrystals. In support of this idea, we have previously shown that sodium ions undergo extremely fast intercalation in ordered mesoporous MoS$_2$. Another advantage of MoS$_2$ is that certain allotropes are highly conductive. As shown in Fig. 5.1(a), MoS$_2$ exists as two predominate polytypes, the semiconducting 2H phase, and the metastable metallic 1T phase. The 2H-MoS$_2$ and 1T-MoS$_2$ phase are both layered structures that consist of S – Mo – S ‘sandwich’ building blocks, but limited miscibility of alkali-ions, such as lithium and sodium-ions, in the 2H-MoS$_2$ phase drives a conversion to the metastable 1T-phase. The phase conversion from 2H to 1T consists of a glide-plane sliding mechanism of the sulfur layers, which changes the molybdenum coordination from trigonal prismatic to octahedral while preserving the
layered vdW gaps for fast sodium-ion migration. This phase change is accompanied by a modification of the electronic structure, which leads to high electronic conductivity. As a result of the large vdW gaps and high electronic conductivity, MoS$_2$ is an ideal material for fast charge storage.

Most of the work on the charge storage properties of MoS$_2$ is focused on the four-electron conversion reaction for its high capacity. The conversion begins when >1.5 moles of sodium ions are inserted in the MoS$_2$ structure leading to the irreversible decomposition of the MoS$_2$ structure into Mo and Na$_2$S. While this reaction indeed leads to higher energy storage, the cycle lifetimes are short, and the kinetics are slow. On the other hand, when the sodium-ion concentration in MoS$_2$ is limited to ~ 1 mole the MoS$_2$ structure does not decompose, the reversibility of the reaction is better, and the kinetics are faster. In this paper we investigate the pseudocapacitive sodium-ion storage in MoS$_2$ nanoparticles that were prepared by a two-step synthesis method. In terms of practical applicability, the high-rate behavior of MoS$_2$ is demonstrated in 10-15 μm thick MoS$_2$ films (≈1 mg cm$^{-2}$). A detailed kinetic analysis has been carried out to quantify the dominant charge storage processes in order to elucidate the charge storage mechanism. The electrochemical determination of the charge storage mechanism is further supported by operando structural characterization using synchrotron based x-ray diffraction. Focusing on the idea that phase transformation suppression is required for charge storage by intercalation pseudocapacitance, we have investigated the markedly different storage properties of sodium-ions in bulk and nanostructured MoS$_2$.
Chapter 5.2. Methods

Chapter 5.2.1. Synthesis

All starting materials were obtained from commercial suppliers and used without further purification. The synthesis of MoO$_2$ nanocrystals has been reported elsewhere,\textsuperscript{115} and is briefly described here. MoO$_2$ nanocrystals were prepared solvothermally by dissolving anhydrous MoCl$_5$ (Strem Chemicals) in a mixture of ethanol and deionized water at a reaction temperature of 180°C for 6 hrs. The MoO$_2$ nanocrystals were converted to MoS$_2$ with H$_2$S gas. The reaction was carried out in a tube furnace at 600°C under flowing H$_2$S/H$_2$ (H$_2$S 5 mol % : H$_2$ 95 mol %, Air Gas) for 10 hours. A graphite boat was used to typically convert ~ 100 - 200 mg of MoO$_2$ to MoS$_2$.

Chapter 5.2.2. Characterization

Powder X-ray diffraction (XRD) was performed in a PANalytical X’Pert Pro operating with Cu Kα (λ = 1.5418 Å) using a 0.03° step size, a voltage of 45kV, and a current of 40mA. XRD patterns were recorded in the range of $10^\circ < 2\theta < 80^\circ$. Transmission electron microscopy (TEM) was performed using a FEI Technai T12 operating at 120 kV. Nitrogen porosimetry was carried out using a Micromeritics TriStar II 3020. The surface area was calculated from the adsorption branch of the isotherm between (0.04 – 0.30 P/Po) using the Brunauer-Emmett-Teller (BET) model. The pore diameter and pore volume was also calculated from the adsorption branch of the isotherm using the Barret-Joyner-Halenda (BJH) model.

Chapter 5.2.3. Electrode formulation

The carbon fiber based electrodes were made from a slurry consisting of 70 wt.% nc-MoS$_2$ or b-MoS$_2$ (Alfa Asear) powder used as active component for Li storage, 10 wt.% vapor
grown carbon fibers (Sigma Aldrich), and 10 wt.% carbon black (Alfa Aesar) used as conductive additive, and 10 wt.% polyacrylic acid solution in ethanol (Mw=250K, Sigma Aldrich) used as binder. The four components were sonicated for 30 minutes to obtain a homogeneous dispersion. Ethanol evaporation over one hour resulted in a homogeneous thick paste that was cast onto 25 µm carbon coated Al foil (gift from Coveris). The slurry was dried at ambient temperature for 1 h, and further dried at 25°C under vacuum overnight to evaporate the excess solvent. The mass loading of the electrode was ~1 mg cm⁻² of active material.

**Chapter 5.2.4. Electrochemical measurements**

Electrochemical measurements of the MoS₂ electrodes were carried out in a 2-electrode SwageLok configuration using a Bio-Logic VMP3 potentiostat. Electrochemical SwageLok cells were all assembled in an argon-filled glovebox with oxygen and moisture levels of <1 ppm. Sodium metal foils served as the auxiliary electrode and the electrolyte used was 1M NaClO₄ in propylene carbonate:fluoroethylene carbonate (PCFEC; 95:5 v/v). Cut-off voltages for both chronopotentiometric and cyclic voltammetric experiments were between 0.7 and 2.5 V vs Na/Na⁺. Current rates were normalized by the theoretical capacity of MoS₂ (167 mAh g⁻¹). Pre-cycling to convert MoS₂ from the 2H to 1T phase was carried out using both chronopotentiometric and cyclic voltammetric experiments cycled between 0.55 and 2.5 V vs Na/Na⁺. AC Impedance was taken after every pre-cycle with an AC amplitude of 10 mV scanned within a frequency range of 100 mHz to 900 kHz.

**Chapter 5.2.5. Operando Synchrotron based X-ray diffraction**

Carbon based slurry electrodes were made for this *in situ* study. The slurry consists of 70 wt.% active material (bulk or nano MoS₂), 10 wt.% vapor grown carbon fibers (Sigma Aldrich),
and 10 wt.% carbon black (Alfa Asaer) used as conductive, and 10 wt.% polyvinylidene fluoride in n-methyl-2-pyrrolidone used as binder. All four components were blended to obtain a homogeneous paste with honey like consistency. The paste was then cast onto 25 μm carbon coated Al foil. The slurry was dried in ambient temperature for a several hours and further dried at 125 °C under vacuum overnight to evaporate the excess NMP. The mass loading of the electrodes is approximately 3-5 mg/cm². These electrodes were cycled from 0.5 V-2.5 V as half cells in swageloc cells using sodium metal as counter electrode, glass fiber (Whatman) as separator, and 1M NaClO₄ in a 1:1 ethylene carbonate/diethylene carbonate solvent (Sigma) as electrolyte. Nano MoS₂ was precycled on a VSP potentiostat/galvanostat (Bio-Logic) using 0.2 C rate that corresponds to 138.6 mAh/g while bulk MoS₂ were cycled on Arbin using 0.2 C rate that corresponds to 50 mAh/g. After precycling, these electrodes were taken out of the Swagelok cells in an Ar filled glovebox and were further reassembled into in-house built coin cell with 3mm holes and kapton tape window to allow transmission of the X-ray during the in situ study. The coin cells were stored in an Ar atmosphere until cycling was performed to prevent exposure. Due to time constraint, in situ studies up at SSRL were done at 0.22C. In situ XRD was performed at beamline 11-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) at 12735 eV. Patterns were collected with exposure times between 1-30 seconds. The diffraction intensity data is plotted as a function of the scattering vector length \( Q = \frac{4\pi}{\lambda} \sin(\theta) \), where \( \theta \) is half of the scattering angle, \( \lambda \) is the wavelength of the incident radiation; the d-spacing thus is simply \( \frac{2\pi}{Q} \). Standard 2032 coin cells were modified with a 3 mm diameter central hole, and used for the operando measurements. The MoS₂ electrodes were assembled into these coin cells using lithium metal as counter electrode, glass fiber (Whatman) as separator, 1M NaClO₄ in 1:1 ethylene carbonate/diethyl carbonate (Sigma Aldrich) with 5% (v/v) fluorinated ethylene
carbonate (TCI America) as the electrolyte. To maintain pressure, the pouch cells were encased within an aluminum frame with a small 4 mm diameter hole to allow for transmission of the X-ray beam through the electrode. The cell was charged and then discharged 4-5 times to drive the 2H-1T phase transition at a current density of 0.2C. -The operando measurement was carried out at 0.2C using a VSP potentiostat/galvanostat (Bio-Logic USA). In order to aid in phase identification, XRD patterns of 2H-MoS$_2$, 1T-Na$_x$MoS$_2$, and triclinic Na$_x$MoS$_2$ were simulated using Mercury 3.5.

Chapter 5.3. Pseudocapacitive Charge-Storage

We have published a detailed report on the synthesis methods, characterization, and pseudocapacitive lithium-ion performance of MoS$_2$ elsewhere$^{141}$. Fig. D.1 shows the structural characterization of the nanostructured MoS$_2$ used in this study. The MoS$_2$ nanoparticles, which are between 10 – 40 nm, have a surface area of 35 m$^2$g$^{-1}$ and show a broad diffraction powder X-ray diffraction pattern that matches the hexagonal 2H MoS$_2$ phase. Furthermore, the vdW gaps are expanded to 0.63 nm from the bulk value of 0.62 nm. An extremely important material property of MoS$_2$ that we leverage in this study is the structural conversion of the semiconducting 2H to the metallic 1T phase$^{27,29,33,34,35}$. As mentioned previously, MoS$_2$ undergoes a topotactic insertion reaction when the concentration of sodium-ions ($x$) is 0 ≤ $x$ ≤ 1.5 moles in MoS$_2$. Fig. 5.1(a) shows the semiconducting trigonal geometry and the metallic octahedral geometry. The conversion to the 1T-phase modifies the electronic structure of MoS$_2$, and ultimately leads to metallic conductivity$^{142}$. In our system, we converted the MoS$_2$ to the 1T-phase by cycling the electrodes at 1C ten times between 0.55 V – 2.50 V vs. Na/Na$^+$. The voltage was limited to above 0.55 V in order to prevent the conversion reaction, which would disrupt the metallic conductivity and layered crystal structure of the 1T-phase. Fig. 5.1(b) shows the
galvanostatic trace of the 1\textsuperscript{st} and 10\textsuperscript{th} formation cycle. The plateau ca. 1 V \textit{vs.} Na/Na\textsuperscript{+} is indicative of the 2H- to 1T-phase transition. After 10 cycles, the plateau corresponding to the 2H to 1T conversion is replaced by the galvanostatic signatures for insertion of sodium-ions into 1T-MoS\textsubscript{2}\textsuperscript{133}. In order to confirm the increased conductivity after the 2H to 1T conversion, impedance spectroscopy was carried out on these half cells. A 23\% decrease in charge transfer resistance from (211 to 177 $\Omega$) is observed between the 1\textsuperscript{st} and 10\textsuperscript{th} formation cycles (Fig. 5.1(b)), and can be attributed to the decrease in impedance as a result of the increased conductivity.

After the formation of the 1T phase through electrochemical precycling as described above, cyclic voltammetry (CV) was performed to study the electrochemical kinetics of MoS\textsubscript{2} nanoparticles. Since the charge storage response times are different for a battery, electrical double layer capacitor (EDLC), and pseudocapacitor, the storage mechanism can be distinguished and quantified using electrochemical kinetic analyses. One such set of analyses utilizes the dependency of the current response on the potential sweep rate in a cyclic voltammetric experiment\textsuperscript{112,113}. Batteries predominately exhibit slow kinetics resulting in voltage separation between cathodic ($V_{p,c}$) and anodic ($V_{p,a}$) peaks in which $\Delta V = V_{p,a} - V_{p,c} > 60$ mV\textsuperscript{145}. This voltage hysteresis results from slow ion-diffusion and phase transitions.\textsuperscript{112} An ideal EDLC, on the other hand, exhibits a box-shaped CV curve\textsuperscript{112}. This electrochemical signature indicates a fast capacitive electrochemical process where the charge exchanged between the material and the electrolyte is independent of the voltage. For capacitive processes, the current ($i$) depends linearly on the scan rate ($\nu$) in a cyclic voltammetry experiment

$$i = C\nu$$

\textit{Equation 1}
where $C$ is the capacitance and is independent of $\nu$. Pseudocapacitance is a mixture between a battery and an EDLC, which exhibits a capacitive box-shaped CV curve superimposed with broad redox peaks. Over a range of sweep rates, a characteristic signature of a pseudocapacitor is a small peak voltage separation of approximately 60 mV. A classic material that exhibits this type of behavior is hydrous RuO$_2$ and displays fast Faradaic charge storage.

Charge storage from the intercalation of sodium ions between the vdW gaps of MoS$_2$ is expressed by the following electrochemical reaction:

$$\text{MoS}_2 + x\text{Na}^+ + xe^- \leftrightarrow \text{Na}_x\text{MoS}_2$$

Equation 2

where the theoretical capacity is 167 mAh g$^{-1}$ ($x = 1$). The cyclic voltammograms, from 0.1 to 10 mV s$^{-1}$, in Fig. 5.1(d) show a capacitive box-shaped curve superimposed with broad redox peaks. This electrochemical signature is similar to hydrous RuO$_2$, which also shows a box-shaped CV curve with broad redox peaks.

The fundamental charge-storage mechanism of MoS$_2$ can be determined by studying the dependency of the current response on the sweep rate ($b$-value analysis). Assuming that the current in a CV experiment obeys a power-law relationship, with the sweep rate, leads to the following relationship:

$$i = av^b$$

Equation 3

where $a$ and $b$ are adjustable parameters. For processes limited by semi-infinite linear diffusion, the $b$-value is 0.5. On the other hand, for a capacitive process the $b$-value is 1. The $b$-value can be obtained by calculating the slope of the line in a plot of log($i$) vs. log($\nu$). These $b$-values are indicated on the CV plots over their corresponding peaks, and are all between 0.88 –
0.95 (Fig. 5.1(d)) indicating that the charge storage of sodium-ions in the MoS\textsubscript{2} vdW gaps are predominantly capacitive.

Another related analysis quantify the capacitive contribution over the entire voltage range of MoS\textsubscript{2} is the $k_1k_2$ analysis\textsuperscript{48}:

$$i(V) = k_2V + k_1V^{1/2} \quad \text{Equation 4}$$

At a given voltage ($V$), electrochemical redox reactions limited by semi-infinite linear diffusion have a corresponding current response varying with $v^{1/2}$ and for capacitive processes, the current varies linearly with $v$. Solving for the values of $k_1$ and $k_2$ at a given potential provides a quantitative distinction between diffusion and capacitive currents. Furthermore, the total capacitive contribution to the charge storage can be calculated by summing the fractional contributions over the entire voltage window. A given CV tells about the energy stored via the area (Fig. 5.1(e)) and over 90\% of the stored energy in this system is capacitive. This is a clear demonstration of sodium-ion intercalation that appears to be capacitive in nature. These intercalation reactions are reminiscent of battery-type intercalation reactions where ions intercalate between the vdW gaps of MoS\textsubscript{2}, but in this nanoparticle based system the charge storage is not limited by solid-state diffusion.

To further support the capacitive storage mechanism of the MoS\textsubscript{2} nanoparticles, the Trasatti analysis was used to quantify the kinetic properties by studying the relationship between capacity and sweep rate\textsuperscript{50,147}. In Fig. 5.1(f), a plot of $q$ (capacity in mAh g\textsuperscript{-1}) versus $v^{-1/2}$ yields a curve demonstrating that the capacity contribution is nearly independent of the sweep rate when cycled from 0.1 to 10 mV s\textsuperscript{-1} whereas at faster rates, linear regions represent diffusion-controlled limitations. At sweep rates below 10 mV s\textsuperscript{-1}, the infinite sweep rate capacity was determined by
extrapolating the y-intercept. Within the range of sweep rates between 1 and 10 mV s\(^{-1}\), the infinite sweep rate capacitance is measured to be 115 mAh g\(^{-1}\) and this capacity represents the available capacity attainable without solid-state diffusion limitations. At a sweep rate of 1 mV s\(^{-1}\), MoS\(_2\) stores 124 mAh g\(^{-1}\), and the \(k_1k_2\) analysis indicated 90% capacitive contribution, which is in excellent agreement with the Trasatti analysis. The question we will address next is the origins of the storage process that enables this cross-over from diffusion limited intercalation reactions, to the fast capacitive controlled intercalation reactions we have just described.

Figure 5.1. (a) MoS\(_2\) 2H semiconducting trigonal geometry and the metallic 1T octahedral geometry. (b) Galvanostatic charge-discharge curve of MoS\(_2\) nanoparticles when converting from the 2H to 1T phase. Voltage plateau at 1 V vs. Na/Na\(^+\) is indicative of the 2H-to-1T phase transition, and after 10 cycles, is replaced by the galvanostatic trace for the insertion of sodium ions into 1T-MoS\(_2\). (c) Nyquist plot of the 2H-to-1T phase transition indicating a decrease in
charge-transfer resistance due to metallic conductivity. (d) b-value analysis indicates capacitive charge-storage mechanism for each pair of redox peaks where a value near unity up to 10 mV s\(^{-1}\) is observed. (e) \(k_1/k_2\) kinetic analysis shows the current response from capacitive processes. The shaded region shows 94% occupation to the overall current response of MoS\(_2\) nanoparticles cycled at 1 mV s\(^{-1}\). (f) Capacity versus \(v^{1/2}\) shows the separation the capacity due to diffusion-controlled and capacitive processes cycled from 0.1 to 100 mV s\(^{-1}\). The dashed diagonal line is extrapolated to identify the infinite sweep rate capacity.

**Chapter 5.4. Operando X-Ray Diffraction**

In order to understand the pseudocapacitive electrochemical response in MoS\(_2\) from a structural perspective we utilized synchrotron based X-ray diffraction to follow the changes in the crystalline structure during operation of a sodium-ion half-cell. The structural work on the lithium and sodium insertion driven 2H to 1T phase transition is vast\(^{27,29,33,34,35}\), so in this paper we focus on structural characterization after the 2H to 1T phase transition has occurred completely. Therefore, the first XRD pattern of bulk MoS\(_2\) shown in the stack plots (Fig. 5.3(a)) correspond to a cell at OCV after being cycled four times between 0.55 V – 2.50 V vs. Na/Na\(^{+}\) (galvanostatic traces for that conversion are shown in Fig. D.2). Three phases can be clearly identified in this first pattern: predominately 1T-Na\(_x\)MoS\(_2\) (0 ≤ \(x\) ≤ 1.0)\(^{137}\), a small amount of 2H-MoS\(_2\), and a trace of triclinic Na\(_x\)MoS\(_2\) (0 ≤ \(x\) ≤ 1.0) (see detailed explanation of phase identification Fig. D.3 – D.4). The presence of triclinic NaMoS\(_2\) in our diffraction patterns indicates that some sodium remains in the structure. In support of this observation, the (001) lattice spacing observed in our first pattern (\(d = 7.09\) Å) is larger than what has been observed as a result of this residual sodium-ion content.\(^{137,148}\) The presence of the 2H phase is related to the
back conversion of the metastable 1T phase to the thermodynamic 2H phase\textsuperscript{149}, and most likely occurred during transportation of these samples (see Fig. D.2).

As sodium is inserted into the structure of bulk MoS\(_2\), a first-order phase change from the 1T phase to the triclinic phase of NaMoS\(_2\) is observed. The (001) peak is indistinguishable from the 1T and the triclinic phase, so they can’t be used to differentiate each other. A clear indication of the 1T to triclinic phase transition, however, is the increasing intensity of the triclinic peak at 1.1 Å\(^{-1}\) seen in Fig. 5.3(a) during sodium ion insertion. Notably, this peak at 1.1 Å\(^{-1}\) is not present in the 2H or 1T phase, so its presence is a clear indicator of the triclinic phase. Peak splitting is also observed (ca. 1 V) between 2-2.5 Å\(^{-1}\), which is another clear signature of a first order-phase transition. This type of behavior is consistent with reports on the phase behavior of the closely related lithium-ion system, showing that the insertion of lithium-ions (\(x\)) between 0 \(\leq x \leq 1.0\) in bulk MoS\(_2\) induces several first order phase transformations\textsuperscript{149}.

In stark contrast to the phase transitions observed during charge and discharge of the micron-sized MoS\(_2\), MoS\(_2\) nanoparticles do not undergo a phase change. Similar to the bulk stack XRD patterns described above, the first XRD pattern of nano MoS\(_2\) in the stack plots shown in Fig. 5.3(b) corresponds to a cell at OCV after being cycled five times between 0.55 V – 2.50 V vs. Na/Na\(^+\) (galvanostatic traces for that conversion is shown in Fig. D.2). Only the 1T phase can be identified in the first XRD pattern. Insertion of sodium does not drive a phase transition as was seen in bulk MoS\(_2\), but the near linear expansion and contraction of the (001) MoS\(_2\) lattice planes suggests that a solid-solution of sodium in MoS\(_2\) is formed instead. The absence of the characteristic triclinic peak at 1.1 Å\(^{-1}\) provides convincing evidence that the 1T to triclinic phase transition is suppressed in the nanostructured form as has been observed for other nanostructured charge storage materials\textsuperscript{72,115,125}. Furthermore, no peak splitting is observed in the 2-2.5 Å\(^{-1}\)
region of the stack plot (Fig. 5.3(b)), again providing evidence that the phase transformation is suppressed here. The modification of phase transition onsets has been clearly established by Tolbert and Alivisatos in their work on the influence of nanocrystal size on the high pressure phase transition in CdSe\textsuperscript{150}. In our work, we speculate that the interfacial energy penalty for two phase coexistence between the triclinic phase and the 1T-phase is too high in the confined space of the nanocrystal. However, it is also interesting to note that the 2H to 1T phase transition was not suppressed in this system, or in our previous work on thin films with even smaller structure sizes\textsuperscript{133}. While it is clear that that more work is needed to understand the underlying mechanism for this suppression, the rich governing physics makes this an interesting fundamental question with real world applicability.

The change in the (001) lattice spacing during the insertion process clearly distinguishes the charge storage mechanism in MoS\textsubscript{2}. After intercalation of 0.4 mol of sodium in bulk MoS\textsubscript{2}, the (001) lattice spacing increases from 0.89 Å\textsuperscript{-1} (\(d = 7.07 \text{ Å}\)) to 0.88 Å\textsuperscript{-1} (\(d = 7.12 \text{ Å}\)) (Fig 5.3(c)), and further insertion drives a contraction of the lattice to 0.94 Å\textsuperscript{-1} (\(d = 6.95 \text{ Å}\)) due to cationic interactions\textsuperscript{148}. During the deinsertion process, the (001) lattice increases to a maximum followed by a contraction of the lattice nearly to the original position. The hysteretic behavior of the lattice expansion suggests that bulk MoS\textsubscript{2} experiences a significant kinetic limitation, such as a phase transition, during the deinsertion of Na-ions (Fig 5.3(c)).

In contrast to bulk MoS\textsubscript{2}, the vdW gaps in the MoS\textsubscript{2} nanoparticles increase linearly during insertion to accommodate sodium ions, up to about 0.4 moles of sodium, followed by a lattice contraction as a result of cationic interaction (Fig. 5.3(d)). The hysteresis in lattice expansion is not observed here indicating again that the phase transformation has been suppressed in nano MoS\textsubscript{2}. A hallmark of charge storage without phase transitions are linear
galvanostatic traces, which are observed for the nanostructured MoS$_2$; in stark contrast to the stepped-plateau galvanostatic traces observed for the micron-sized samples. Finally, the XRD peaks return to their original position after deinsertion, which indicates that the insertion and deinsertion process is structurally reversible.

Our operando study demonstrates that the trigonal (1T) to triclinic phase transition is suppressed in nanostructured MoS$_2$, and that sodium is incorporated as a solid solution in MoS$_2$. Even if the solid-state diffusion lengths are short enough to afford fast kinetics in a nanostructured material, if it undergoes a phase transition, the rate limiting step may become the phase conversion – regardless of the size. We believe that the fast kinetics result from phase transition suppression, and not simply the reduced ion migration path lengths. In Fig. 5.3(b) the MoS$_2$ lattice clearly expands and contracts during charge and discharge further demonstrates that the majority of the stored charge originates from intercalation of sodium-ions into the bulk of the MoS$_2$ nanocrystals – not simply the surface of the nanocrystal. Another benefit of this modified charge storage mechanism is the structural reversibility it affords the system, which leads to increased cycle lifetimes as will be described in the next section. By combining the detailed electrochemical kinetic analysis and this structural understanding of the charge storage process, we can provide compelling data that sodium intercalates into the bulk of this nanocrystal while not being governed by solid-state diffusion kinetics – i.e. intercalation pseudocapacitance. This characterization distinguishes this system as a clearly identifiable capacitive system, and not simply a nanostructured battery material. While this latter statement may seem to be parsing nomenclature, it is important to distinguish the two different charge storage mechanisms as unique as they both undergo Faradaic processes that are typically confused with each other.
Figure 5.2. Simulated powder X-ray diffraction patterns (a) Hexagonal (2H)-MoS$_2$, (b) Trigonal (1T)-MoS$_2$, (c) Triclinic NaMoS$_2$, (d) and the inset of (c) demarcated by the dashed box. * Triclinic (11-1), (101), (01-1)
Figure 5.3: X-ray diffraction patterns collected during the intercalation and de-intercalation processes of a pre-cycled Na half-cell containing (a) bulk MoS$_2$, (b) nano MoS$_2$ as positive electrode (with charging/discharging rate of C/4.5). The sharp peak at 2.08 Å$^{-1}$ is attributed to Na counter electrode in the cell. Change in d-spacing of (c) bulk MoS2 and (d) nano MoS2 during the sodiation process.

Chapter 5.5. Superior Electrochemical Properties

MoS$_2$ nanoparticle based electrodes were cycled galvanostatically between 1C to 100C to demonstrate their practical applicability as sodium-ion pseudocapacitors. As discussed
previously, the sloping voltage profiles shown in Fig. 5.4(a), at all measured C-rates, is an electrochemical signature of solid-solution behavior. As a result, the MoS$_2$ nanoparticles exhibit fast rate performance, delivering about 150 mAh g$^{-1}$ at a rate of 1C. At a modest rate of 5C, our nanostructured MoS$_2$ preforms similarly, or slightly better, with other nanostructured MoS$_2$ materials (Table 5.2). For example, Wu et al. showed that closed shell, fullerene-type MoS$_2$ nanocrystals deliver 115 mAh g$^{-1}$ at 5C, and 60 mAh g$^{-1}$ at 20C. In another study, Bang et al. reported on exfoliated MoS$_2$ nanosheets that delivered 120 mAh g$^{-1}$ at 800 mA g$^{-1}$ (≈5C). While these rates are still more typical of battery-type reactions, these studies reported here demonstrate that MoS$_2$ is an example of a material that stores charge by intercalation pseudocapacitance. At rates > 20C, our material outperforms the fullerene-type MoS$_2$ by nearly two-fold. At a much faster rate of 100C (charging time of only 36 seconds), a capacity of 65 mAh g$^{-1}$ is still achieved, making MoS$_2$ the first Na$^+$ conducting material to exhibit intercalation pseudocapacitance. Materials that do not undergo a phase transition upon intercalation also tend to exhibit long lifetimes, and MoS$_2$ is no exception. Very little degradation to the delivered capacity (retention of 97%) is observed even after 1800 cycles at a rate of 20C (Fig. 5.4(c)). In comparison to other reports, this nanostructured MoS$_2$ demonstrates up to sixty-fold greater cycle lifetimes (Table 5.2). It is clear that suppressing intercalation-induced phase transitions leads to new and useful properties in MoS$_2$, which are not observed in the corresponding bulk material.
<table>
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<th>Material type</th>
<th>Slow rate C-rate, mAh/g</th>
<th>Fast rate C-rate, mAh/g</th>
<th>Ultra fast rate C-rate, mAh/g</th>
<th>Capacity retention cycles, % retention</th>
<th>Ref.</th>
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<td>20, 111</td>
<td>100, 65</td>
<td>1800, 97</td>
<td>this work</td>
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<td>20, 60’</td>
<td>n/a</td>
<td>30, 47</td>
<td>[148]</td>
</tr>
<tr>
<td>Exfoliated MoS$_2$</td>
<td>5, 120’</td>
<td>Not reported</td>
<td>n/a</td>
<td>100, ~95’</td>
<td>[151]</td>
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</table>

Table 2. Gravimetric capacity of nanostructured MoS$_2$ based on sodium-ion half-cells. *Capacity estimated from plot.
Figure 5.4. (a) Galvanostatic cycling of MoS$_2$ at various c-rates (1C, 5C, 10C, 20C, 40C, 60C, 100C) (b) Galvanostatic cycling performance of MoS$_2$ showing attainable capacity as a function of cycle number at various rates. Corresponding coulombic efficiencies are well above 99%. (c) Long-term cycling performance of MoS$_2$ cycled at 20C showing minimal capacity fade (97% capacity retention) up to 1800 cycles.

Chapter 5.6. Conclusion

We have demonstrated that the energy storage mechanism associated with Na+ intercalation in MoS$_2$ is from intercalation pseudocapacitance. While most reports on MoS$_2$ largely focus on the high capacity conversion reaction at low potentials, this study demonstrates
several attractive properties of the intercalation reaction. The quantitative electrochemical kinetic analysis shows that over 90% of the storage in this system is capacitor-like. As a result, this material system can be charged to nearly 50% of its 1C capacity in just under 40 seconds. These fast rates overlap with the performance characteristics of double-layer electrochemical capacitors, while delivering much higher capacities as a result of the Faradaic based charge storage. We have performed synchrotron based operando XRD on this system to elucidate the structural origins of the fast pseudocapacitive charge storage. We confirmed that micrometer size MoS$_2$ undergoes a trigonal to triclinic first-order phase transition during the charge storage process. This phase transition is suppressed in nanostructured MoS$_2$ and enables charge storage to occur with capacitor-like kinetics (i.e., extremely fast). We believe that the sodium ions can migrate very rapidly through the VdW gap when they are not impeded by a slow phase transition. In addition, the nanostructured MoS$_2$ shows almost no capacity decay even after being cycled 1800 times. These results demonstrate the prospect of using chalcogenide based materials as high performance sodium-ion hosts. In addition, these results provide a clear basis for establishing the intercalation pseudocapacitance charge storage mechanism and distinguishing it from materials which possess battery-like kinetics.
Chapter 6. Overview

The accumulation of the work presented in the five chapters constitute the work I have carried out as my dissertation. The overall focus of my work has been to both structurally and electrochemically characterize novel materials and determine the extent of Na-ion intercalation, and in some cases Li-ion intercalation. As much as Na-ion intercalation is important, so is fast charge-storage properties. The materials presented here demonstrate that the electrochemical performance (high capacity, long cycle-life, and safety) of certain materials can be improved drastically by modulating different nanoscale morphologies, as well as optimizing electrode formulations for practical applications.

The first system studied, sodium titanate (Na$_2$Ti$_3$O$_7$), compared the differences in electrochemical properties between nanosheets and nanotubes. We identified that particle morphologies and assembly as an electrode material dramatically affected the electrochemical performance due to surface area and porosity for ion-accessibility; nanotubes exhibited much higher surface areas and porosity compared to nanosheets. Ultimately, reduced graphene oxide composites of nanotubes showed the best electrochemical properties by exhibiting broad voltammetric CV profiles coupled with sloping voltage profiles when imposed constant currents, and this was highly reminiscent of pseudocapacitance.

For the second system, we addressed the issue of low capacities of single-layer nanosheets by retracing our steps of the exfoliation process and deriving nanoplatelets (few-layered nanosheets) that allow for Na-ion insertion. This work on the nanoplatelets showed interesting changes and advantages utilizing 2D morphologies of Na$_2$Ti$_3$O$_7$ (a combination of nanoplatelets and nanosheets, Na$_2$Ti$_3$O$_7$ NP-NS) in comparison to bulk materials. These include the extension of the electrochemically active voltage window and improved fast rate capability.
In addition, we used ex-situ XPS coupled with cyclic voltammetry to investigate the phenomenon of increasing capacity upon cycling of 2D Na$_2$Ti$_3$O$_7$. With its low operating voltage, expanded electrochemical window, and high capacities, Na$_2$Ti$_3$O$_7$ NP-NS shows promise as a prospective negative electrode for NIBs.

For the third system, we prepared sodium iron fluorophosphates (Na$_2$FePO$_4$F) as a nanoparticle and assessed its electrochemical properties as a prospective positive electrode material. In this work, we utilized a polyol medium to synthesize 10-15 nm Na$_2$FePO$_4$F particles. These nanoparticles were then carbon coated (1 – 2%) and composites of reduced graphene oxide demonstrated (Na$_2$FePO$_4$F -rGO) improved rate capability. Electrochemical impedance spectroscopy was performed to complement cyclic voltammetric studies used in the kinetic analyses. Overall, the $R_{CT}$ decreased with rGO and $D_{Na}$ increased an order of magnitude compared to non-carbon-coated Na$_2$FePO$_4$F nanoparticles. With high capacities at high voltages, Na$_2$FePO$_4$F -rGO is a promising material for use as a positive electrode for both aqueous and non-aqueous NIBs.

The final system we investigated was the pseudocapacitive properties of MoS$_2$ nanoparticles. This material demonstrated a sodium-ion energy storage system that was characterized by intercalation pseudocapacitance. The quantitative electrochemical kinetic analysis shows that over 90% of the storage in this system is capacitive. These fast rates overlap with the performance characteristics of double-layer electrochemical capacitors, while delivering much higher capacities as a result of the Faradaic based charge storage. We also coupled the electrochemical information with synchrotron based *operando* XRD on this system to elucidate the structural origins of the fast pseudocapacitive charge storage. We demonstrated that the sodium ions can migrate through the VdW gaps extremely fast when they are not impeded by a
slow phase transition. We believe that these results demonstrate the attractiveness of chalcogenide based material as high performance sodium-ion hosts. Moreover, our results provide a clear metric in determining and distinguishing the intercalation pseudocapacitance charge storage mechanism.

In the last section of this dissertation (Appendix A), I will discuss the studies that were carried out at the Naval Research Laboratory in Washington, D.C. where we investigated the effect of cation vacancies on ion-intercalation (both Li- and Na-ions). Vanadium-substituted iron oxide aerogels (2:1 Fe:V ratio; VFe$_2$O$_x$) were synthesized using an epoxide-initiated sol–gel method to form high surface-area, mesoporous materials in which the degree of crystallinity and concentration of defects are tuned via thermal treatments under controlled atmospheres. We correlated the electrochemical charge-storage properties of a series of VFe$_2$O$_x$ aerogels with their degree of order and chemical state, as verified by X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy. We found that the disordered O$_2$-heated VFe$_2$O$_x$ aerogel yielded the highest Li$^+$- and Na$^+$-insertion capacities.
Chapter 7. References


35. Tsai, C.-C. & Teng, H. Structural features of nanotubes synthesized from NaOH treatment


68. Miyamoto, N., Kuroda, K. & Ogawa, M. Aggregation of a cationic cyanine dye


92. Kawabe, Y. *et al.* A comparison of crystal structures and electrode performance between Na$_2$FePO$_4$F and Na$_2$Fe$_{0.5}$Mn$_{0.5}$PO$_4$F synthesized by solid-state method for rechargeable Na-ion batteries. *Electrochemistry* **80**, 80–84 (2012).


99. Song, W. *et al.* Na$_2$FePO$_4$F cathode utilized in hybrid-ion batteries: a mechanistic

100. Lee, I. K., Shim, I.-B. & Kim, C. S. Phase transition studies of sodium deintercalated Na$_{2-x}$FePO$_4$F ($0 \leq x \leq 1$) by Mössbauer spectroscopy. *J. Appl. Phys.* **109**, 07E136 (2011).


131. Liang, Y. *et al.* Rechargeable Mg batteries with graphene-like MoS$_2$ cathode and


Appendix A. Supporting Information for Chapter 2. Modulation of Titanate Morphologies in Graphene Composites for High-Performance Lithium and Sodium-Ion Insertion

Figure A.1. BJH desorption dV/dlog(D) pore volume plots for (a) NS and (b) NT.

Figure A.2. Raman spectra of (a) NS and NS:RGO and (b) NT and NTG to show the existence of RGO.
Figure A.3. Cyclic voltammograms of all Ti$_3$O$_7$ samples swept at 1 mV s$^{-1}$ in a (a) Li and (c) Na-ion system. Capacity vs. charge time for all Ti$_3$O$_7$ samples cycled in a (b) Li and (d) Na-ion system.
Figure A.4. Galvanostatic charge-discharge curves of (a) NT, (b) NTG, (c) NS, and (d) NSG cycled in a Li-ion system.
Figure A.5. (a) Summary of galvanostatic performance (capacity vs. cycle number) for NT, NTG, NS, and NSG cycled in a Li-ion system. Individual galvanostatic performance plots showing capacity and coulombic efficiency vs. cycle number for (b) NT, (c) NTG, (d) NS, and (e) NSG for Li-ion system.
Figure A.6. Galvanostatic charge-discharge curves of (a) NT, (b) NTG, (c) NS, and (d) NSG cycled in a Na-ion system.
Figure A.7. (a) Summary of galvanostatic performance (capacity vs. cycle number) for NT, NTG, NS, and NSG cycled in a Na-ion system. Individual galvanostatic performance plots showing capacity and coulombic efficiency vs. cycle number for (b) NT, (c) NTG, (d) NS, and (e) NSG for Na-ion system.
Appendix B. Supporting Information for Chapter 3. \( \text{Na}_2\text{Ti}_3\text{O}_7 \) Nanoplatelets and Nanosheets Derived from a Modified Exfoliation Process for Use as a High Capacity Sodium-Ion Negative Electrode

Energy Dispersive Spectroscopy and X-Ray Diffraction of Proton-Exchanged \( \text{Na}_2\text{Ti}_3\text{O}_7 \)

![Energy Dispersive Spectroscopy and X-Ray Diffraction](image)

Figure B.1. Energy Dispersive Spectroscopy tracking the amount of atomic sodium upon proton-exchanging \([\text{H}_x\text{Na}_{2-x}]\text{Ti}_3\text{O}_7\) for 1, 2, and 3 days.
Figure B.2. X-ray diffraction patterns of (a) proton-exchanged $[\text{H}_x\text{Na}_{2-x}]\text{Ti}_3\text{O}_7$ and (b) exfoliated Na$_2$Ti$_3$O$_7$ after 1-day, 2-day, and 3-days of reaction. Based on integrated intensities, it is evident that the concentration of Na$_2$Ti$_3$O$_7$ NP decreases with longer duration of proton exchange.
Figure B.3. Exfoliation flowchart of Na$_2$Ti$_3$O$_7$ for obtaining Na$_2$Ti$_3$O$_7$ NP-NS, Na$_2$Ti$_3$O$_7$ NP, and PA/Ti$_3$O$_7$ NS.

For the current project, where there are two different nanoscale morphologies, nanosheets and nanoplatelets (Na$_2$Ti$_3$O$_7$ NP-NS), differential centrifugation was used to isolate a specific morphology. Differential centrifugation is commonly employed for biological systems where progressively higher centrifugation force is used to isolate cellular components of decreasing size and density$^{69}$. The separation of these cellular components is based on their sedimentation rate through an imposed centrifugal force which, in turn, is dependent on the size and shape of the cellular components. This added step is illustrated in Fig. B.3 as Step 4, where pure nanoplatelets (Na$_2$Ti$_3$O$_7$ NP (in green)) are isolated and used as a control sample. Nanosheets (PA/Ti$_3$O$_7$ NS) were previously isolated during Step 3 and this is used as the control sample for pure nanosheets. Experimentally, the Na$_2$Ti$_3$O$_7$ NP-NS solution was subjected to an additional centrifuge step at
1000, 2500, 5000, 7500, 10000, and 14500 rpm for 10 minutes (Fig. B.4). Based on the size and density of the nanoplatelets and nanosheets, we evaluated two separate solutions, one of the sedimented particles and the other being the supernatant. As illustrated in Fig. B.4, the sedimented particles which are centrifuged 1000 rpm contained the highest concentration of nanoplatelets (Na$_2$Ti$_3$O$_7$ NP). With the use of higher speeds of at least 5000 rpm, the supernatant contained pure nanosheets (PA/Ti$_3$O$_7$ NS).

As mentioned above, slower centrifuge speeds led to a higher concentration of Na$_2$Ti$_3$O$_7$ NP while higher speeds led to the isolation of pure PA/Ti$_3$O$_7$ NS. X-ray diffraction (XRD) was used to verify the phase and quantify the ratio of nanoplatelets to nanosheets. The XRD pattern of the control sample for PA/Ti$_3$O$_7$ NS is shown in Fig. B.5. The control sample for Na$_2$Ti$_3$O$_7$ NP shows a sharp (100) reflection at 10.5° accompanied by an additional (004) reflection at 28°. Although there is a small peak at 8° which indicates the presence of some nanosheets, we have used this sample as the control since it is comprised of a high concentration of Na$_2$Ti$_3$O$_7$ NP. The relative concentration of the two different morphologies can be estimated by the ratio of the
integrated intensities of the two most intense XRD reflections (8° for nanosheets, 10.5° for nanoplatelets). For Na$_2$Ti$_3$O$_7$ NP, the percentage of nanoplatelets was determined to be 70%. It will become apparent from cyclic voltammetry measurements described below that the electrochemical behavior of this material presents itself as pure Na$_2$Ti$_3$O$_7$ NP.

We used cyclic voltammetry to identify the electrochemical behavior of the two nanoscale morphologies of interest, nanoplatelets and nanosheets. As shown in Fig. B.5(b), the presence of only low potential redox peaks in cyclic voltammograms (CVs) between 0.1 and 0.5 V $\text{vs. } \text{Na/Na}^+$ closely resembles the electrochemical response of bulk Na$_2$Ti$_3$O$_7$.$^{52,58,152}$ On the other hand, PA/Ti$_3$O$_7$ NS are electrochemically active between 0.5 and 2.5 V $\text{vs. } \text{Na/Na}^+$ (Fig. B.5(c)). Thus, the specific redox peaks associated with nanoplatelets and nanosheets occur at very different potentials. Na$_2$Ti$_3$O$_7$ NP occur at 0.18 and 0.26 V ($\text{vs. } \text{Na/Na}^+$) for the cathodic and anodic peaks, respectively, whereas the of PA/Ti$_3$O$_7$ NS shows redox peaks at 1.1 and 1.2 V ($\text{vs. } \text{Na/Na}^+$) for each cathodic and anodic peak, respectively. The CVs in Figs. S5(b) and S5(c) provide the control measurements needed to independently assess the electrochemical properties of the nanoplatelets and nanosheets. As shown in Fig. S3, we are able to adjust synthesis conditions and prepare materials which contain both nanoplatelets and nanosheets (Na$_2$Ti$_3$O$_7$ NP-NS). As illustrated in Fig. B.5(d), the electrochemical signature of Na$_2$Ti$_3$O$_7$ NP-NS exhibits two coupled redox peaks, one which comes from the nanoplatelet morphology and the other arising from the nanosheet geometry. The presence of these low potential redox peaks in the CVs between 0.1 and 2.5 V $\text{vs. } \text{Na/Na}^+$ for Na$_2$Ti$_3$O$_7$ NP-NS enables this material to be considered a prospective negative electrode. The CVs for both the sedimented particles and supernatant from differential centrifugation experiments are shown in Fig. B.6.
Figure B.5. (a) X-ray diffraction patterns of control samples. Corresponding cyclic voltammograms cycled at 5 mV s\(^{-1}\) from 0.1 to 2.5 V vs. Na/Na\(^{+}\) for (b) Na\(_2\)TiO\(_7\) NP (inset CV is of bulk Na\(_2\)TiO\(_7\)). Slower rates were required to clearly exhibit redox peaks at low potentials), (c) PA/TiO\(_3\) NS, and (d) Na\(_2\)TiO\(_7\) NP-NS.
Figure B.6. Cyclic voltammograms for Na$_2$Ti$_3$O$_7$ NP-NS samples centrifuged between 1000 and 14500 rpm (a) sedimented particles (b) supernatant.

**Atomic Force Microscopy**

Figure B.7. Atomic force microscopy images and depth profile for two separate spots of pure PA/Ti$_3$O$_7$ NS.
Estimating the Number of Layers using X-Ray Diffraction

The estimated number of layers for all samples are tabulated in Table B.1\textsuperscript{72}. For bulk Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}, the crystallite thickness and number of layers were calculated to be 39 nm and 47 layers, respectively. Upon exfoliation of this compound, the crystallite size of PA/Ti\textsubscript{3}O\textsubscript{7} NS was found to be 9.1 nm with roughly 9 layers. For pure Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} NP, the number of layers was estimated to be 37. Clearly, the partial exfoliation of bulk Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} reduces the size of this material with a preferential orientation in the (h00) direction.

The number of layers was estimated by dividing the crystallite size, $t$, by the d-spacing $d$ (Equation 1).

$$\text{Number of Layers} = \frac{t}{d}$$  

(1)

The crystallite size was calculated using Scherrer’s equation (Equation 2) where $k$ is the shape factor, $\lambda$ is the x-ray wavelength (1.54 Å), $\beta$ is the FWHM, and $\theta$ is the Bragg angle.

$$t = \frac{k \lambda}{\beta \cos \theta}$$  

(2)

The $d$-spacing was calculated using Bragg’s Law where $n$ is an integer (1 for 1\textsuperscript{st}-order diffraction), $\lambda$ is the x-ray wavelength (1.54 Å), $d$ is the spacing between layers of atoms, and $\theta$ is the Bragg angle

$$n \lambda = 2d \sin \theta$$  

(3)
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<th>Material</th>
<th>$\theta$</th>
<th>t (nm)</th>
<th>d (nm)</th>
<th>No. of layers</th>
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<td>47</td>
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<td>PA/(\text{Ti}_3\text{O}_7) NS</td>
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<td>9.1</td>
<td>1.1</td>
<td>9</td>
</tr>
<tr>
<td>(\text{Na}_2\text{Ti}_3\text{O}_7) NP</td>
<td>10.6</td>
<td>37.0</td>
<td>0.84</td>
<td>37</td>
</tr>
</tbody>
</table>

Table B.1. Estimated number of layers calculated using Scherrer’s equation and known \(d\)-spacing.
Figure B.8. Total X-ray scattering measurements for Na$_2$Ti$_3$O$_7$ NP-NS, bulk Na$_2$Ti$_3$O$_7$, and calculated Na$_2$Ti$_3$O$_7$ NP.

Figure B.9. Azimuthal scan of Na$_2$Ti$_3$O$_7$ NP-NS showing morphological anisotropy.
Figure B.10. X-ray photoelectron spectra of survey scans for (a) Bulk Na$_2$Ti$_3$O$_7$ (b) PA/Ti$_3$O$_7$ NS (c) Na$_2$Ti$_3$O$_7$ NP-NS and (d) Na$_2$Ti$_3$O$_7$ NP-NS after cycling in 1M NaClO$_4$ in PC:FEC.
Figure B.11. N 1s high-resolution fitted X-ray photoelectron spectra of (a) bulk Na$_2$Ti$_3$O$_7$ (b) PA/Ti$_3$O$_7$ NS (c) Na$_2$Ti$_3$O$_7$ NP-NS (d) Na$_2$Ti$_3$O$_7$ NP-NS after cycling in 1M NaClO$_4$ in PC:FEC.
Figure B.12. Na 1s high-resolution fitted X-ray photoelectron spectra of (a) bulk Na$_2$Ti$_3$O$_7$ (b) PA/Ti$_3$O$_7$ NS (c) Na$_2$Ti$_3$O$_7$ NP-NS (d) Na$_2$Ti$_3$O$_7$ NP-NS after cycling in 1M NaClO$_4$ in PC:FEC.
<table>
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<th>Material</th>
<th>Na 1s at%</th>
<th>N 1s at%</th>
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</thead>
<tbody>
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<td>3.6</td>
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<tr>
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<td>3.3</td>
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<td>$\text{Na}_2\text{Ti}_3\text{O}_7$ NP-NS after cycling</td>
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<td>0.6</td>
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Table B.2. Quantitative atomic percentages of Na 1s and N 1s for bulk $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{PA/}\text{Ti}_3\text{O}_7$ NS, $\text{Na}_2\text{Ti}_3\text{O}_7$ NP-NS, and $\text{Na}_2\text{Ti}_3\text{O}_7$ NP-NS after cycling in 1M NaClO$_4$ in PC:FEC.
Supplemental Electrochemical Characterization

Figure B.13. (a) Cyclic voltammograms of Na$_2$Ti$_3$O$_7$ NP swept from 1 – 20 mV s$^{-1}$ and $b$-value extrapolation from 1 – 20 mV s$^{-1}$ for both (a) Na$_2$Ti$_3$O$_7$ NP and (b) PA/Ti$_3$O$_7$ NS.

Figure B.14. (a) 1$^{st}$ and 5$^{th}$ cycle discharge curve at 1C. The irreversible capacity on the 1$^{st}$ cycle is associated with forming a stable SEI layer. (b) Long-term cycling for Na$_2$Ti$_3$O$_7$ NP-NS cycled at 10C for 1000 cycles.
Figure B.15. Comparison of capacity vs. cycle number for PA/Ti$_3$O$_7$ NS and Na$_2$Ti$_3$O$_7$ NP-NS. Stable capacities are observed after 10 cycles for Na$_2$Ti$_3$O$_7$ NP-NS.

Figure B.16. Cyclic voltammogram of Na$_2$Ti$_3$O$_7$ NP and Na$_2$Ti$_3$O$_7$ NP-NS cycled at 5 mV s$^{-1}$ at the (a) 1$^{st}$ cycle and (b) 2$^{nd}$ cycle.
References


Appendix C. Supporting Information for Chapter 4. Na₂FePO₄F Nanoparticles for High-Rate Sodium-Ion Cathodes

Figure C.1. Transmission electron microscopy image of NFPF-SSR.

Figure C.2. TGA/DSC analysis of NFPF-P heat-treated at 450°C under argon atmosphere with an isothermal hold for 5 minutes at 450°C.
Figure C.3. X-ray diffraction patterns of NFPF-P heat-treated at various temperatures. Dotted red line indicates decomposition of Na$_2$FePO$_4$F to oxidized Fe$_2$O$_3$ and metallic Fe.
Figure C.4. \( \log (\text{peak current, } i) \) versus \( \log (\text{sweep rate, } mV/s) \) of (a) NFPF-SSR, (b) NFPF-P, (c) NFPF-450CAr, and (d) NFPF-rGO.
Figure C.5. $b$-value determination of (a) NFPF-SSR, (b) NFPF-P, (c) NFPF-450CAr, and (d) NFPF-rGO.
Figure C.6. Capacitive contribution determination of (a) NFPF-SSR, (b) NFPF-P, (c) NFPF-450CAr, and (d) NFPF-rGO cycled at 1 mV s⁻¹.
Figure C.7. Galvanostatic charge-discharge curves of (a) NFPF-SSR, (b) NFPF-P, (c) NFPF-450CAr, and (d) NFPF-rGO with C-rates imposed from C/10 to 20C.
Figure C.8. Electrochemical cycling performance of (a) NFPF-SSR, (b) NFPF-P, (c) NFPF-450CAr, and (d) NFPF-rGO.
Appendix D. Supporting Information for Chapter 5. Crossover from Slow Sodium-Ion Storage in MoS$_2$ to Ultrafast Intercalation Pseudocapacitance in MoS$_2$ Nanoparticles by Phase Transition Suppression

MoS$_2$ was prepared by a two-step synthesis process, which enables control over the final nanostructure. MoO$_2$ nanocrystals were synthesized using a scalable hydrothermal method, which were then converted to MoS$_2$ using thermal annealing in hydrogen sulfide gas. While single-step solution methods do exist to synthesize MoS$_2$ directly, these low temperature routes tend to produce poorly crystalline material. The thermal sulfurization method we use in this study produces well crystallized MoS$_2$, which positively impacts the fast pseudocapacitive charge storage mechanism observed in this system. Fig. D1(a) – D1(c) shows the transmission electron microscope (TEM) images of the MoS$_2$ nanocrystals at several different magnifications, and illustrates that the primary particle size is between 20-50 nm. The (002) lattice fringes can clearly be seen in Fig. D1(c), and guest species, like sodium ions, can intercalate between these layers reversibly. Fig. D1(d) shows the powder X-ray diffraction (PXRD) pattern of the MoS$_2$ nanocrystals, which matches the hexagonal MoS$_2$ polytype (JCPDS No. 37-1492). Significant peak broadening is observed in the PXRD pattern, and the calculated Scherrer size from the (002) peak is 7 nm (Fig. D1(e)). The broadening due to finite size effects, lattice defects, and curvature of the MoS$_2$ sheets can be seen in Fig. D1(c). The VdW gap width was calculated from the (002) peak in PXRD using aluminum foil as an internal reference, and the results show this gap is expanded to 0.63 nm – a 2.4% expansion compared to bulk MoS$_2$. Another important structural feature for pseudocapacitive charge storage is high surface area, which allows high ionic flux at the surface of the electrode-electrolyte interface. The nitrogen isotherms shown in Fig. D1(f) were used to calculate a surface area of 35 m$^2$g$^{-1}$ using the Brunauer-Emmett-Teller method.
Figure D.1. Transmission electron microscopy images of the MoS$_2$ nanocrystals at different magnification. These images show that the primary particle size is sub-50 nanometer (a-c) Powder X-ray diffraction of the MoS$_2$ nanocrystals indicating that the material is phase pure and crystallize in the hexagonal MoS$_2$ polytype. (d,e) The Scherrer width was calculated from the deconvoluted (002) MoS$_2$ peak, and the 7 nm width indicates a high degree of lattice disorder. Nitrogen isotherms of the MoS$_2$ nanocrystals collected at 77K. (f) The surface area was calculated using the Brunauer-Emmett-Teller method.
Figure D.2. Pre-cycling galvanostatic traces of bulk (a) and nano (b) MoS$_2$ that were carried out in order to convert the MoS$_2$ from the semiconducting 2H phase to the conductive 1T phase. The disappearance of the plateaus below 1V in (a) indicate that the majority of the 2H phase of MoS$_2$ was converted to the 1T phase of MoS$_2$ after the 1$^{st}$ cycle. The same 2H to 1T phase transition occurs more slowly in the MoS$_2$ nanocrystals because many nucleation events are required to fully convert this material to the 1T phase.

In Fig. D.3 a, the first XRD pattern of bulk MoS$_2$ shown in the stack plots correspond to a cell at OCV after being cycled four times between 0.55 V – 2.50 V vs. Na/Na$^+$. Three phases are present, and the identification of those phases will be described in more detail in this ESI: predominately 1T (0.89 Å$^{-1}$, $d$ = 7.08), a trace of triclinic phases (1.11 Å$^{-1}$, $d$ = 5.66), and a small amount of 2H (0.97 Å$^{-1}$, $d$=6.48). The 1T phase can convert back to the 2H phase, which most likely occurred while our samples were transported to the synchrotron for analysis (voltage during transportation was ~2.50 V vs. Na/Na$^+$). The peak at 0.97 Å$^{-1}$ corresponding to the 2H (002) lattice is demarcated with a red circle and corresponds to the broad electrochemical signature, also demarcated by a red circle, in the dQ/dV plot in Fig. S3 b. As Na-ions are inserted, the XRD peak at 0.97 Å$^{-1}$ decreases in intensity as it is converted into the 1T and triclinic phase.
Figure D.3. (a) Magnified operando X-ray diffraction data for bulk MoS$_2$ displaying a peak at 0.97 Å$^{-1}$, which corresponds to the 2H phase of MoS$_2$. (b) dQ/dV-V plot shows the redox peak for 2H to 1T phase transition.

In addition to the 1T phase converting to the 2H phase at rest, the conversion can also be driven galvanostatically above 2.46 V vs. Na/Na$^+$. Therefore, the pseudocapacitive kinetics described in this paper along with the long cycle lifetimes are contingent on limiting the upper cut-off voltage to 2.50 V vs. Na/Na$^+$. 
Figure D.4. (a) charge-discharge curve of bulk MoS$_2$ at C/4.5 rate with a voltage window of 0.55 – 2.7 V. (b) selected diffraction pattern of In-situ X-ray diffraction of bulk MoS$_2$ discharged to 2.69 V. Discharging above 2.5 V leads to the re-appearance of the starting 2H-MoS$_2$ phase.

Most micrometer MoS$_2$ powders consist of anisotropic particles (typically plates), which align in the plane of the current collector. When XRD patterns of those electrodes are collected in reflection geometry, as is standard in most operando studies on this material,$^{137,156}$ only the (00$l$) planes are in the appropriate geometry to diffract Fig. D.5. We collected our diffraction in transmission geometry, using extremely high synchrotron photon flux, so we observed weakly-scattering peaks in our diffraction patterns, related to the covalent crystallinity in a triclinic NaMoS$_2$ phase, that are not typically observed in other studies.$^{137}$ Cartoon representations of the different collection geometries are shown in Fig. D.5. Diffraction of an anisotropic sample like MoS$_2$ in these different collection geometries can lead to systematic peak absences. The bulk samples we measured are anisotropic, so in this geometry the (hk0) planes will diffract strongly allowing us to clearly observe reflections for triclinic NaMoS$_2$. The ability to distinguish this peak in our diffraction patterns enables clear identification of the phases present during charge storage.
In order to aid in phase identification, XRD patterns of 2H-MoS\(_2\), 1T-Na\(_x\)MoS\(_2\), and triclinic Na\(_x\)MoS\(_2\) were simulated (shown in Fig. 5.2 of the main text). These patterns all share the intense peak ca. 1.0 Å\(^{-1}\), corresponding to the vdW gaps in MoS\(_2\). The reduction in symmetry of the 1T crystal structure (trigonal crystal symmetry) compared to the 2H crystal structure (hexagonal crystal symmetry) leads to patterns with clearly distinguishable features above Å\(^{-1}\). The triclinic phase has the least symmetry, and many more peaks in the simulated patterns. One clearly identifiable peak in the triclinic phase that is not present in the 2H or 1T phases shows up at 1.1 Å\(^{-1}\), which enables clear identification of that phase.

While the triclinic phase of NaMoS\(_2\) has not been described often in the literature, Petkov et al. identified a triclinic phase of LiMoS\(_2\) using atomic pair distribution analysis\(^{157}\). The small coherence length of the triclinic structure made identification by powder XRD elusive. We think in our study the high synchrotron photon flux combined with the ideal crystallite orientation (leading to amplification of signal compared to a randomly oriented sample) has enabled us to observe the triclinic phase of NaMoS\(_2\) in this study.
Figure D.5. Cartoon representation of different collection geometries and their resulting systematic X-ray diffraction peak absences.

References


Appendix E. Defective by Design: Vanadium-Substituted Iron Oxide Nanoarchitectures as Cation-Insertion Hosts for Electrochemical Charge Storage

Chapter E.1. Introduction and Background

High-performance materials used as positive electrodes for rechargeable Li-ion batteries often contain expensive, toxic, and/or strategic metals (in the form of pure or mixed-metal oxides such as LiCoO$_2$), driving the search for less expensive, nontoxic alternatives. One such example is LiFePO$_4$, which offers a thermodynamically favorable Li$^+$-insertion potential of $\sim$3.5 V vs. Li and a high reversible capacity (160 mA h g$^{-1}$), in conjunction with the cost and environmental benefits inherent to iron-based materials.\(^1\) Certain iron oxides (FeO$_x$), particularly those that have cation-defective structures, also exhibit promise as positive electrode materials. For example, maghemite ($\gamma$-Fe$_2$O$_3$, more accurately denoted as Fe$^{3+}_{2.67}$\(\square_{0.33}\)O$_4$) is a cation-deficient spinel phase that inserts Li$^+$ into structural cation vacancies at more positive potentials than observed in the defect-free analogue, magnetite (Fe$_3$O$_4$).\(^2,3,4,5\)

The cation-vacancy population of the $\gamma$-Fe$_2$O$_3$ structure can be further increased by substituting a fraction of the Fe$^{3+}$ sites with metal cations of higher oxidation state, such as Mo$^{6+}$ or V$^{5+}$.\(^6\)\(^,\)\(^7\) We recently reported that a nanocrystalline Mo-substituted ferrite (Mo$_{0.59}$Fe$_{1.50}$\(\square_{0.91}\)O$_4$·$n$H$_2$O) provides $>4\times$ improvement in specific capacity for Li$^+$-insertion relative to an analogous $\gamma$-Fe$_2$O$_3$ material.\(^8,9\) The population of electrochemically active defects in metal oxides can also be amplified when these materials are expressed in nanoscale forms,\(^10\) ranging from hollow nanospheres\(^11,12\) to three-dimensionally (3D) ultraporous nanoarchitectures such as aerogels.\(^13\) Aerogels exhibit high specific surface areas (100–600 m$^2$ g$^{-1}$) that encourage surface-sited defect formation, while providing other structural characteristics beneficial to
electrochemical functionality: (i) through-connected, covalently bonded networks of nanometric particles that electrically wire the electrode architecture; (ii) through-connected networks of mesopores and/or macropores that enable efficient diffusion and transport of molecules and ions; and (iii) nanoscale domains that minimize the solid-state diffusion distance for ion insertion.

Previous investigations of V\textsubscript{2}O\textsubscript{5} aerogels as Li\textsuperscript{+}-insertion hosts illustrate how the aerogel framework can enhance electrochemical performance\textsuperscript{13, 14, 15, 16}. For example, while microcrystalline V\textsubscript{2}O\textsubscript{5} only intercalates \(\sim 2\) Li\textsuperscript{+} per formula unit\textsuperscript{17}, V\textsubscript{2}O\textsubscript{5} aerogels insert \(> 4\) Li\textsuperscript{+} per formula unit (chemically or electrochemically)\textsuperscript{13, 18, 19}. Spectroelectrochemical analysis of Li\textsuperscript{+}-insertion into V\textsubscript{2}O\textsubscript{5} aerogels implies that beyond 2 Li\textsuperscript{+} per V\textsubscript{2}O\textsubscript{5}, the increase in Li\textsuperscript{+} content may not occur by traditional insertion mechanisms but rather by processes at accessible defect sites that are not accompanied by a change in the oxidation state of vanadium\textsuperscript{20}.

Herein, we combine these two materials design strategies to produce deliberately defective cation-insertion hosts based on V-substitution into a \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}–like structure that is expressed as an ultraporous, high surface-area aerogel. Vanadium-substituted iron oxide (2:1 Fe:V ratio; VFe\textsubscript{2}O\textsubscript{x}) aerogels are achieved using an epoxide-driven sol–gel synthesis\textsuperscript{21, 22, 23, 24} that yields amorphous oxides of the desired stoichiometry, but whose crystallinity and defective nature can be tuned by subsequent thermal processing under controlled atmospheres. We explore the cation-insertion properties of VFe\textsubscript{2}O\textsubscript{x} aerogels as a function of crystalline order, V and Fe oxidation state, and surface area/porosity. Direct thermal processing under flowing O\textsubscript{2} at 300°C produces X-ray-amorphous VFe\textsubscript{2}O\textsubscript{x} aerogels that exhibit reversible Li\textsuperscript{+}- and Na\textsuperscript{+}-insertion specific capacities approaching 130 mA h g\textsuperscript{−1} and 70 mA h g\textsuperscript{−1}, respectively, a result of high specific surface area (231 m\textsuperscript{2} g\textsuperscript{−1}), a defective \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3} local structure, and V present in the +5 oxidation state. The local and long-range atomic structures and the chemical state of the VFe\textsubscript{2}O\textsubscript{x} aerogels as a function of
thermal treatment were elucidated by X-ray absorption spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy; material morphology and composition were examined by electron microscopy and energy-dispersive spectroscopy.

Chapter E.2. Experimental

Chapter E.2.1. VFe₂Oₓ Aerogel Synthesis and Processing

The VFe₂Oₓ aerogels were synthesized by adapting the alkoxide-precursor, epoxide-initiated sol–gel method\(^{25}\) using an Fe-to-V ratio of 2:1. The use of vanadium salts rather than an alkoxide precursor led to precipitates rather than gels. In a typical synthesis, FeCl₃•6H₂O (3.0846 g; 97%, Sigma-Aldrich) was dissolved in 10 mL of ethanol (200 proof, Warner-Graham Company) via sonication and then chilled in an aqueous ice bath. In a second container, vanadium triisopropoxide (1.3832 g; 96%, Alfa Aesar; stored in a refrigerator at 35°C before use) was added drop-wise into 20 mL of ethanol pre-chilled in an aqueous ice bath. The vanadium solution was equilibrated for a few minutes and then chilled to –78°C in a dry ice–ethanol bath. The two chilled solutions were combined with an additional 10 mL rinse with ethanol to ensure quantitative transfer of the Fe\(^{3+}\); the V-Fe solution was equilibrated for ~3 min in the dry ice–ethanol bath. Next, 12 mL of propylene oxide (Sigma-Aldrich 99%; passed through a column of activated alumina and stored in a refrigerator at 35°C before use) was quickly added to the container and the solution was covered with Parafilm\textsuperscript{TM}. The solution was equilibrated for ~5 min in the –78°C bath and then placed in an aqueous ice bath and stirred for ~45 min, during which time the solution changed from translucent orange to dark reddish-brown. The sol was removed to ambient temperature and gelation occurred within 10 min. The gel was aged overnight with the Parafilm\textsuperscript{TM} seal maintained; the mother liquor within the gel pores was then exchanged with several 200-mL
The acetone-exchanged gels were transferred under excess acetone into a supercritical drier (Polaron, Quorum Technologies), and solvent-exchanged with liquid CO$_2$ at 10°C. The CO$_2$ was then taken to 44°C and 9 MPa, well beyond its supercritical point of 31°C and 7.4 MPa, before the pressure was released. For comparison, unsubstituted FeO$_x$ aerogels were prepared by the epoxide method using the FeCl$_3$•6H$_2$O precursor, ethanol solvent, and propylene oxide gel-initiator as described above (i.e., the same molar ratio of cations to epoxide and cation to solvent), but carried out under ambient temperature (~20°C).

The as-synthesized VFe$_2$O$_x$ and FeO$_x$ aerogels were calcined to 300°C in alumina boats within a calibrated tube furnace (MTI Corporation OTF-1200X) under flowing Ar or O$_2$ at ~50 cm$^3$ min$^{-1}$ with heating and cooling ramp rates of 1°C min$^{-1}$ and 4-h dwell times at the calcining temperature. Samples heated under high and low partial pressure of oxygen (p$_{O_2}$) are referred to as 300-O$_2$ and 300-Ar, respectively. The samples designated as 300-Ar-O$_2$ were first subjected to a low p$_{O_2}$ heat treatment, cooled to room temperature and then heated under high p$_{O_2}$ using the same temperature, ramp rate, and dwell time.

### Chapter E.2.2. Materials Characterization

Surface areas and pore-size distributions of the VFe$_2$O$_x$ and FeO$_x$ aerogels were measured using nitrogen physisorption (Micromeritics ASAP 2020 porosimeter). All samples were degassed at 80°C for 12 h, backfilled with N$_2$ at room temperature, and then immediately placed on the instrument for characterization. Surface area was determined from the linear portion of the adsorption isotherm using the model of Brunauer–Emmet–Teller. Pore size distributions were
calculated from the entire adsorption isotherm data using Micromeritics DFTPlus software (DFT model for a cylindrical geometry and Halsey curve thickness).

Aerogel morphology was imaged using scanning electron microscopy (SEM; Carl Zeiss Leo Supra 55 microscope operating at 5 keV) and transmission electron microscopy (TEM; JEOL JEM 2200FS microscope operating at 200 kV). Elemental analysis was made with the SEM using energy dispersive spectroscopy (EDS; operating at 20 keV). For SEM measurements, the aerogel powders were mounted onto aluminum SEM stubs using double-sided carbon tape; for TEM measurements, the powders were ground in isopropanol and drop cast onto lacey carbon substrates.

The temperatures necessary for crystallization and volatilization of synthesis byproducts as a function of calcining atmosphere were characterized using simultaneous thermoanalytical and calormetric measurements with a Netzsch STA 449 F1 Jupiter thermogravimetric analyzer (TGA/DSC). Approximately 10 mg of as-synthesized aerogel was placed in an alumina crucible and equilibrated under the desired atmosphere for ~1 h before heating. The samples were heated to 550°C at 10°C min⁻¹ in either Ar or O₂.

Powder X-ray diffraction (PXRD) profiles were collected on a Rigaku SmartLab X-ray diffractometer with a fixed CuKα radiation (λ = 1.5406 Å). Scans were recorded from 20 to 80°2θ, with a 0.02° step size and an integration time of 1 s per step. For materials where the PXRD indicated crystallinity, average crystallite sizes were calculated from the peak indexed to the (400) peak of the magnetite crystal structure; we chose the (400) reflection because it is intense and sufficiently isolated to avoid peak overlap from other reflections. Synchrotron PXRD data for 300-Ar and 300-Ar-O₂ VFe₂Oₓ aerogels were collected at beamline 11-BM at the Advanced Photon
Source at Argonne National Laboratory ($\lambda = 0.413851 \text{ Å}$). The data were refined with the General Structure Analysis System (GSAS) with EXPGUI;\textsuperscript{26,27} models of maghemite ($P4_32_12$ ICDS #87121) and magnetite ($Fd-3m$, ICDS #20596) and assuming the stoichiometry for the aerogel was $\text{Fe}_{8x/(8+x)}\text{V}_{(24-8x)/(8+x)}\text{O}_4$ ($x \approx 2$).

X-Ray Photoelectron Spectroscopy (XPS) was used to examine the chemical state and relative concentrations of Fe, V, and O using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer at a chamber pressure $<5.0 \times 10^{-8}$ torr and equipped with a monochromatic Al Kα source (1486.68 eV) using a 400-μm elliptical spot size. The VFe$_2$O$_x$ aerogel specimens were packed into wells of the powder module sample holder. The spectra were obtained at an energy step-size of 0.15 eV by averaging 25 scans of the Fe$2p$, V$2p$, O$1s$, C$1s$, and Cl$2p$ regions (the Cl region was examined to ensure $>99\%$ conversion/removal of chloride). The spectra were analyzed with Avantage® software version 5.35 using a Shirley-derived background subtraction model and peak-shifting relative to the adventitious C$1s$ peak of 284.6 eV. The V$2p_{3/2}$ peaks were fitted with a floating Gaussian–Lorentzian ratio.

Room-temperature V and Fe K-edge X-ray absorption spectra of VFe$_2$O$_x$ and FeO$_x$ aerogels for as-synthesized materials and following heat treatments were collected in transmission mode at beamline 10-ID-B at the Advanced Photon Source at Argonne National Laboratory. The samples were prepared by attaching the powders to scotch tape and then folding several layers of the powder-tape assembly together; a method that gives reasonable results for homogenized powders such as aerogel materials. The energy scale was calibrated with respect to the first inflection point energies of the Fe and V foil standards at 7112.0 and 5465.0 eV, respectively. The pre-edge background was determined from a linear fit to the energy range of $-150$ to $-30$ eV relative to the edge energy. The normalization step was determined from a cubic polynomial fit.
over the energy range 150 to ~800 eV relative to the edge energy. The half-height energy was used
to define the wave number \( k = 0 \). The background for the extended X-ray absorption fine structure
(EXAFS) was determined using cubic spline procedures over the range 2–12 Å\(^{-1}\) with the FT range
set to 3–11 Å with \( k^3 \)-weighted EXAFS spectra and a Hanning window of 1.0 Å\(^{-1}\). The XAFS data
analysis was carried out using the IFEFFIT suite of programs (Athena and Artemis).\(^{28,29}\)

**Chapter E.2.3. Electrode Preparation**

Aluminum foil current collectors (Alfa Aesar; either 0.5-mm thick, 99.9% metals basis or
0.13-mm thick, 99.9995% metals basis) for three-electrode and coin-cell configurations were
prepared by sanding one side of the foil with 120-grit sand paper and then alkaline-etching in 1 M
NaOH at ambient temperature for 20 min, rinsing with deionized water, and acid-etching at 80°C
in 1 M HCl. The etched foils were rinsed with deionized water and air-dried at 100°C overnight.
The current collectors for three-electrode half-cell configurations were 0.5-mm thick and cut into
2 cm × 1 cm pieces, whereas the foils for coin-cells were 0.13-mm thick and cut into \( \frac{1}{2} \)“-diameter
disks.

Active cathode material inks were prepared by making a slurry in N-methyl-2-pyrrolidone
(NMP; 99.5% anhydrous, Sigma-Aldrich) of 85% active material, 8% Super P carbon black
(source) and 7% polyvinylidene fluoride binder (PVdF; Kynar® HSV 900). Approximately 15–
20 mg of active material powder was combined with carbon in a mortar and pestle and ground for
~3 min to ensure that the powders were well-mixed to which a 5% PVdF solution in NMP was
added and the wet mixture ground for 15 min. As necessary, NMP was added drop-wise to
maintain a consistency of warm honey. The slurry was applied to the current collector with a
spatula and then air dried for ~1 h followed by vacuum drying overnight at 120°C. After drying,
the electrodes were sandwiched between two weigh papers and pressed at 5000 psi and then immediately weighed and pumped into an Ar atmosphere glove box. For the half-cell electrodes, the slurries were painted onto a 1 cm × 1 cm area of the aluminum current collector, whereas for the coin-cell disks, the entire ½” face was painted with the slurry. The mass of active material was calculated as 85% of the weight of the applied film, as determined by the mass difference of the aluminum substrate before and after applying, drying, and pressing the film.

Chapter E.2.4. Electrochemical Characterization

Cyclic voltammetric measurements were made with a Solartron SI1286 Electrochemical Interface using a three-electrode configuration in an Ar atmosphere glove box. For Li⁺-insertion experiments an electrolyte of 1 M LiPF₆ in 1:1:1 ethylene carbonate:diethyl carbonate:dimethyl carbonate (BASF) was used and the reference and auxiliary electrodes were made from Li foils (250-µm thick). The Na⁺-insertion experiments were made with Na-foil auxiliary and reference electrodes in an electrolyte comprising 1 M NaClO₄ in propylene carbonate (99.7% anhydrous, Sigma-Aldrich), which was prepared in an Ar atmosphere glove box and dried with molecular sieves (3 Å, Sigma-Aldrich) before use. The cathodes were cycled between 2.0 and 4.0 V vs. Li/Li⁺ or 1.7 and 3.7 V vs. Na/Na⁺ from 0.5 to 50 mV s⁻¹. The specific capacity was determined by averaging the integrated anodic and cathodic currents and normalizing to the mass of active material on the film.

Coin-cell measurements were performed in CR 2032 coin cells (MTI corporation) that consisted of (working outward from anode side) a Teflon®-separated negative electrode can, a stainless-steel spring, two stainless-steel spacers with a 250-µm–diameter Li-foil disc attached to the second spacer, two 2400 Celgard separators, the cathode film deposited on aluminum-foil
current collector as described above, and a positive electrode can. The cells were assembled in an
Ar-filled glove box. The cathode and the Celgard separator were infiltrated with the LiPF$_6$
electrolyte at 20 mm(Hg) for 4 h in the glove box antechamber and excess electrolyte was applied
to the Li anode during cell assembly. The coin-cell cycling was controlled with an Arbin BT2000
cycler, in the range of 2 V to 4 V at 10 mA g$^{-1}$ of active material, starting with an initial charge
step.

Chapter E.3. Results and Discussion

Chapter E.3.1. Synthesis of VFe$_2$O$_x$ Aerogels

The VFe$_2$O$_x$ aerogels were synthesized using sol–gel protocols in which a proton-
scavenging epoxide (propylene oxide) drives hydrolysis and condensation of metal(aquo-hydroxy)
complexes to form metal-oxide gel networks; subsequent supercritical CO$_2$ extraction of the
liquid-filled gels produces monolithic aerogels.$^{21}$ Epoxide-based sol–gel chemistry is a versatile
route to synthesize iron oxides$^{21,22,23,24}$ as well as other transition metal and rare-earth oxides (e.g.,
Y$_2$O$_3$-stabilized ZrO$_2$, La$_{0.85}$Sr$_{0.15}$MnO$_3$, NiCo$_2$O$_4$, La$_{9.33}$Si$_6$O$_{26}$, and Gd$_{0.1}$Ce$_{0.9}$O$_2$).$^{25,30,31,32,33,34}$
Hydrated metal chlorides are the most common precursors due to their high solubility in alcohols
and water, and because chloride anions act on the protonated epoxide via nucleophilic attack to
shift the equilibrium of the hydrolysis/condensation reactions. Iron(III) chlorides behave ideally
for epoxide-based sol–gel methods,$^{35}$ but vanadium(III) chloride precursors hydrolyze too rapidly,
preferentially forming precipitates rather than stable gels. We adapted our prior strategy for
bimetallic oxide gels in which one of the metals was introduced as an alkoxide,$^{25}$ and used
vanadium tri-isopropoxide (V(′OPr)$_3$), a well-known precursor for synthesizing V$_2$O$_5$ aerogels.$^{36}$
While more stable than vanadium chloride, V(′OPr)$_3$ is still hydrolytically sensitive under ambient
conditions, thus our sol–gel reactions were performed at reduced temperatures (dry ice–ethanol bath, −72°C). In the present case, propylene oxide is added to an ethanolic solution of V(OPr)$_3$ and Fe(III) chloride, resulting in robust VFe$_2$O$_x$ gels that are ultimately processed into high surface-area, ultraporous aerogels.

**Chapter E.3.2. Characterization of VFe$_2$O$_x$ Aerogel Structure and Composition**

The as-synthesized VFe$_2$O$_x$ aerogels comprise interpenetrating networks of through-connected solid and pores with feature sizes on the order of tens of nanometers, typical for aerogel-type materials (Fig. E.1 and Fig. S1). The porous, nanostructured nature of this material is confirmed by N$_2$-sorption porosimetry, which shows specific surface area of 535 m$^2$ g$^{-1}$, cumulative pore volume of 1.6 cm$^3$ g$^{-1}$ (Table E.1), and a wide distribution of pore sizes with an average of 13 nm (Fig. S2). As expected from a low-temperature sol–gel synthesis, the as-prepared VFe$_2$O$_x$ aerogel is amorphous when examined by XRD.

![Figure E.1. Scanning electron micrographs of VFe$_2$O$_x$ aerogels: (a) as-synthesized and (b) 300-O$_2$.](image)

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The disordered, as-synthesized VFe\(_2\)O\(_x\) aerogel was subjected to thermal processing under controlled atmospheres to tune the crystallinity of the VFe\(_2\)O\(_x\) structure and to remove organic byproducts of the epoxide-driven reactions. Thermal analysis (simultaneous TGA and DSC) under flowing O\(_2\) or Ar was performed to determine the lowest temperature necessary to transform and/or purify the as-synthesized VFe\(_2\)O\(_x\) aerogel (Fig. S3). Under either atmosphere the VFe\(_2\)O\(_x\) aerogel exhibits weight loss up to \(~27\%\), mostly occurring before 300°C; we attribute this weight loss to the volatilization of organic residues from the sol–gel synthesis.\(^{31,37}\) On the basis of these findings, we chose 300°C as our endpoint for thermal processing—a temperature sufficient to remove unwanted byproducts and to induce partial crystallization, but also mild enough to minimize particle ripening and concurrent loss of surface area. Following similar protocols reported earlier for FeO\(_x\) aerogels,\(^{22}\) we also applied a two-stage treatment at 300°C, first under Ar to induce crystallization and then under O\(_2\) to oxidize the metal sites in the VFe\(_2\)O\(_x\) aerogels to obtain a more defective, \(\gamma\)-Fe\(_2\)O\(_3\)–like form. Elemental analysis of thermally processed VFe\(_2\)O\(_x\) aerogels by EDS confirms that the 2:1 Fe:V stoichiometry from the initial synthesis is retained.

Oxidative heat treatment of the as-synthesized VFe\(_2\)O\(_x\) aerogel partially densifies the networked structure while retaining the ultraporous morphology and broad pore-size distribution as determined by SEM, TEM, and N\(_2\)-porosimetry (Figs. E.1, E.2, and S2); total pore volume decreases \(~20\%\) to 1.3 cm\(^3\) g\(^{-1}\) and the specific surface area is reduced to 231 m\(^2\) g\(^{-1}\) (Table 1). Heat treatment under low pO\(_2\) (300-Ar) also retains the ultraporous aerogel morphology (Figs. E.2, S2, and S4) but further reduces surface area to 165 m\(^2\) g\(^{-1}\) and pore volume to 0.95 cm\(^3\) g\(^{-1}\) (Table 1). Subsequent oxidative heat treatment of the 300-Ar aerogel does not alter the pore-size distribution or surface area (Table E.1 and Fig. S2). For comparison, a pure FeO\(_x\) aerogel calcined to 300°C in O\(_2\) has a higher surface area (416 m\(^2\) g\(^{-1}\)) and a narrower pore-size distribution centered
at 38 nm, in contrast to the broad distribution of mesopores observed for all VFe$_2$O$_x$ aerogels (Fig. S2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area$^a$, m$^2$g$^{-1}$</th>
<th>BJH pore volume, cm$^3$g$^{-1}$</th>
<th>Discharge capacity in Li$^{+}$-electrolyte$^b$, mAhg$^{-1}$</th>
<th>Discharge capacity in Na$^{+}$-electrolyte$^b$, mAhg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VFe$_2$O$_x$ as-synthesized</td>
<td>535</td>
<td>1.6</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>VFe$_2$O$_x$ 300-O$_2$</td>
<td>231</td>
<td>1.3</td>
<td>130</td>
<td>70</td>
</tr>
<tr>
<td>VFe$_2$O$_x$ 300-Ar</td>
<td>165</td>
<td>0.95</td>
<td>77</td>
<td>40</td>
</tr>
<tr>
<td>VFe$_2$O$_x$ 300-Ar-O$_2$</td>
<td>156</td>
<td>0.87</td>
<td>105</td>
<td>58</td>
</tr>
<tr>
<td>FeO$_x$ 300-O$_2$</td>
<td>416</td>
<td>2.3</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Values are ±2% for replicate analyses within batch and ±10% for batch-to-batch analysis.

$^b$ Capacities derived by integration of voltammetric curves at 0.5 mV s$^{-1}$ scan rate.

Table E.1. Brunauer–Emmett–Teller (BET) surface areas, Barrett–Joyner–Halenda (BJH) pore volumes, and specific discharge capacities for select VFe$_2$O$_x$ and FeO$_x$ aerogels.
Figure E.2. Transmission electron micrographs of VFe$_2$O$_x$ aerogels: (a) as-synthesized, (b) 300-O$_2$, (c) 300-Ar, and (d) 300-Ar-O$_2$.

The XRD-amorphous nature of the as-synthesized VFe$_2$O$_x$ aerogel is retained with calcination in high p$_{O_2}$ (300-O$_2$; Fig. E.3), whereas heating to 300°C under inert atmosphere (300-Ar) produces a nanocrystalline cubic phase with peaks corresponding to either maghemite ($\gamma$-Fe$_2$O$_3$; ICDD# 00-039-1346) or magnetite (Fe$_3$O$_4$; ICDD# 01-073-9877). Further oxidative heat treatment of the nanocrystalline 300-Ar VFe$_2$O$_x$ aerogel induces a decrease in atomic order as evidenced by broadened diffraction peaks, reduced peak intensity, and the appearance of a broad
amorphous feature centered around 30°20 (Fig. E.3). Using Scherrer analysis of the (400) peak, the average crystallite sizes for the 300-Ar and 300-Ar-O₂ samples are calculated to be 9.2 and 7.9 nm, respectively. The average crystallite sizes are comparable to the distribution of primary particle sizes (5–15 nm) observed by TEM (Fig. E.2); the slightly larger particle size derived from TEM is attributed to partial atomic disorder in the particles, which will not contribute to the average crystallite size. Although we established crystallinity of the VFe₂Oₓ materials by XRD, the phase and degree of order in the VFe₂Oₓ nanoarchitectures can also be qualitatively accessed by color and magnetic susceptibility. The amorphous aerogels (as-synthesized and 300-O₂–treated) are light brown and paramagnetic, whereas the nanocrystalline 300-Ar and 300-Ar-O₂ aerogels strongly interact with a permanent magnet and are black and dark brown, respectively.

The magnetite and maghemite spinel phases are isostructural and therefore difficult to differentiate, particularly in nanocrystalline materials where diffraction peaks broaden. To further elucidate the crystalline phase for the 300-Ar and 300-Ar-O₂ VFe₂Oₓ aerogels, we used bright X-rays from a synchrotron source, combined with Rietveld analysis of the PXRD pattern (Fig. S5). We observe two phases in their diffraction profiles: (i) a nanocrystalline structure and (ii) an amorphous component (as evidenced by the presence of a large background despite the use of a synchrotron source). For Rietveld refinement, the ratio of Fe:V was fixed at 2:1 and it was assumed that vanadium occupy tetrahedral sites, as observed by Gillot and Nivoix for VₓFe₃₋ₓO₄ phases where x < 1; the amorphous component was accounted for with a ninth-order Chebyschev polynomial. When using the magnetite structure as a starting point, we obtain a better fit to the diffraction profile than when starting with the maghemite structure (see supporting information). We attribute the amorphous region at low 2θ to the disordered nature of aerogel surfaces and the
large surface-to-bulk ratio present in these ultraporous oxide nanoarchitectures.

The relative diffraction peak intensities for \((0,k,l)\) reflections are anomalously high for the 300-Ar VFe\(_2\)O\(_x\) aerogel, as is the \((0,4,4)\) peak intensity for the 300-Ar-O\(_2\) aerogel. These anomalies indicate that stacking faults are present within the crystalline component although fitting a model of the stacking faults to the PXRD is inhibited by the amorphous contribution to the profile and nanocrystalline peak broadening.\(^{38}\) This structure refines to a cubic unit cell with \(a = 8.33\) Å and with coherent crystallite sizes of the 300-Ar and 300-Ar-O\(_2\) samples calculated to be 9.50 and 7.53 nm, respectively, in good agreement with the Scherrer analysis of diffraction profiles from XRD.

Figure E.3. X-ray diffraction profiles of VFe\(_2\)O\(_x\) aerogels: (300-O\(_2\) —), 300-Ar (—), and 300-Ar-O\(_2\) (—). Diffraction peaks for 300-Ar and 300-Ar-O\(_2\) index to either maghemite (\(\gamma\)-Fe\(_2\)O\(_3\); ICDD# 00-039-1346) or magnetite (Fe\(_3\)O\(_4\); ICDD# 01-073-9877).

The oxidation states of V and Fe in the VFe\(_2\)O\(_x\) aerogels were assessed by deconvolving XPS regional spectra for V\(2p_{3/2}\) (Fig. A.4) and Fe\(2p_{3/2}\) (Fig. S6). The 300-O\(_2\) aerogel had a single V\(2p_{3/2}\) peak at 517.7 eV, which corresponds to V\(^{5+}\) state.\(^{39}\) Spectra for the 300-Ar VFe\(_2\)O\(_x\) show
two overlapping V2p3/2 peaks at 517.2 and 516.1 eV that indicate a mixture of V5+ and V4+, a result of partial reduction of V5+ sites during low-pO2 heat treatment. Subsequent heating in O2 (300-Ar-O2) returns the vanadium to +5, as indicated by a single V2p3/2 peak at 517.3 eV. The Fe2p regions for the three VFe2Ox aerogels consist of broad peaks that generally do not differ between the various heat treatments. The position of the Fe2p3/2 satellite suggests that the predominant oxidation state is Fe3+, but the peak for 300-Ar has a slightly lower binding energy at 719.4 eV, which indicates the presence of Fe2+. The O1s spectra of all three samples are similar, and indicative of hydrated or defective oxides.
Figure E.4. X-ray photoelectron spectra of the V2p\textsubscript{3/2} binding energy for VFe\textsubscript{2}O\textsubscript{x} aerogels: 300-O\textsubscript{2} (---), 300-Ar (--), 300-Ar-O\textsubscript{2} (----), background fit (---), and peak fit (-----).

X-ray absorption spectroscopy was also performed on this series of VFe\textsubscript{2}O\textsubscript{x} aerogels, as well as analogous unsubstituted FeO\textsubscript{x} aerogels, to determine oxidation state and local structure. The XANES region includes contributions from dipole-allowed transitions from 1s states to
unoccupied final states with $p$ character (Figs. E.5, S7, and S8). The pre-edge peak, however, is due to transitions from $1s$ states to final states with $3d$ character, which are forbidden by dipole selection rules but allowed by quadrupole selection rules. The intensity of quadrupole-allowed transitions is usually weaker than those of dipole-allowed transitions, as is the case for the Fe XANES (Figs. E.5, S7, and S8). For vanadium oxides, the intensity of the pre-edge peak is significantly enhanced due to lack of centrosymmetry as a result of the high degree of distortion of the VO$_6$ octahedral geometry. The X-ray edge energy (at half-height beyond the pre-edge peak) and the pre-edge peak energy display a positive shift with increase in V oxidation state. The pre-edge peak intensity also increases with greater VO$_6$ octahedral distortion and to a lesser degree with increasing density of unoccupied $d$ states that accompany higher V oxidation states.

The Fe oxidation state in the as-synthesized and 300-O$_2$ FeO$x$ aerogel is close to +3; thermal treatment under Ar shifts the Fe oxidation state to ~+2.8 (Fig. S7). The VFe$_2$O$x$ aerogel samples also have Fe oxidation states that remain within a narrow window very close to +3 (2.94–3.12), with the lowest Fe oxidation state exhibited by the 300-Ar aerogel (Fig. E.5a and Fig. S8). In agreement with XPS, the V K-edge XANES results indicate a +5 oxidation state for the as-synthesized VFe$_2$O$x$ aerogel and for the aerogels treated under oxidizing environments (300-O$_2$ and 300-Ar-O$_2$), whereas the heating under low p$_{O2}$ reduces the vanadium toward +4 (Fig. E.5b and Fig. S8). However, an increase in pre-edge peak intensity indicates a greater degree of distortion in the 300-Ar VFe$_2$O$x$ aerogel than that of the V$^{+4}$ standard, VO$_2$. 
The local structure of the as-synthesized FeO\textsubscript{x} aerogel, as determined by EXAFS, is highly disordered, evidenced by a lack of significant contributions from higher coordination spheres in the region of the Fourier transform data above 2 Å (Fig. S9). Disorder decreases following calcination at 300°C in O\textsubscript{2} as evidenced by the increase in the amplitude of the structure in the 2.2–3.6 Å region of the Fourier transform. Thermal treatment in Ar induces significant changes, particularly in the first coordination sphere (Fe–O peak centered at ~1.5 Å in the Fourier transforms data) of FeO\textsubscript{x}, resulting in a local structure that is closely related to γ-Fe\textsubscript{2}O\textsubscript{3} (maghemite), especially in the region dominated by Fe–Fe interactions (2.2–3.6 Å region). The shift in the Fe–O peak to slightly higher distance is consistent with the presence of a small fraction of Fe\textsuperscript{2+} as a result of heating in Ar. The local structure of Fe in VFe\textsubscript{2}O\textsubscript{x} is similar for the as-synthesized, 300-O\textsubscript{2}, and 300-Ar-O\textsubscript{2} aerogels, and may be interpreted as a disordered form of γ-Fe\textsubscript{2}O\textsubscript{3} (Fig. 6 and Fig. S10). The local structure of V for VFe\textsubscript{2}O\textsubscript{x} heated to 300°C in Ar is clearly distinct from the structure that emerges under oxidative conditions (Fig. E.6 and Fig. S11).
increase in the amplitudes of the structure in the 2.2–3.6 Å region of the Fourier transforms of the EXAFS spectra indicates that the 300-Ar VFe$_2$O$_x$ aerogel exhibits a more ordered form related to γ-Fe$_2$O$_3$.

Figure E.6. Fourier transform plots of (a) V and (b) Fe K-edge EXAFS spectra for VFe$_2$O$_x$ aerogels: 300-O$_2$ (—), 300-Ar-O$_2$ (— — —), 300-Ar (— — — —), and as-synthesized (•••).

Based on the synchrotron PXRD, EXAFS, and TEM results, we posit that our material consists of domains of nanocrystalline magnetite-like and amorphous, maghemite-like oxide, similar to our previous assessment of FeO$_x$ aerogels that showed mixed magnetite/maghemite character. This broad, amorphous PXRD pattern has previously been observed for core–shell maghemite/magnetite FeO$_x$ nanoparticles.

Chapter E.3.3. Electrochemical Cation-Insertion as a Function of Structure and Composition

We use these VFe$_2$O$_x$ and FeO$_x$ aerogels as model electrode materials with which to investigate the influence of structural order/disorder, cation-vacancy content, and V substitution
on electrochemical charge-storage properties, focusing primarily on Li$^+$-insertion reactions in nonaqueous electrolytes. Cyclic voltammetry (CV) provides an initial assessment of capacity and active potential window, as seen when $\text{VFe}_2\text{O}_x$ or $\text{FeO}_x$ aerogel powders are processed into conventional composite electrodes and cycled at 0.5 mV s$^{-1}$ in a three-electrode cell (Fig. E.7). In all cases, most of the capacity is delivered between 3.2 and 2.0 V vs Li, with broad voltammetric profiles reminiscent of pseudocapacitive processes.

Integration of the voltammograms to obtain capacity values shows that the 300-\text{O}_2 $\text{VFe}_2\text{O}_x$ aerogel provides the highest specific capacity of the series, reaching 130 mA h g$^{-1}$. The impact of V substitution on electrochemical performance is clear when compared to an analogously processed $\text{FeO}_x$ aerogel, which delivers only 60 mA h g$^{-1}$. The ideal stoichiometry for these respective oxides in their fully oxidized, cation-defective forms is $[\text{Fe}^{3+}_{8/3} \cdot \Box^{1/3}]\text{O}_4$ and $[\text{V}^{5+}_{8/11}\text{Fe}^{3+}_{16/11} \cdot \Box^{9/11}]\text{O}_4$, with greater vacancy content for V-substituted $\text{FeO}_x$ due to the need for additional charge compensation when $\text{V}^{5+}$ replaces $\text{Fe}^{3+}$ in the spinel lattice. Assuming a 1:1 correlation between vacancy content and Li-ion capacity, and accounting for the difference in formula mass, $\text{VFe}_2\text{O}_x$ should provide 2.90 times the specific capacity of an analogous cation-defective $\text{FeO}_x$ material; experimentally, we observe capacity improves by a factor of 2.17.

Heating the as-synthesized $\text{VFe}_2\text{O}_x$ aerogel directly in Ar produces a nanocrystalline and partially reduced form that exhibits much lower specific capacity (77 mA h g$^{-1}$) than the poorly crystalline, 300-\text{O}_2 aerogels. The diminished capacity expressed by 300-Ar $\text{VFe}_2\text{O}_x$ is recovered by $\sim 35\%$ to 105 mA h g$^{-1}$ after subsequent heating in O$_2$, which oxidizes all V to the +5 state and creates more cation vacancies, while also increasing overall structural disorder, all without altering specific surface area or pore structure. However, the fully oxidized, nanocrystalline 300-Ar-\text{O}_2 VFe$_2$O$_x$ still does not achieve the Li-ion capacity of the X-ray-amorphous 300-\text{O}_2 analog. The
difference in specific surface area (230 vs. 160 m$^2$ g$^{-1}$) for these two VFe$_2$O$_x$ aerogels may play a role in establishing Li-ion capacity, as vacancies and defects are favored at surface sites. Similar trends are also observed for VFe$_2$O$_x$ cycled in a Na-ion electrolyte, albeit achieving a lower total capacity due to the larger size of the Na$^+$ cation (Fig. 7); VFe$_2$O$_x$ 300-O$_2$ yields 70 mA h g$^{-1}$ in Na$^+$ electrolyte compared to 130 mA h g$^{-1}$ in Li$^+$ electrolyte.

Figure E.7. Cyclic voltammograms at 0.5 mV s$^{-1}$ of composite cathodes prepared with (—) VFe$_2$O$_x$ 300-O$_2$, (---) VFe$_2$O$_x$ 300-Ar-O$_2$, (•••) VFe$_2$O$_x$ 300-Ar, and (•••) FeO$_x$ 300-O$_2$ in (a) Li$^+$-containing electrolyte and (b) Na$^+$-containing electrolyte.

The oxygen-calcined, X-ray-amorphous VFe$_2$O$_x$ aerogel was selected for galvanostatic cycling experiments (at 10 mA g$^{-1}$) in Li coin cells. Representative charge–discharge profiles are shown in Fig. E.8a; the sloping nature of these curves is consistent with the broad shapes observed in the voltammetric tests. Capacity values were also derived from these galvanostatic experiments, returning 186 mA h g$^{-1}$ and 157 mA h g$^{-1}$ on first and second discharge, respectively; the capacity drop in this case is likely due to solid electrolyte–interface (SEI) formation. Thereafter, capacity fades gently with specific capacity maintained at ~100 mA h g$^{-1}$ through 50 cycles. Charge–discharge coulombic efficiency ranges between 87–89% over the 50 cycles examined, which may
indicate parasitic side reactions occurring during charging or some incremental irreversibility in the Li\(^+\)-insertion process. Further work is underway to enhance cycling stability, understand SEI formation, and further amplify specific capacity in this new class of cation-insertion materials.

![Figure E.8](image.png)

Figure E.8. (a) Galvanostatic charge–discharge cycling of a 300-O\(_2\) VFe\(_2\)O\(_x\) aerogel at 10 mA·g\(^{-1}\) between 4.0 and 2.0 V vs. Li/Li\(^+\) in 1 M LiPF\(_6\) in 1/1/1 EC/DEC/DMC; (b) discharge capacity versus cycle number for the galvanostatic cycling.

**Chapter E.4. Conclusion**

Using a combined strategy of cation-substitution and nanostructuring, we synthesize deliberately defective VFe\(_2\)O\(_x\) aerogels and demonstrate that increasing concentrations of cation vacancies concomitantly enhances their specific capacity for Li\(^+\)- and Na\(^+\)-insertion. Aerogel frameworks create a defect-rich structure with high accessibility to the defect sites, and the substitution of tetrahedral iron sites with V\(^{5+}\) induces further vacancy formation. We observe the highest specific capacity (130 mA h g\(^{-1}\)) in Li\(^+\)-containing electrolyte when the VFe\(_2\)O\(_x\) aerogel is calcined in oxidizing atmospheres such that high surface area is retained and the X-ray amorphous oxide expresses \(\gamma\)-Fe\(_2\)O\(_3\)–like local structure.
Chapter E.5. References


