

**Metal oxyhalides and halides for use as electrode
materials in Li-ion batteries**

A Dissertation Presented for the
Doctor of Philosophy
Degree

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I would like to thank my parents, Mark and Linda, because without their love and support none of my accomplishments would have been possible. I thank my brother, Christopher, whose constant example provided me with the strength I needed to achieve this goal. I thank my best friend, James, who while being across the country always found the time to provide me with encouragement. Most of all I would like to thank Kiran, my girlfriend, who while pursuing a Ph.D. of her own always put my needs ahead of her own and provided the support and understanding that I needed to reach this goal. Thank you to all of my friends and family, including those that have been lost along the way, that have encouraged and provided the much-needed support that helped me to achieve this goal.

ABSTRACT

Synthesis of select metal halides and oxyhalides are explored in the form of direct fluorination using a fluidized bed reactor system, direct chlorination using hydrogen chloride gas, and a degradation dehydration reaction as novel methods towards the synthesis of these select metal halides and oxyhalides. The flexibility of the direct fluorination technique is demonstrated by the ability to vary the degree of fluorination based on the reaction conditions of temperature, time, and fluorine concentration. Conversion electrodes in the form of metal halides and metal oxyhalides are investigated as both anode and cathode materials for lithium ion batteries. The resulting electrochemical properties of the materials are reported. In the case of titanium oxydifluoride it is shown how the precursor material can alter the properties of the final product. Alpha ruthenium (III) chloride is demonstrated to be an excellent compound for the study of metal chlorides in lithium ion batteries as it shows a high reversible capacity over many cycles. Reversible cycling data for iron (III) oxychloride is shown using both standard organic and ionic liquid electrolytes. This demonstrates the importance of using the proper electrolyte with a specific active material to achieve the optimal properties from the battery system. Collectively what is shown is the viability of conversion type metal halide and oxyhalide electrodes to be used in lithium ion batteries.

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CHAPTER ONE

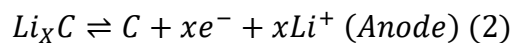
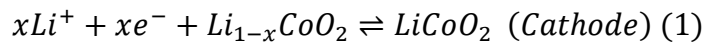
INTRODUCTION AND GENERAL INFORMATION

The past few decades have shown a push for a new direction away from fossil fuels towards more renewable sources of energy to become the energy economy of the future. Batteries have become increasingly integrated into our daily lives and have become a major field of active research. Batteries consist of three major components, two electrodes and an ionically conductive but electronically insulating electrolyte. Batteries operate by the fairly simple idea that potential arises from a difference in chemical potential of two electrodes that have been physically separated so that electrons transferred can do work on an external circuit while simultaneously ions are transported through the electrolyte to maintain charge balance.¹ A battery can either be primary, meaning that the battery only discharges, or secondary, meaning that the battery can be reversibly charged and discharged many times. The innovation of personal electronics that has been seen in recent years is due to the rechargeable lithium ion battery (LIB). New applications continue to drive the need for lighter, smaller, and more energy dense batteries. There are many different types of batteries being researched including lithium-air, lithium-organic, sodium ion, and magnesium sulfur. In order for batteries to become a viable alternative to fossil fuels, in areas such as electric vehicles, advancements in battery materials need to be made.

Batteries can only be as good as the active materials used inside that battery. Each component of a battery is important but it is the electrode active materials that can provide the most drastic improvements to battery performance. The electrode active material is directly responsible for many of the battery properties including cycle stability and energy density. Current LIBs consist of a LiCoO_2 cathode and a graphite anode which only stores about 180 watt-hours per kilogram, Wh kg^{-1} .² To increase the energy that can be stored in a battery either the potential difference between the two electrodes must be increased or the amount of lithium that can be stored inside of the active material of the electrode must be increased since energy density is the product of capacity and voltage. The ideal battery would contain the highest potential versus Li/Li^+ positive electrode coupled with the lowest potential versus Li/Li^+ negative electrode, resulting in the highest possible voltage while keeping the capacities of both electrodes as high as possible. The open circuit voltage is the difference in electrochemical potentials of the anode and the cathode. There are many different classes of materials used for both positive and negative electrodes with their respective potentials and capacities. There is a large difference in the capacity between lithium metal and other negative electrode materials, but lithium metal also has dendrite formation which causes cell failure. Due to its high capacity there is still a large amount of research trying to solve the safety issue of dendrite formation when using lithium metal as the negative electrode.³ The electrolyte

must also be considered because this provides the electrochemical window in which the battery is cycled to minimize electrolyte decomposition, and have high cycle stability. The window created by the electrolyte is the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). If the potential of the anode is above the LUMO the electrolyte will be reduced and if the potential of the cathode is below the HOMO the electrolyte will be oxidized.² In order to create better batteries new electrode materials need to be investigated.

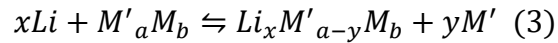
There are four main types of electrode materials that are used in batteries, including intercalation, alloying, displacement, and conversion. The most used and commercialized type is the intercalation compound. Intercalation compounds can act as both cathodes and anodes. Intercalation is a special case of topochemical reaction in which a guest species is inserted inside the lattice of the crystalline host.⁴ The ability of these compounds to intercalate is valuable because the intercalation is reversible, which means by applying the proper potential the lithium ions can be deintercalated from the cathode and intercalated into the anode, recharging the battery. Both LiCoO_2 and graphite are intercalation compounds and have general reactions given by



Intercalation compounds are limited by the structural aspects of the crystal lattice. An example of this would be graphite which can only store one mole of lithium for every six moles of carbon.

The second type of compound is the alloying compound which can only act as an anode material. These compounds are metals that can alloy with lithium. Alloying type electrode materials that have been heavily studied include silicon, tin, and antimony, and form compounds of the form Li_xM_y . These alloying compounds are an interesting class of materials because they can typically achieve much higher capacities than the intercalation compounds. This is because they can alloy more lithium per unit of the alloying element. A prime example of this is with the alloying element silicon which can alloy with up to 4.4 lithium per silicon, which gives a theoretical capacity of 4200 mAh g^{-1} .⁵ Although these materials have incredibly large capacities they have a major flaw. During lithium insertion and extraction these materials undergo extremely large volume changes, up to 400% for some silicon alloys.⁶ The stress of these expansions and contractions of the particles causes a pulverization, which leads to poor electrical contact between the current collector and the active material causing rapid capacity fade.⁷ One way of trying to overcome this shortcoming is by depositing the alloying metal such as silicon onto a support such as carbon to provide structural stability.⁸

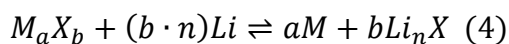
The third type of electrode material is the displacement type, which can only be used as an anode material. Displacement type materials are a special type of alloying material that contains both an alloying and non-alloying element in the structure. These alloying electrodes can be understood as being MM' compounds where M is the alloying element and M' is the non-alloying element. When these compounds react with lithium they have generally been described as forming domains of Li_xM inside of a M' matrix.⁹ Compounds of this type include SnAg, Sn_xFe, Cu₂Sb, InSb and Cu₆Sn₅. Including these inactive species is believed to provide structural stability and combat the volume changes of the active particles.⁹ The general reaction that is observed with these materials is the reversible Li-ion insertion and metal displacement as shown below



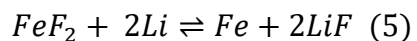
These are interesting materials because they still provide the possibility of high capacities like that of the alloying materials but because of the inactive metal that is displaced the volume changes during lithium insertion and extraction are not nearly as drastic. With antimony, for example, a volume expansion of approximately 135% is seen when Sb forms Li₃Sb, but in a compound like InSb the volume expansion is only 46.5%.^{10, 11} By reducing the volume changes there

is a smaller chance of structural pulverization during cycling which leads to better cycle stability.

The fourth type of compound used in batteries is the conversion compound which can be used as cathodes or anodes. Typical conversion compounds include metal oxides, sulfides, and fluorides. The basic reaction for these conversion materials can be represented as



where M is the transition metal, X is the anion, and n is the oxidation state of the anion. Conversion materials show a lot of promise because unlike the intercalation materials that are limited by the redox reaction to one Li^+ per metal center, conversion materials can transfer more than one Li^+ per metal center. An example of this would be



which can reversibly exchange two lithium ions giving it a higher specific capacity than many intercalation compounds.¹² Although conversion compounds show promise for becoming battery electrode materials they also have several problems that must be solved before they will be a viable option. Conversion compounds

such as Fe_2O_3 , similar to alloying compounds, undergo large volume changes of around 80% resulting in poor cycle stability and in most cases there is a large overpotential between the charging and discharging steps.^{13, 14}

Metal halides are one specific class of conversion electrode compounds that have recently been of much interest, due to their high theoretical specific capacities and intermediate operating voltages. There are however several drawbacks to these materials including poor conductivity, large voltage hysteresis, and dissolution of the active material.¹⁵ The cause for the poor conductivity is due to the large band gap of the materials caused by the ionic nature of the metal halide bond.¹⁵ Large voltage hysteresis are thought to be caused by either asymmetric reaction pathways or compositional inhomogeneity.¹⁶ Material dissolution is caused by the high solubility that many ionic compounds exhibit, especially metal chlorides. In order for metal halides to be considered for active materials these issues must be addressed through either smarter material choice or modifying material microstructure.

There has been a large amount of research involving the use of nanomaterials as the active materials in electrodes to overcome some of the inherent limitations of standard bulk electrode materials. The use of nanomaterials for electrodes has been used to address several issues, especially rate capability and cycling stability.¹⁷ Rate capability is essentially the speed at which the electrode can be fully discharged and charged. It has been established that the

limits on rate capabilities is caused by slow solid-state diffusion of lithium into and out of the electrode.¹⁸ The time it takes for the Li^+ to diffuse into an electrode is given by

$$t = L^2/2D \text{ (6)}$$

where t is time, L is the length or distance that the ion is diffusing, and D is the diffusion coefficient. By using a nanomaterial the size of the particle is greatly decreased and the surface area is greatly increased which lowers the L term. This makes the time it takes for lithium ions to diffuse in and out of the electrode much smaller. In many materials, such as tin, the poor cyclability is due to structural breakdown from volume changes during lithium insertion and extraction. It has been shown that smaller particles can more easily accommodate these structural changes during lithium insertion and extraction leading to better cycle stability.¹⁹ Another advantage of using nanomaterials is the large surface area gives more interfacial space and this increase makes it easier to observe specific properties of the interface between the electrolyte and the electrode.

Although the basic theory of how a battery functions is simple the chemistry that takes place is very complex. There are many subtle mechanisms that need to be understood and controlled in order to achieve the goal of making a better battery material. A battery consists of many different parts that undergo reactions

that can affect battery performance including the electrode components, the separator, and the packaging materials. There are many components that go into the making of an electrode. The electrode consists of a current collector, binder, carbon black, and active material. The current collector is usually copper foil for the anode and aluminum foil for the cathode electrode. The current collector provides support for the active material as well as decreases the internal resistance of the battery because many active materials are not highly conducting. The binder, carbon black and active material are mixed together in a slurry and cast onto the current collector. Although the active material is the primary component that gives the functional characteristics to the electrode it is not sufficient to consider this alone. A binder is used to ensure a strong contact between the current collector and the active material, as well as helping to prevent the negative effects of volume changes during the cycling of the battery.²⁰ The carbon black is used to increase the conductivity between the particles of the active material.²⁰ The separator allows ions to flow freely while mechanically separating the cathode and anode. Separators can be made of many different materials including cellulosic papers, polymers, and glass wools.^{21, 22} Each of the separator materials has unique characteristics that can affect the battery performance. The packaging material is the casing that contains all of the components of the battery. Reactions can occur between the electrolyte and the casing which can affect the battery. These different interactions must all be accounted for and precisely

controlled in order to build a working battery. All of the components of the electrode must be considered in order to gain a deeper understanding into the reactions taking place during the battery cycling process.

It is also necessary to understand the side reactions taking place inside the battery. There are reactions that can occur between the current collector and electrolyte, and more importantly reactions that occur between the surface of the electrode and the electrolyte. In order to enhance the understanding of what happens during battery cycling the formation of a solid electrolyte interphase (SEI) layer must be considered. This interfacial layer is critically important to the function of the battery. The SEI forms during cycling from the decomposition of the electrolyte and the formation of lithium salts.²³ This is a passivating layer which protects the electrolyte from further decomposition at the electrode. It is because of this layer that allows the use of electrode materials with electrochemical potentials outside of the electrolyte window. The SEI layer can affect many different battery properties including rate capability and cycle stability. The formation of the SEI layer passivates the electrode which can be unstable in the presence of the electrolyte and causes an irreversible consumption of lithium which leads to overall capacity loss.²⁴ This passivating SEI layer is crucially important and can affect many aspects of the battery including the shelf life, cycle life, safety, and power capability.²⁵ The SEI layer can be degraded at elevated temperatures due to the hydrofluoric acid that forms and causes exothermic reactions with the

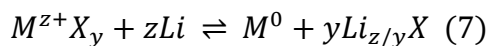
SEI layer which can lead to a thermo-runaway reaction that can cause the battery to explode.²⁶ The morphology, chemical composition, and physical properties of the SEI layer all depend upon what type of electrolyte is being used and what types of additives have been included.

CHAPTER TWO

TITANIUM OXYDIFLUORIDE

Introduction

There are a number of chemistries which are attractive for application to lithium ion batteries beyond traditional intercalation compounds such as graphite and LiCoO_2 . One such class of materials is the so-called conversion electrodes, such as the metal (oxy)fluorides FeF_3 , FeOF , CuF_2 , or TiOF_2 . These materials have capacities in the range of $1,000 \text{ mAh g}^{-1}$, almost three times that of the standard graphite electrode,²⁷ due to the ability to access multiple oxidation states of the transition metal and follow the generalized reaction:



where M is a cation with multiple oxidation states, and X is an anion such as oxygen or fluorine. Fluoride materials are an important class of conversion materials because of their relatively high potentials, which result in higher energy densities than the corresponding metal oxides or sulfides.²⁸ However, metal fluorides are electrically insulating due to large band gaps, and as electrode materials they typically exhibit a large voltage hysteresis between charge and

discharge cycles that results in poor efficiency.²⁹⁻³¹ Various approaches have been used to improve the electrochemical activity of metal fluorides, which include reducing the crystal size, adding a highly conductive carbon to ensure electrical connection to the metal fluoride particles, and the addition of oxygen to improve the cycle stability while slightly lowering capacity.^{30, 32} Although conversion materials have been studied for decades the underlying mechanisms of these conversion reactions are still not well understood.^{13, 33-34}

Fluorination reactions to form the electrode materials can be performed by a variety of methods including precipitation from a fluorinated solution, reaction with HF,³⁵ direct reaction with F₂(g), solid-state reactions with a fluorinating agent such as NH₄F, CuF₂, ZnF₂, XeF₂, AgF₂ or NH₄HF₂³⁶⁻³⁷, electrochemical fluorination³⁸ and reaction with poly(vinylidene fluoride) (PVDF).³⁹ Experimental conditions including reaction time, temperature and fluorine concentration can be used to control the level of fluorine insertion and the homogeneity of the products. This control could be beneficial for cycling stability and lowered impedance which are believed to be caused by a passivating fluoride layer on the electrode surface.^{40 41} The elevated temperature, fluidized bed reactor fluorination route is capable of modifying electrochemical properties by modifying composition (e.g., TiO_{2-x}F_x), and through a change in structure (e.g., from anatase TiO₂ to TiOF₂). Other methods to form TiOF₂ have included solvothermal, hydrothermal synthesis and direct fluorination in a standard tube furnace.⁴²⁻⁴⁶ For the fluidized bed system,

the degree of fluorination can be controlled by varying the time and temperature at which the fluorination reaction is performed.

The goal of this work is to explore the role of precursor chemistry in the formation of fluoride electrodes. Specifically, we sought to explore whether a pre-reduced, more electrically conducting metal oxide precursor would influence the electrical transport and electrochemical behavior of the fluorinated product. Furthermore, we note that many reduced metal oxides have lower electronic reactivities than the fully oxidized materials, e.g. Ti_2O_3 vs TiO_2 , such that the fluorination process could be modified by pre-reduction of the metal oxide precursor. We present the direct fluorination of nanoscale titanium oxide precursors and the effect on the electrochemical behavior in lithium ion batteries. Through variation in temperature in a fluidized bed reactor system the overall capacity and cycle stability are shown to increase in response to higher levels of fluorination. Furthermore, the electrochemical properties of TiOF_2 were found to differ based upon whether a TiO_2 or TiO_xN_y precursor was used, with the partially reduced TiO_xN_y precursor providing a higher reversible capacity.

Experimental

Fluorination of TiO₂ nanoparticles to form TiOF₂

Nanoparticles of TiOF₂ were synthesized via the direct fluorination of high surface area anatase TiO₂ nanoparticles (Nanostructured and Amorphous Materials Inc., ~15 nm APS, 99.7 %) in a fluidized bed reactor (FBR) system shown schematically in Figure 1. Before fluorination, the precursors were dried in vacuo for 24 hours at 250 °C using a hot oil bath. Drying is essential to remove any adsorbed water from the nanoparticles, which if present will react with fluorine gas to form hydrofluoric acid. Titania powder samples of 0.5- 1.0 g size were loaded into the FBR within a nitrogen filled glovebox and sealed, then removed and weighed before being connected to the fluorination line. The FBR and sample were heated to 225 °C under flowing helium, at which point a flow of 2.0 sccm fluorine (Air Products) mixed with helium carrier gas (23 sccm) was initiated. After 24 h the fluorine flow was shut off, and the system was allowed to cool to room temperature under helium flow. The FBR was weighed again to determine any weight loss or gain that occurred during the reaction before collecting the sample in the glovebox. The fluorinated sample produced from titanium oxide is labelled O-TiOF₂. Reaction at lower temperatures (175 °C and 200 °C) produced mixed phase (MP) TiO₂/TiOF₂ products (MP175-TiOF₂ and MP200-TiOF₂) according to

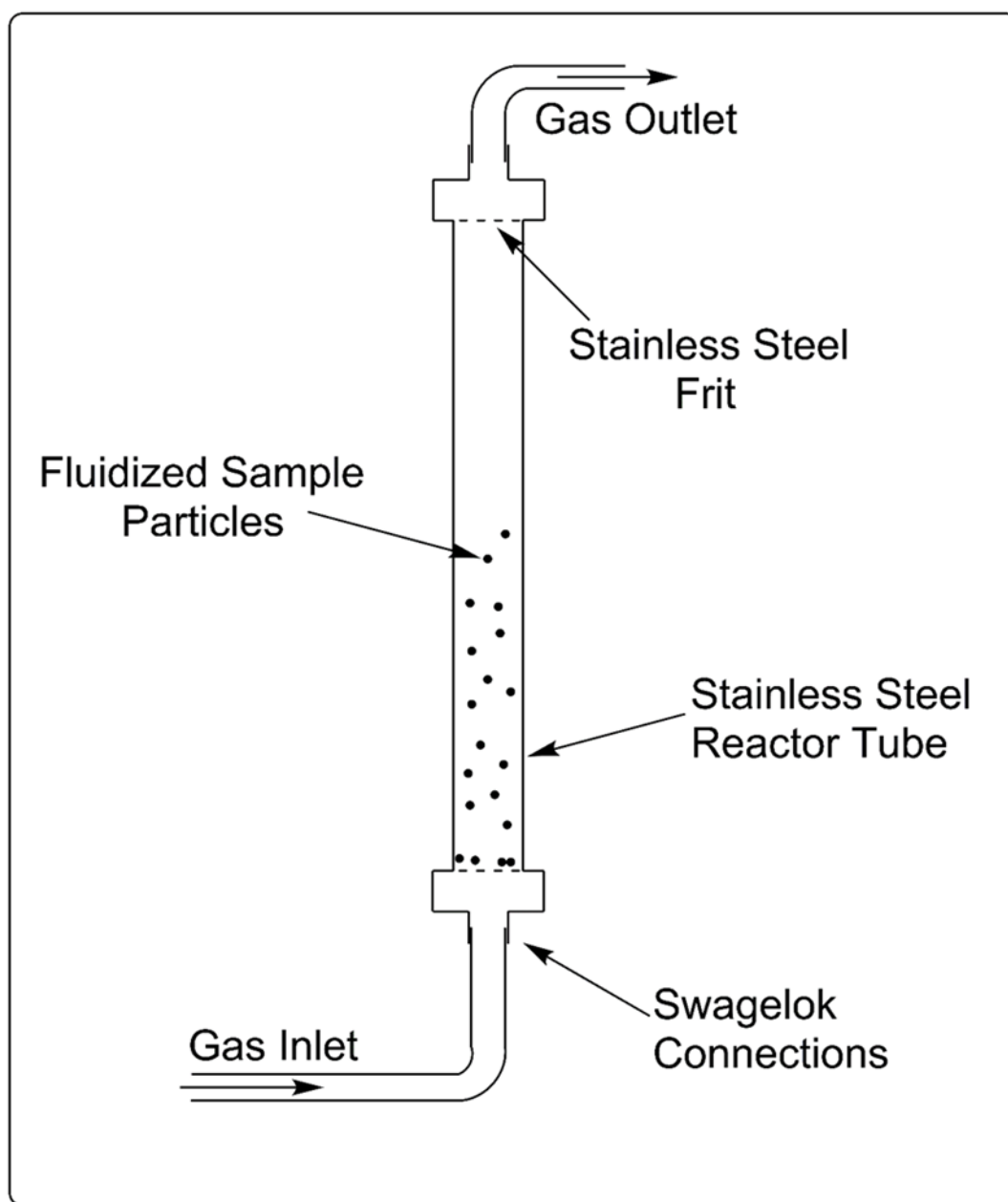


Figure 1: Fluidized Bed Reactor FBR system used to perform the direct fluorination of the TiO_2 and TiO_xN_y precursor materials.

analysis of X-ray diffraction data (Figure 2), as discussed further in the supplemental information.

Fabrication of pre-reduced Ti-O-N precursor

Titanium oxynitride nanoparticles were synthesized via the direct nitridation of TiO₂ nanoparticles. The TiO₂ samples were placed in alumina crucibles and reacted under a 200 sccm ammonia flow (Air Gas, Electronic Grade, 99.9995%) at 860 °C over 19 h and cooled under flowing ammonia. Nitride powders were subsequently fluorinated using the procedure detailed in the previous section. Elemental analysis was carried out by Galbraith Laboratories, Knoxville, Tennessee, to determine the nitrogen (method GLI procedure E7-1) and titanium (method GLI procedure ME-70) weight percentages. The fluorinated sample produced from a nitrogen containing precursor is labelled N-TiOF₂.

Characterization of TiOF₂ nanoparticles

The nanoparticles were characterized using a Panalytical Empyrian powder X-ray diffractometer employing Cu K_α radiation. Data was collected within the 2θ range of 10-90°, using a spinning reflection sample stage and Si zero background sample holder. Crystal structures were refined using the Rietveld method in FullProf Suite.⁴⁷⁻⁴⁸ X-ray diffraction (XRD) data collected on silicon powder

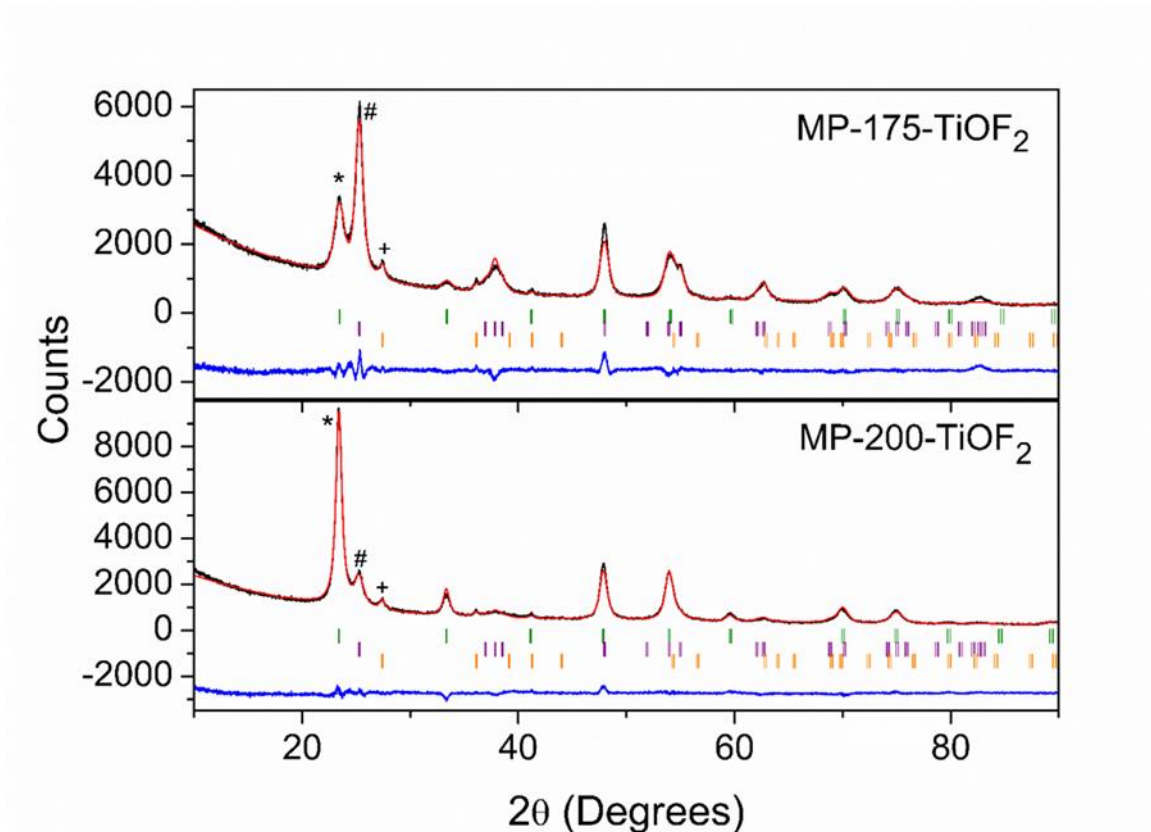


Figure 2: Rietveld refined X-ray diffraction data for $\text{TiO}_2/\text{TiOF}_2$ mix phases which indicates that the sample consists of three phases a TiOF_2 phase (*), a TiO_2 anatase phase (#) and a TiO_2 rutile phase (+). The red line is the calculated pattern, black is the experimental diffraction pattern, and blue is the difference between the calculated and the observed. Reflection positions for TiOF_2 are shown in green, reflection positions for anatase TiO_2 are shown in purple and reflection positions for rutile TiO_2 in orange. Refinement shows that MP-175- TiOF_2 shows a composition of 25.6 ± 0.12 % TiOF_2 , 66.3 ± 0.42 % anatase TiO_2 and 7.46 ± 0.12 % rutile TiO_2 . Refinement shows that MP-200- TiOF_2 shows a composition of 69.5 ± 0.26 % TiOF_2 , 25.7 ± 0.18 % anatase TiO_2 and 4.8 ± 0.09 % rutile TiO_2 . MP-175- TiOF_2 refinement χ^2 is 2.17 and Rwp is 13.5. MP-200- TiOF_2 refinement χ^2 is 2.53 and Rwp is 15.7.

standard under identical run conditions were used to obtain instrument profile parameters for microstructural analysis. The specific surface areas were evaluated with a Quantachrome analyzer from the results of N₂ physisorption at 77 K.

XPS measurements

The surface chemistry of the precursor materials, electrode powders and cycled electrodes were investigated using a PHI 3056 XPS spectrometer equipped with an Al K_α source (1486.6) at a measurement pressure below 10⁻⁸ Torr. After electrochemical cycling the electrodes were immediately disassembled in an Ar filled glovebox and rinsed with anhydrous DMC (less than 0.5 mL - Aldrich). Samples were transferred to the XPS chamber using an air-tight vacuum transfer system. High resolution scans were acquired at 350 W with 23.5 eV pass energy and 0.05 eV energy step. Survey scans were measured at 350 W with 93.9 eV pass energy and 0.3 eV energy step. The binding energies were shifted by setting the adventitious carbon signal to 284.8 eV to account for charging (0.1 – 0.3 eV). The intensities of the presented spectra are not normalized and are simply shifted vertically for clarity. The spectra were deconvoluted using Gaussian-Lorentzian functions and a Shirley-type background. Powders of TiO₂ (Sigma Aldrich) were measured as references.

Electrochemical measurements

The electrochemical measurements were carried out at room temperature using 2 electrode CR2032 type coin cells. The working electrodes were prepared from a slurry of active material (TiOF_2 nanoparticles), conductive agent (carbon black), and a binder (poly(vinylidene difluoride)) at a ratio of 90:5:5 percent by weight. The mixture was cast onto copper foil using the slurry method and dried to form the electrode. All electrodes contained a mass loading of between 1.3-1.6 mg cm^{-2} of active material. All coin cells were assembled in an argon filled glove box using pure lithium foil as the counter electrode and polypropylene as the separator. The electrolyte solution consisted of 1M LiPF_6 in a 1:1:1 volume ratio of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) from Novolyte with water impurity < 20 ppm. The assembled cells were cycled galvanostatically using a LAND CT2001A battery testing system. The battery cells were tested galvanostatically, with a current constant of 33.5 mA g^{-1} while cycling between 3.0 and 0.05 V, which corresponds to a C/10 rate relative to the maximum theoretical capacity of 335 mAh g^{-1} for LiTiO_2 . To provide a direct comparison, other electrode materials in this study were also tested at 33.5 mA g^{-1} between 3.0 and 0.05 V.

Results and Discussion

Precursor chemistry

The X-ray diffraction patterns of TiO_2 and TiO_xN_y starting materials are shown in Figure 3 and Figure 4, respectively. The anatase TiO_2 nanopowder consists of a mixture of anatase (ICSD 9852; tetragonal $I4_1/amd$ structure) and a small amount of rutile (ICSD 9161) crystal structures, with a surface area of $163.2 \pm 1.1 \text{ m}^2 \text{ g}^{-1}$ and estimated crystalline domain size of 11 nm based upon X-ray diffraction data analysis. After ammonolysis at 860 °C, the rock salt structure (ICSD 152807) of TiN was observed. The Ti-N has a refined lattice parameter of 4.2184(2) Å and domain size of 36 nm calculated using the Scherrer formula via microstructural analysis with FullProf Suite. The lattice parameter of TiN is expected to be 4.235 Å, whereas the refined value is 4.218 Å, which is intermediate between that of TiN and stoichiometric TiO ($a = 4.1766 \text{ Å}$; ICSD 77692). Bulk elemental analysis of the Ti-N precursor showed the concentration of titanium and nitrogen in the material to be 67.0 %Ti and 20.76 %N. The balance is most likely O (12.24 at%) given the known reactivity of TiN in air, or from residual oxygen during ammonolysis, indicating the Ti-N precursor is actually an oxynitride, i.e. TiO_yN_x . The lattice parameter derived from Rietveld refinement is similar to other TiO_xN_y materials seen in the literature, which has been reported to vary between

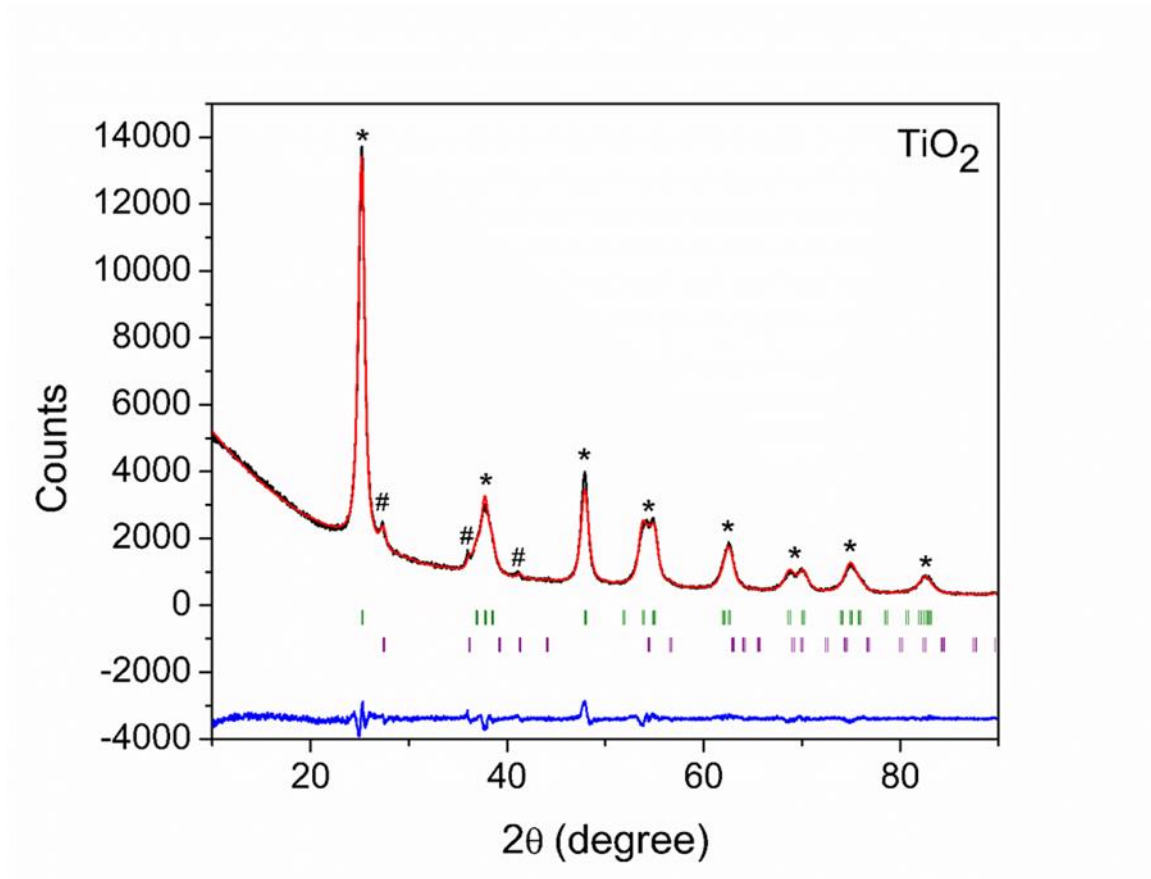


Figure 3: Rietveld refined X-ray diffraction data for TiO_2 , which indicates that the sample is primarily of the anatase phase (*) with a small amount of rutile impurity (#). The red line is the calculated pattern, black is the experimental diffraction pattern, and blue is the difference between the calculated and the observed. Reflection positions for anatase TiO_2 are shown in green and reflection positions for rutile TiO_2 are shown in purple. Refinement shows the TiO_2 has a composition of 95.9 ± 0.53 % anatase and 4.1 ± 0.12 % rutile. Refinement χ^2 is 3.12 and R_{wp} is 11.0.

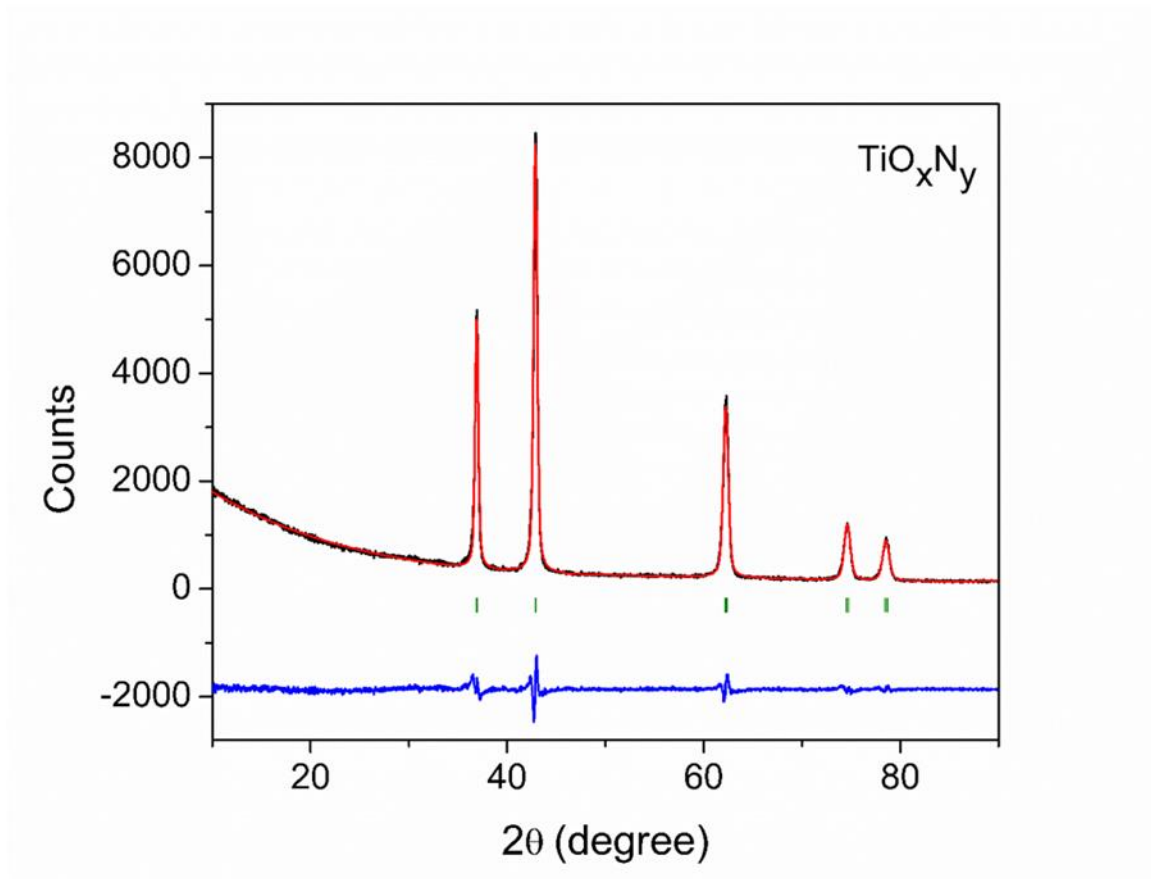


Figure 4: Rietveld refined X-ray diffraction data for TiN which indicates that the sample is an oxynitride species TiO_xN_y. The red line is the calculated pattern, black is the experimental diffraction pattern, and blue is the difference between the calculated and the observed. Reflection positions for TiOF₂ are shown in green. The χ^2 is 2.14 and the R_{wp} is 13.8. The remaining difference is likely due to slight compositional inhomogeneity.

the lattice parameters of the TiN and TiO based on the ratio of oxygen to nitrogen.⁴⁹⁻⁵⁰

Fluorinated electrode materials

After fluorination of the TiO₂ and TiO_xN_y precursors at 225 °C the resulting materials were white powders. XRD data indicated the formation TiOF₂ ((ICSD160661); $a = 3.8019 \text{ \AA}$), which has a cubic ReO₃-type structure in space group *Pm-3m*. This is surprising given the different reaction precursors. However during fluorination of the TiN_xO_y precursor, there is a significant weight loss of ~ 80% of the mass of the starting material, which is associated with sublimation of a TiF₄. XPS results, detailed ahead, indicate that no measurable N is left on or near the surface of the material. Weight loss similarly occurs during fluorination of the oxide precursor, but only ~ 20% of the mass of starting material is lost. These results suggest that the N containing precursor is much more reactive, and the nitrogen is likely easily displaced forming N₂ while the Ti bound to N readily reacts to form the volatile TiF₄, which accounts for the weight loss. BET analysis of nitrogen adsorption-desorption isotherms finds surface areas of 46.7 m²/g for O-TiOF₂ and 52.9 m²/g for N-TiOF₂, indicating similar surface areas for both samples of aggregated nanopowders (Figure 5 and Figure 6). Rietveld refinements of X-ray diffraction data for TiOF₂ synthesized from anatase TiO₂ nanoparticles and TiO_xN_y nanoparticles are shown in Figures 7 and 8, respectively, and indicate that

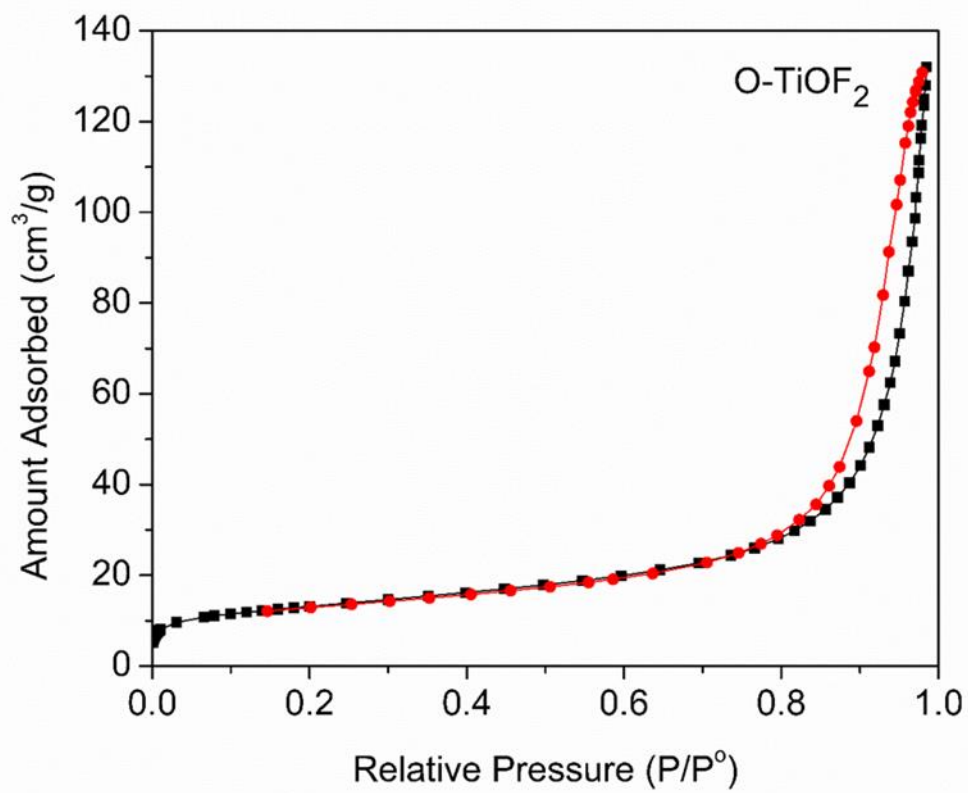


Figure 5: Isotherm of nitrogen adsorption for O-TiOF₂ used in the calculation of the BET surface area.

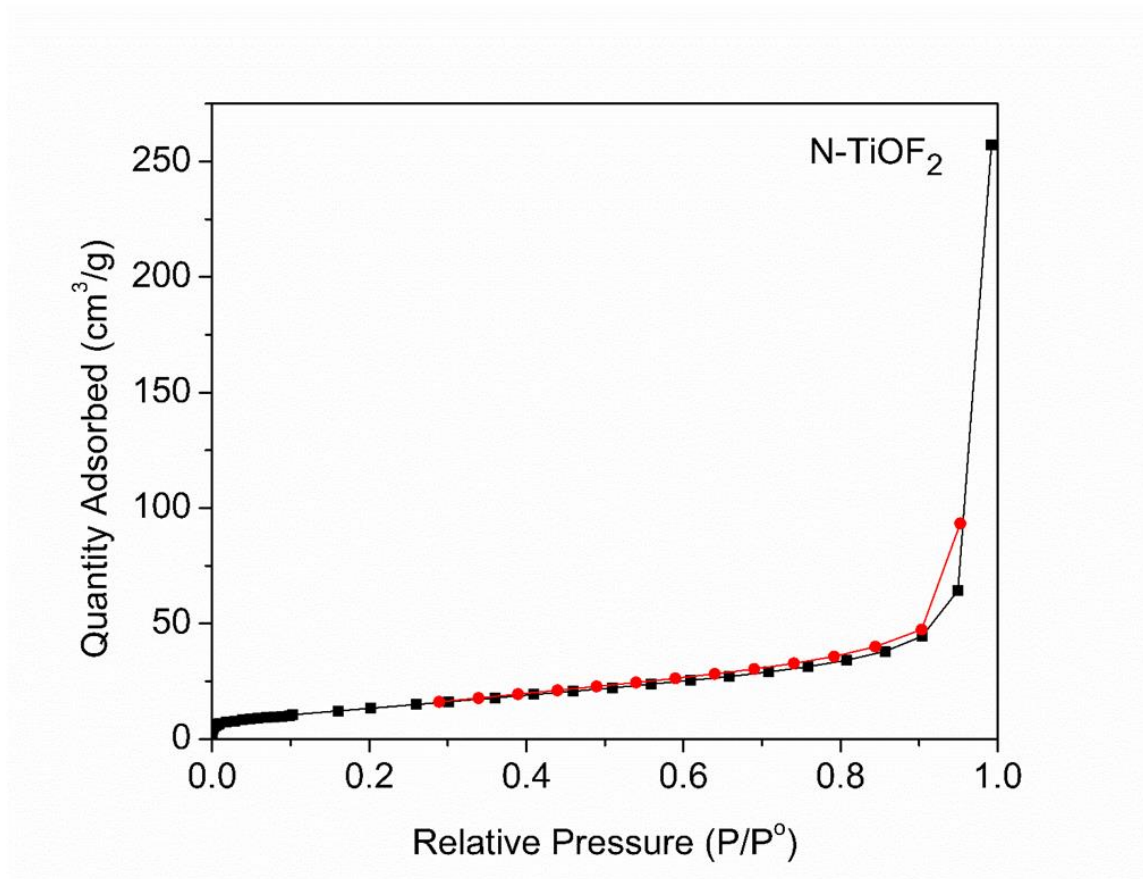


Figure 6: Isotherm of nitrogen adsorption for N-TiOF₂ used in the calculation of the BET surface area.

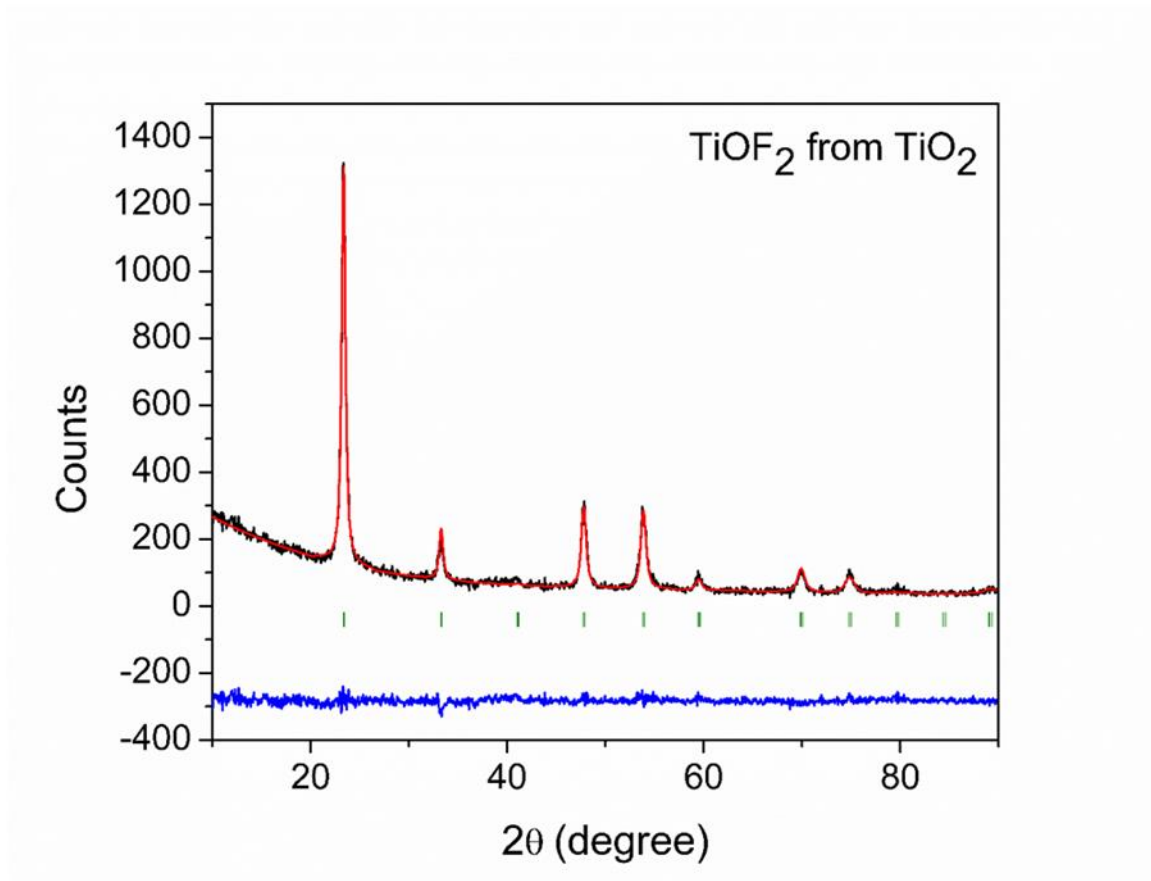


Figure 7: Rietveld refined X-ray diffraction data for O-TiOF₂. The red line is the calculated pattern, black is the experimental diffraction pattern, and blue is the difference between the calculated and the observed. Reflection positions for TiOF₂ are shown in green. The statistical goodness-of-fit parameters are χ^2 of 0.807 and Rwp of 25.8.

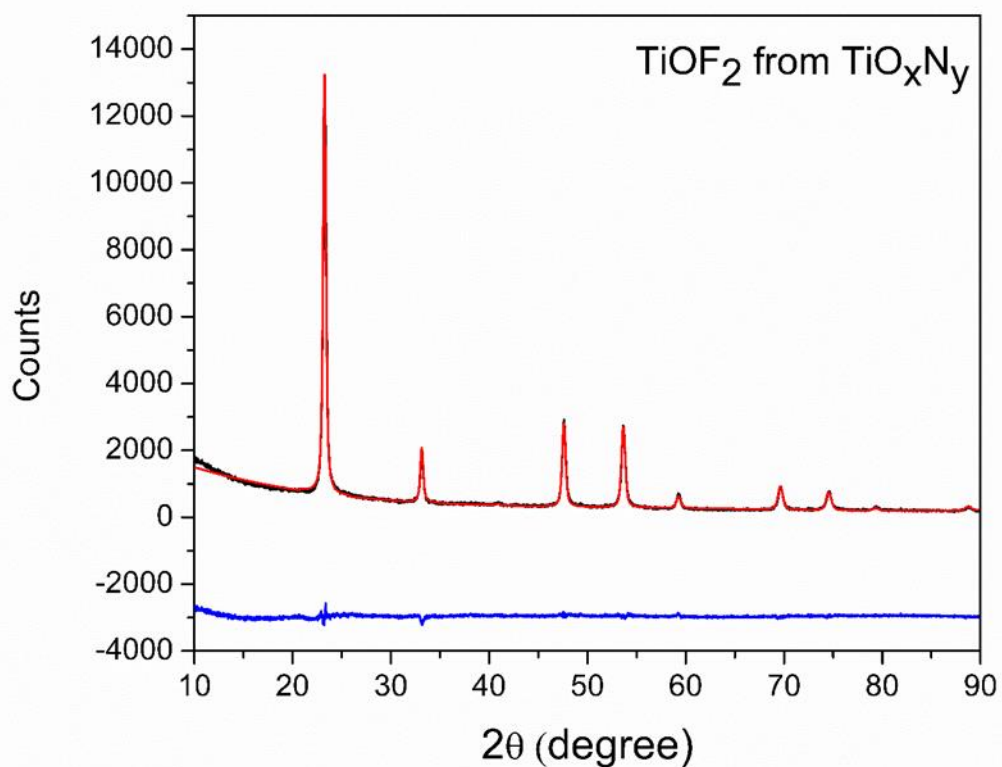


Figure 8: Rietveld refined X-ray diffraction data for pure N-TiOF₂. The red line is the calculated pattern, black is the experimental diffraction pattern, and blue is the difference between the calculated and the observed. Reflection positions for TiOF₂ are shown in green. The statistical goodness-of-fit parameters are χ^2 of 1.97 and the Rwp of 13.8.

at 225 °C the fluorination route produces largely phase pure powders. It is notable that a TiOF_2 phase prepared through a low temperature metathetic reaction with SiO_2 has also been reported to crystallize in a rhombohedral structure with $a = 5.333 \text{ \AA}$ and $c = 13.232 \text{ \AA}$, and to undergo a reversible transition to a high temperature cubic structure near 60-65 °C.⁵¹ The clearest distinction between the diffraction patterns of cubic TiOF_2 and the rhombohedral structure can be made with peaks near to $2\theta = 40^\circ$; the $(113)_\text{H}$ reflection of the R-3c TiOF_2 structure is reported at $39.4^\circ 2\theta$, as compared to $38.5^\circ 2\theta$ for the $(113)_\text{H}$ of TiF_3 , and there is no peak from the cubic structure present in this 2θ range. There is no strong $(113)_\text{H}$ present, whereas there is a $(111)_\text{C}$ reflection of the cubic Pm-3m TiOF_2 structure present near $41^\circ 2\theta$, and Rietveld refinements of TiOF_2 powders prepared at 225 °C with direct fluorination clearly favor a cubic structure. It should be noted that a very weak, broad peak near $38.2^\circ 2\theta$ is observed in some samples that can be assigned either to a partially fluorinated TiO_2 anatase structure, or to a rhombohedral TiF_3 or $\text{TiO}_{1-x}\text{F}_{2+x}$ structure. The Rietveld refinements in the cubic structure give lattice parameters of $a = 3.8052(3) \text{ \AA}$ and $a = 3.81594(6) \text{ \AA}$, as well as average crystalline domain sizes of 21 nm and 30 nm, for the TiOF_2 synthesized from the TiO_2 and the TiO_xN_y precursors, respectively. This indicates that a slight increase in domain size during conversion to the fluoride from the TiO_2 precursor, but a slight decrease in domain size during the conversion to the fluoride from the TiN precursor, though the results are similar within the error of the method. The

approximately 0.01 Å higher lattice parameter of the N-TiOF₂ may indicate a slight difference in composition, possibly due partial reduction of the sample to form the slightly larger Ti³⁺ cation as implied by the TiO_{1-x}F_{2+x} formula. Therefore, the two fluorinated materials exhibit the same structure and similar crystallinity, with slight differences in composition on the basis of which precursor was used.

Surface analysis

Ti2p, O1s, F1s, and N1s XPS data collected for the TiO_xN_y precursor material and the TiOF₂ compounds derived from the TiO₂ and TiO_xN_y precursors are presented in Figure 9. Data collected for the TiO_xN_y precursor (bottom row) are consistent with the presence of both oxygen and nitrogen. The data show the formation of a complex mixture of Ti species on the surface of the TiO_xN_y. From the curve fits of the Ti 2p_{3/2} peak we see evidence for the presence of three Ti species. The low energy peak is centered around 454.7 eV which is due to Ti³⁺-N bonding.^{49, 52-68} A second, higher energy species is located at 455.9 eV which is attributed to Ti^{3+/4+}-O/N bonding or satellite peaks for the Ti³⁺-N species.^{49, 52-53, 59, 62-77} Given the clear evidence of O on the surface (Figure 9, lower middle), it is likely this species is due to the Ti-O/N species. Finally, there is a high energy feature at 458.2 eV due to Ti⁴⁺-O bonds. The intensity of this peak, and the apparent corresponding concentration, may be a bit misleading given the overlap between the Ti 2p_{1/2} peak originating from the Ti³⁺-N which overlaps with the Ti

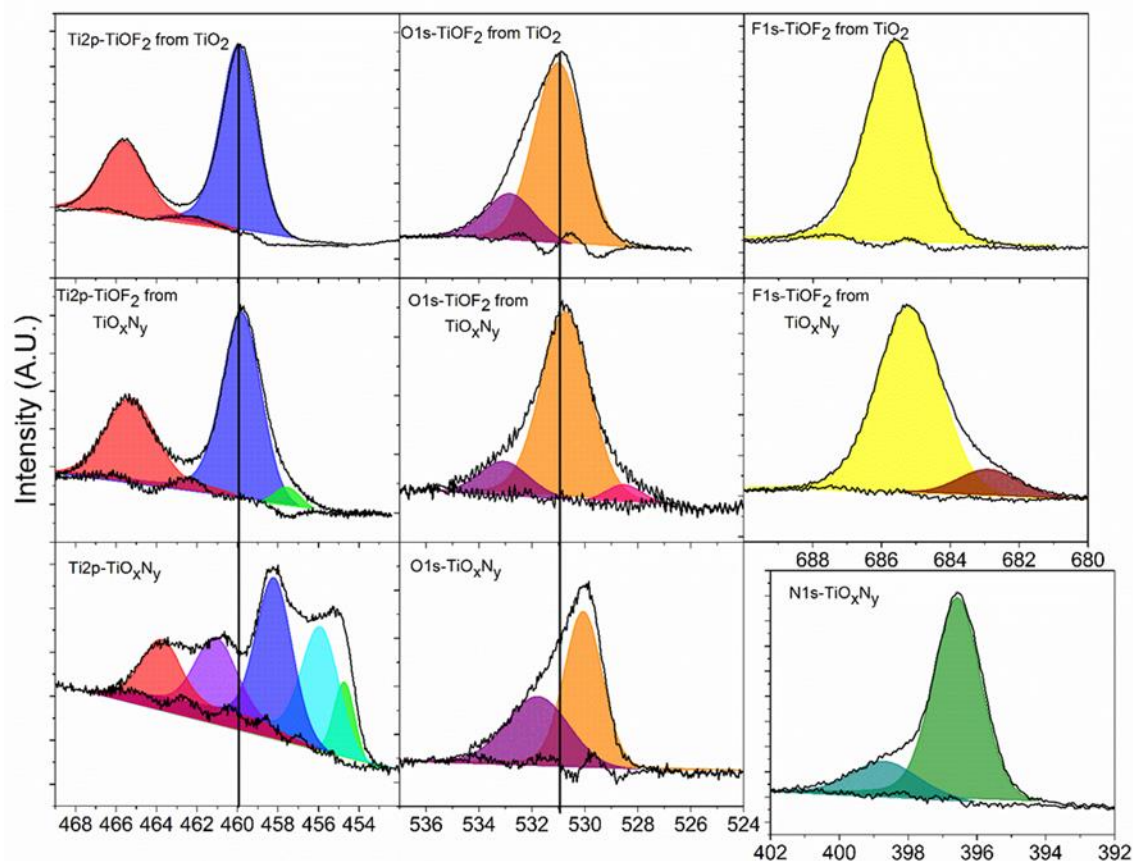


Figure 9: XPS data for O-TiOF₂ and N-TiOF₂ in the Ti2p, O1s and F1s regions, are shown in the upper and middle rows, respectively. Data show similar binding energy (BE) peaks for both TiOF₂ materials, but there are additional peaks in the N-TiOF₂ spectra at lower BE indicating the presence of reduced species. N-TiOF₂ showed no nitrogen peaks in XPS data. For comparison, XPS of TiO_xN_y in the Ti2p, O1s and N1s regions are shown in the bottom row, indicating a large contribution of nitrogen and reduced titanium species.

$2p_{3/2}$ peak of $Ti^{4+}-O$.^{49, 52-53, 55, 58-59, 62-66, 68-74, 76-81} The O1s data collected for the TiO_xN_y precursor shows clear evidence for the presence of two O species. The first O species has a binding energy of ~ 530 eV and is due to the Ti-O bonds evident in the Ti 2p data.^{49, 52, 55, 59, 64, 66-67, 72-73, 75-78} The second species is located at a higher binding energy (~ 532 eV) and can be attributed to either an oxynitride species, adsorbed water or oxygen on the surface, or metal hydroxy species.^{49, 52, 59, 64, 66, 72, 77} We believe that this peak is attributed to either the oxynitride species or the adsorbed water/oxygen. The N1s data also shows the presence of two N containing moieties. The main N species has a binding energy of 396.4 eV and is due to the Ti-N bonds discussed for the Ti 2p XPS data.^{49, 52-55, 59, 64, 66-68, 72-73, 75-79} The second N species has a binding energy of 399 eV and is due to Ti-O/N species.^{52-53, 64, 66-68, 72, 76, 79} However, it has similarly been debated as to whether the peaks in this region are intrinsic to TiN and other metal nitrides, and can be attributed to shake up peaks.^{55, 64} Together this data indicates the surface chemistry of the TiO_xN_y is a complex mixture of N, O/N and O species. This is not surprising given the reactivity of metal nitrides in air, however, the data clearly shows the presence of reduced Ti in the top few nanometers of the TiO_xN_y precursor.

XPS data for the fluorinated TiO_xN_y samples in the Ti2p, O1s, and F1s regions are dominated by the peaks expected for $TiOF_2$. From the curve fits of the Ti $2p_{3/2}$ peak we see evidence for the presence of two Ti species shown in Figure

9 (middle left). The high energy peak at 459.8 eV is attributed to Ti^{4+} $2p_{3/2}$ peak for TiOF_2 .⁸²⁻⁸³ This +0.6 eV shift relative to Ti^{4+} in the precursor is due to the more electronegative F added to the surface. The small peak at lower binding energy (457.6 eV) indicates the presence of a reduced Ti species, likely Ti^{3+} .^{72, 80, 84} This species is similar to the peak reported at 457.6 eV for “TiOFN” due to Ti^{3+} .⁸⁵ The O1s data collected for N-TiOF₂ shows clear evidence for the presence of three O species as shown in Figure 9 (middle center). The first peak is located ~531 eV and is attributed to a Ti-O species.^{83-84, 86-87} The next peak is seen at ~533 eV and is attributed to adsorbed water.⁸³⁻⁸⁴ The third smaller peak is located at 528.5 eV, which is attributed to oxygen bound to a reduced Ti^{+3} species shown to be present in the Ti2p spectrum of N-TiOF₂. The F1s data also shows the presence of two F containing moieties shown in Figure 9 (middle right). The main species has a binding energy of 685.2 eV and is due to the Ti-F bond in TiOF_2 .^{83, 86, 88-92} Two other possibilities exist for the presence of an F 1s peak near this binding energy, which are adsorbed fluorine (683.9 to 684.3 eV) or fluorine bound in the TiO_2 lattice (687.2 to 688.6 eV); based upon the XRD data, the main contribution is likely to be from Ti-F in TiOF_2 .⁸⁸⁻⁹³ We also see a small peak centered at 682.9 eV, which again we believe to be evidence of some binding to a reduced Ti^{+3} species. An N1s spectrum was taken for N-TiOF₂ but shows no peaks, indicating no nitrogen was left near the surface of the material after fluorination. However,

the presence of Ti^{3+} in N-TiOF_2 is a direct result of the reduced oxynitride precursor.

XPS data for the fluorinated TiO_2 samples in the $\text{Ti}2\text{p}$, $\text{O}1\text{s}$, and $\text{F}1\text{s}$ regions are solely peaks expected for TiOF_2 . From the curve fits of the $\text{Ti } 2\text{p}_{3/2}$ peak we see evidence for the presence of one Ti species shown in Figure 9 (top left). The high energy peak at 459.9 eV is attributed to $\text{Ti}^{4+} 2\text{p}_{3/2}$ peak for TiOF_2 .⁸²⁻⁸³ The $\text{O}1\text{s}$ data collected for O-TiOF_2 shows clear evidence for the presence of two O species as shown in Figure 9 (top center). The first peak is located ~ 531 eV and is attributed to a Ti-O species.^{83-84, 86-87} The next peak is seen at ~ 533 eV and is attributed to adsorbed water.⁸³⁻⁸⁴ The $\text{F}1\text{s}$ data also shows the presence of only one F containing species shown in Figure 9 (top right). This peak shows a binding energy of 685.6 eV and is due to the Ti-F bond in TiOF_2 .^{83, 86, 88-92} The O-TiOF_2 showed no peaks at lower binding energies as seen in the N-TiOF_2 material. Therefore, there is no reduced titanium species present in the fluorinated TiO_2 sample, which is expected since there was no reduced titanium species in the precursor. The main difference in surface chemistry between N-TiOF_2 and O-TiOF_2 is the presence of Ti^{3+} in N-TiOF_2 , which may enhance the electrical conductivity of the material through doping into a conduction band.

Electrochemistry of TiOF_2 formed through direct fluorination

The electrochemical performance of the precursor powders was characterized for comparison with the fluorinated products. The electrochemical performance of TiO_2 and TiO_xN_y between 3.0 and 0.05 V at a rate of C/10 are shown in Figure 10. The theoretical capacity of TiO_2 as an intercalation compound is 335 mAh g^{-1} , for the intercalation of 1 mole of Li per formula unit. For these commercial materials we measure a capacity of $\sim 138 \text{ mAh g}^{-1}$ as compared to values of up to 235 mAh g^{-1} (or a composition near $\text{Li}_{0.7}\text{TiO}_2$) for more optimized nanophase electrodes. A plateau is observed at approximately 1.75 V vs Li/Li^+ , as expected for the intercalation reaction of Li into TiO_2 in nanosized anatase (the majority phase) particles.⁹⁴ This intercalation plateau corresponds to a partial reduction of titanium from the +4 to +3 oxidation state, and to a phase transition to orthorhombic *Imma* for a composition near $\text{Li}_{0.5}\text{TiO}_2$.⁹⁵ For the high surface area TiO_2 nanoparticles employed in this study, the capacity quickly fades with cycling from 520 mAh g^{-1} in the first cycle, to under 250 mAh g^{-1} in subsequent cycles. The high initial capacity is due in part to SEI formation, and the subsequent capacity fade is due to a pulverization of the material from the expansion and contraction of the lattice as lithium is intercalated and deintercalated. The TiO_xN_y precursor displayed a reversible specific capacity of less than 50 mAh g^{-1} during cycling versus lithium (Figure 10, top right), consistent with a low level of SEI formation and the capacity of carbon present in the electrode formulation; the poor

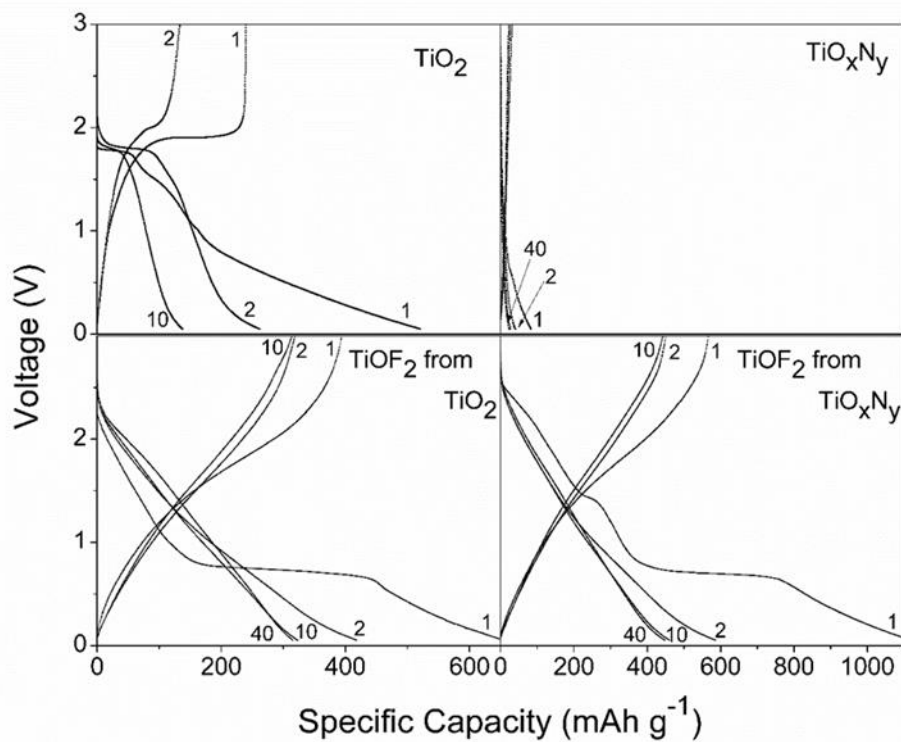


Figure 10: Galvanostatic cycling data of voltage versus specific capacity for O-TiOF₂ and N-TiOF₂, with their corresponding precursor materials shown in the upper row. All cells were cycled at a rate of 33.5 mA g⁻¹, equivalent to C/10 for TiO₂, and cycled between 3.0 and 0.05 V. The fluorinated materials show improved reversible capacity and cycle stability relative to their precursor.

diffusion rate of lithium in the rock salt structure, combined with the fact that most of the titanium has already been reduced from Ti^{4+} , is likely responsible for the lack of capacity.⁹⁶ Due to contributions from non-optimal crystal structure and morphology, the capacities of the precursor TiO_2 and TiO_xN_y powders are relatively low.

The electrochemical profiles of the N- and O- TiOF_2 materials are shown in Figure 10 and Figure 11, for data collected from 3.0-0.05 V at a rate of C/10. There are significant differences between the TiOF_2 samples over all cycles due to the different precursor chemistry: during the first discharge O- TiOF_2 has a capacity near 650 mAh g^{-1} and N- TiOF_2 has a capacity of over 1100 mAh g^{-1} , such that the initial capacity of the N- TiOF_2 is over 30% higher than that of O- TiOF_2 . There is a large irreversible capacity loss between the first and second discharge cycles; O- TiOF_2 gives a second discharge capacity of 418 mAh g^{-1} and N- TiOF_2 a second discharge capacity of 587 mAh g^{-1} , which suggests an irreversible capacity loss of 47% and 51%, respectively. This compares well with results for TiOF_2 materials produced by other methods (with morphologies such as nanotubes, nanocubes and nanospheres), which give initial discharge capacities between 860 and 1045 mAh g^{-1} , and show irreversible capacity losses between the first and second discharge cycles of 44% to 48%.^{42-44, 97} The large irreversible capacity loss, along with the first discharge capacity above the theoretical maximum for N- TiOF_2 , clearly indicates that some Li is being consumed in the formation of an SEI layer.

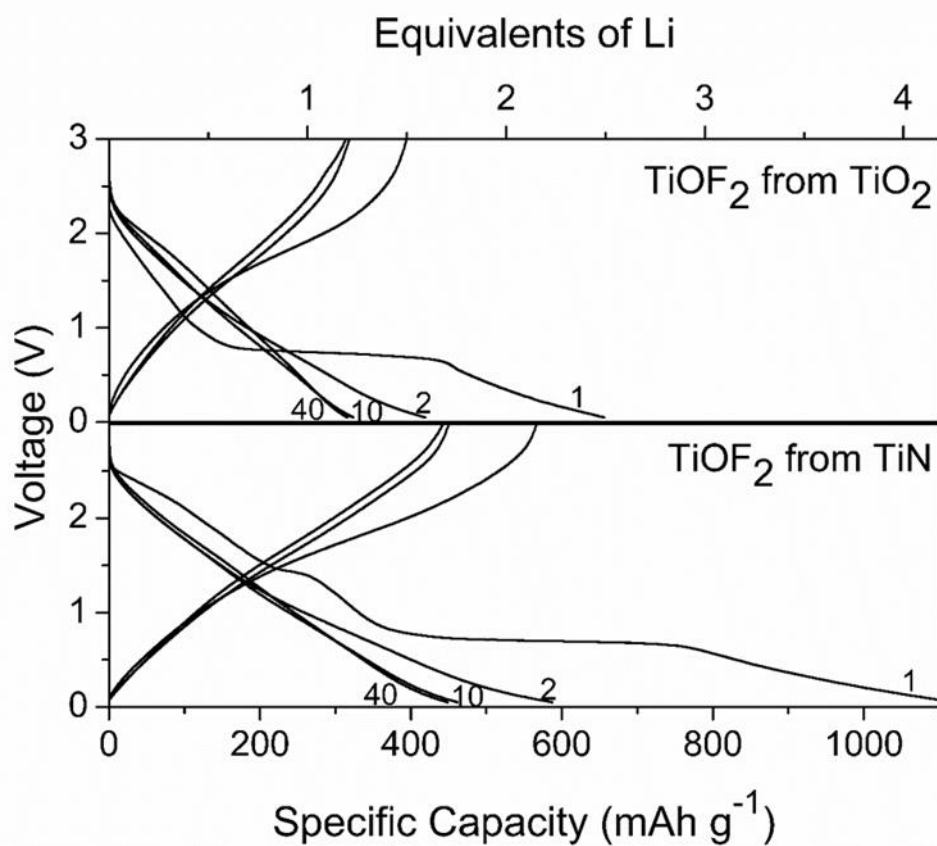


Figure 11: Galvanostatic cycling data comparing O-TiOF₂ and N-TiOF₂. Both cycled between 3.0-0.05 V at a current density of 33.5 mA g⁻¹ (C./10 for TiO₂). N-TiOF₂ shows an approximate 71 % increase in initial capacity from the first discharge over that of the O-TiOF₂. N-TiOF₂ shows an approximate 43 % increase in reversible capacity at the 40th discharge over that of the O-TiOF₂.

Fluorination of the precursors has resulted in a large increase in reversible capacity beyond the initial cycles. After 10 cycles, where the SEI should presumably be relatively constant, the capacities for N- and O-TiOF₂ are 470 and 325 mAh g⁻¹, respectively, whereas the TiO₂ capacity is near 140 mAh g⁻¹. Electrochemical cells for each material were run in triplicate and cycling capacities were within 10% of the given value. In the literature reversible capacities of TiOF₂ materials were seen to range from 377 to 510 mAh g⁻¹ at a current density of 30 mA g⁻¹, which is in the range of materials reported here.^{43-44, 90} This compares with theoretical capacities of 263 mA g⁻¹ for 1 Li per TiOF₂ and 1052 mA g⁻¹ for complete reduction to titanium metal. The results are consistent with a maximum of close to 2 Li per formula unit of reversible capacity, due to the difficulty in reducing Ti below an oxidation state of +2.

While there is an increase in reversible capacity for both fluorinated samples, there are clear differences between the two samples in the voltage profile during the first cycle lithiation. For example there is a second plateau at higher voltage evident at 1.4 V during lithiation for the N-TiOF₂ sample (~80 mAh g⁻¹) that is absent in the O-TiOF₂ sample. Secondly, the large plateau at 0.7 V is much larger for N-TiOF₂ (~410 mA g⁻¹) as compared to O-TiOF₂ (~300 mA g⁻¹). XPS results have shown that the surface chemistries and compositions of the electrodes are similar, with the exception of partial reduction in the case of N-TiOF₂. Although N-TiOF₂ and O-TiOF₂ appear to have the same structure from

XRD analysis, N-TiOF₂ exhibits a higher reversible capacity in addition to having a second plateau at 1.4 V in the first discharge cycle. The differences between the N- and O-TiOF₂ raises questions about the role of structure and composition in the reaction mechanism of TiOF₂.

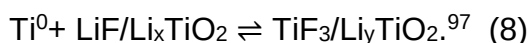
There has been a significant discussion in the literature regarding the details of the reaction mechanism. Li-ion half-cell batteries containing TiOF₂ electrodes have been reported to show a plateau at 1.3 V by Zeng et. al. and Dambournet et. al., while others do not show any plateau in this region.^{42-44, 97} The studies that contain the plateau at 1.3 V attribute it to a phase transition of TiOF₂ from a cubic ReO₃-type structure to a rhombohedral structure upon lithiation, a structure which has been independently reported in a sample prepared by chemical lithiation.⁹⁸ The chemical lithiation study was carried out using n-butyl lithium, which corresponds to a potential of 1 V vs. Li⁰, meaning that only reactions that occur above that potential can be observed.⁹⁷⁻⁹⁸ This provides support for the possibility that the plateau at 1.3 V is from an intercalation reaction and the associated structural change of TiOF₂. It has not been clearly explained in the literature why TiOF₂ prepared through some routes show this small plateau at 1.3 V, while others do not. Given that amorphization at lower voltages appears to remove this plateau in subsequent cycles, the presence of this peak may be related to the initial crystallinity of the TiOF₂ sample, or subtle structural and compositional changes due to precursor chemistry.

It is worth further examining the role that structure and composition may play in the reaction mechanism, through consideration of the relationship between the electrochemistry TiOF_2 and that of similarly structured MF_3 compounds ($\text{M}=\text{Ti}, \text{Fe}, \text{V}, \text{Co}, \text{Cr}$). Metal fluorides such as these crystallize in a VF_3 -type rhombohedral structure which is derived from the ReO_3 cubic structure type.⁹⁹ Comparing the electrochemical data of TiF_3 to N-TiOF_2 when cycled versus lithium, a similar voltage profile is observed. TiF_3 shows two plateaus: the first is a smaller plateau near 1.4 V, and the second is a larger plateau at 0.9 V.¹⁰⁰⁻¹⁰¹ The plateau near 1.4 V is attributed to intercalation to form a Li_xMF_3 ($\text{M}=\text{Fe}, \text{Ti}, \text{V}$) phase, where x can be up to 0.5, and the second plateau to the conversion reaction to form LiF and Ti .¹⁰⁰⁻¹⁰² TiF_3 , Li_xTiF_3 and Li_xTiOF_2 have rhombohedral ReO_3 -type structures, and consequently have very similar diffraction patterns. Chemical lithiation of the oxyfluoride was carried out by Dambournet et. al. with a Ti/Li ratio of 3:1 and was refined using $R\text{-}3c$ space group and achieved a fit with refined lattice parameters of $a=5.143 \text{ \AA}$ and $c=13.928 \text{ \AA}$.⁹⁷ This compares to the chemical lithiation of TiOF_2 by Murphy et. al., who for a structure of $\text{Li}_{0.43}\text{TiOF}_2$ gave the lattice parameters of $a=5.12 \text{ \AA}$ and $c=13.615 \text{ \AA}$.⁹⁸ Murphy et. al. also gave lattice parameters for a $\text{Li}_{1.5}\text{TiOF}_2$ phase of $a=5.131 \text{ \AA}$ and $c=13.998 \text{ \AA}$ which more closely matches the lattice parameters given by Dambournet et. al., despite a much higher level of lithiation than was reported in the Dambournet et. al. experiments.⁹⁸ Furthermore, a non-lithiated $R\text{-}3c$ rhombohedral phase of TiF_3 is reported to have lattice

parameters of $a = 5.144 \text{ \AA}$ and $c = 13.845 \text{ \AA}$ with reflections in the same positions as is seen in ICSD 52160.¹⁰³ It should be noted that due to the structural similarity between the various possible lithiated and non-lithiated rhombohedral phases, and the variations in lattice parameter reported in the literature, it is difficult to definitively state the composition of lithiated materials on the basis of XRD data. The presence of a plateau near 1.4 V in N-TiOF₂ is a sign of a lithium intercalation mechanism, which by comparison with rhombohedral TiF₃ may reflect the presence of Ti³⁺ in a fluorine-rich TiO_{1-x}F_{2+x}. The presence of Ti³⁺ near the particle surface is supported by XPS data, and the possibility of fluorine-rich TiO_{1-x}F_{2+x} by the slightly larger lattice parameter of N-TiOF₂. The lack of the 1.4 V plateau in O-TiOF₂ may relate to the lack of Ti³⁺ in this structure. Furthermore, the partial reduction may contribute to the improved reversible capacity of the N-TiOF₂, as this could lead to a slight increase in electronic conductivity resulting in better electrode utilization.

As the crystallinity of the electrodes decreases upon cycling to the point at which XRD data are no longer useful in identifying the phases present, alternative spectroscopic techniques must be used to gain further information on the mechanism of reversible lithiation. Such studies have been reported on materials related to TiOF₂. Li et. al. performed ex situ micro-Raman spectroscopy on TiF₃ at various stages of Li insertion during cycling that indicated the formation of Li_xTiF₃ for $x \leq 0.5$, beyond which a conversion reaction is initiated to form LiF and Ti⁰;

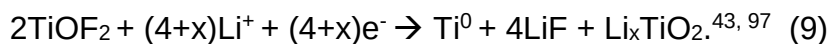
traces of TiF_3 can be seen in the spectra up to an insertion of 2.5 Li.¹⁰⁰ Upon Li extraction the reappearance of TiF_3 peaks in the spectra are apparent below 2.5 Li, which confirms that TiF_3 can be cycled reversibly. A reversible capacity of 400 mAh g^{-1} at a current density of 50 mA g^{-1} has been reported for a related titanium hydroxyfluoride material.⁹⁷ Dambournet et. al. have performed ^7Li NMR on cycled titanium hydroxyfluoride material from discharged and charged cells which gave spectra that were consistent with the presence of a Li_xTiO_2 phase. By combining the NMR data with the pair distribution function (PDF) approach and XPS data, Dambournet et. al. proposed a mechanism for the reversible capacity of nanoscale titanium hydroxyfluoride that involved parallel conversion and intercalation reactions written as



It was further suggested that a similar mechanism may be active in reversible cycling of TiOF_2 . Essentially, after the first discharge cycle of TiOF_2 , a composite would form of fluoride and oxide phases that undergoes reversible cycling. More detailed investigations into the reaction of TiOF_2 and Li at higher potentials need to be carried out in order to determine whether an Li_xTiOF_2 phase can be formed after the first cycle, or whether the formation of a titanium fluoride

and titanium oxide composite is the only available mechanism for reversibly cycling TiOF_2 .

The large plateau at 0.7 V has been attributed to three different possibilities. First it could be a reaction with two different lithiated phases in equilibrium, expressed as Li_xTiOF_2 and Li_yTiOF_2 where $y > x$.^{42, 44, 83} This would imply a phase transition that has not been directly observed due to the low crystallinity at higher levels of lithiation. The second possibility proposed is the direct conversion reaction



The third possibility is that all or part of this plateau around 0.7 V is caused by SEI formation, which for a cell with LiPF_6 in EC:DEC electrolyte typically occurs near this potential.²⁵ Given the possible mechanisms for the 0.7 V plateau, the disappearance of this plateau in later cycles suggests either that an irreversible structural change has occurred or that a stable SEI has formed. Given the large irreversible capacity in the first discharge cycle, it is likely that SEI formation contributes significantly to this plateau. Furthermore, ex situ XPS data collected seen in Figure 12 confirms the presence of reduced titanium species after discharging to 0.05 V, as expected for both intercalation and conversion mechanisms. However, because of the large SEI layer formation that occurs when

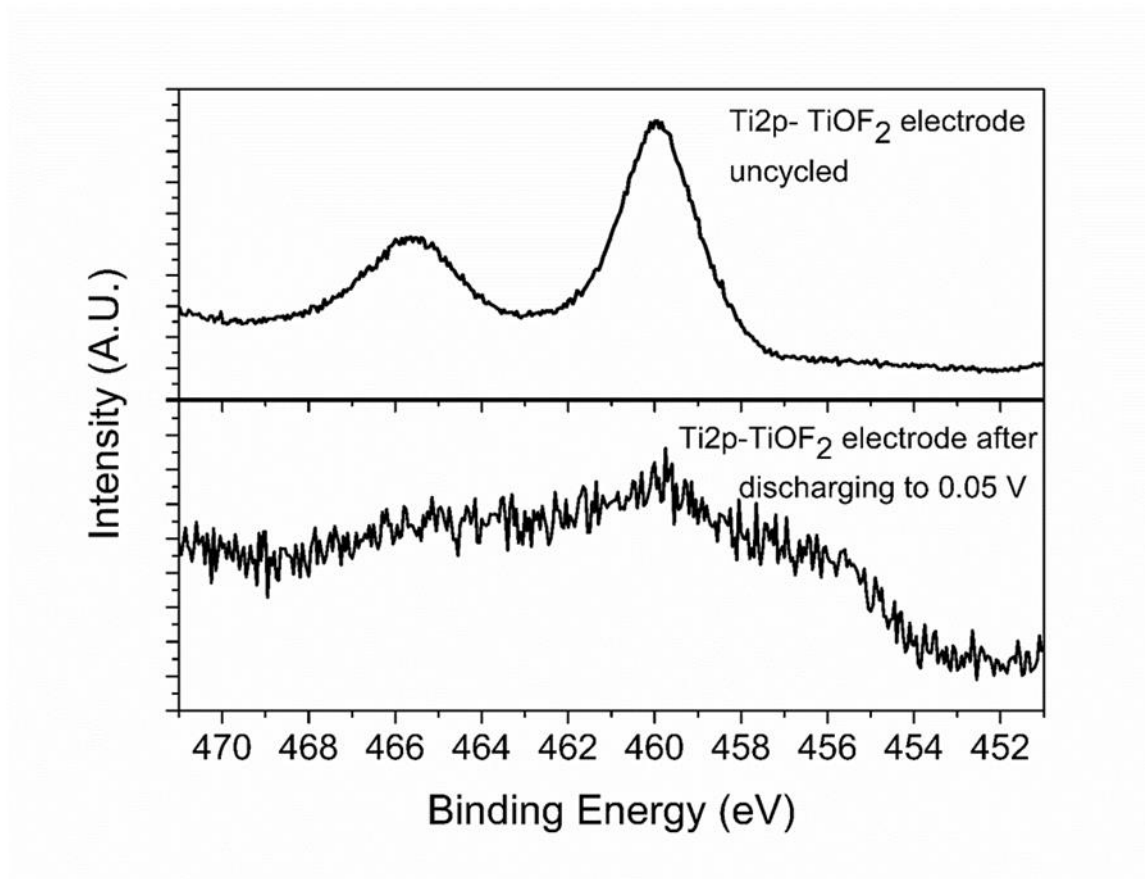


Figure 12: Ex situ XPS spectra in the Ti2p region for O-TiOF₂ electrodes before cycling (Top) and after discharging to 0.05 V (Bottom) at a rate of 33.5 mA g⁻¹ are shown. The spectrum of the discharged electrode is much noisier due to the large amount of SEI layer formation that occurs when discharging to low potentials. However, it can still clearly be observed by the shift in peak position to lower binding energy shown by the circled region that there is the presence of reduced Ti species, such as Ti³⁺.

cycling to this voltage the noise in the spectrum is quite high and does not allow a concrete assignment of fully reduced or partially reduced Ti species. In consideration of the evidence for intercalation at higher voltages, and the apparently irreversible conversion reaction to a mixed phase fluoride/oxide in the related titanium hydroxyfluoride, the lithiation mechanism in TiOF_2 is likely a combination of the reported possible mechanisms. This would involve lithium intercalation at higher voltage, followed by SEI formation and conversion reaction at lower voltage during the initial discharge, forming a mixed composite electrode that exhibits reversible cycling (as in reaction (7)).

A rate capability experiment was also performed on the O- TiOF_2 and N- TiOF_2 to determine the stable capacity of the electrode material at current densities of C/10, C/2, C, 5C, 10C, 20C and 50C. The capacity quickly fades to below 70% of the initial stable capacity as the current is increased by a factor of ten, as can be seen in Figure 13. The capacity returns to the initial capacity when the current is reduced, meaning that no irreversible reactions occurred from the use of increased current, and the capacity loss is largely due to polarization and diffusion limitations. Only one prior report of rate capability for TiOF_2 was found in the literature, which was for TiOF_2 nanotubes prepared by Zeng et. al. Similar results were obtained in this study and for the nanotubes, with a reversible decrease in capacity as current density was raised.⁴³ The rate capability was found to be

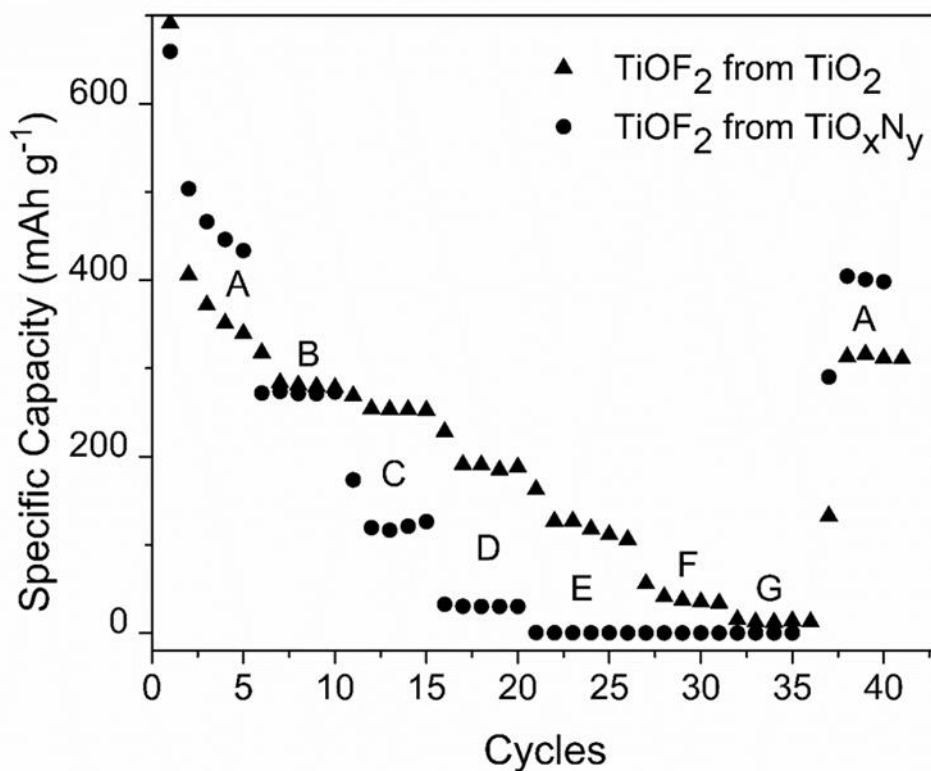


Figure 13: Rate capability test showing specific capacity of TiOF₂ formed from TiO₂ and TiO_xN_y at increasing charge-discharge current densities of A 33.5 (C/10), B 167.5 (C/2), C 335 (C), D 1675 (5C), E 3350 (10C), F 6700 (20C), and G 16750 (50C) mA g⁻¹. All measurements taken within the voltage window of 3.0 -0.05 V. Capacity quickly fades as current density is increased, but capacity is returned when the current density is decreased.

similar, though slightly higher in the nanotubes reported by Zeng et. al. for a similar current density, due to the lower diffusion length of the nanotube wall.

Fluorination of TiO_2 nanoparticles produces an enhancement of electrochemical performance, and the fluidized bed method provides the capability to readily form mixed phase or single phase powders from any given precursor powder. The method allows for the possible control over anion composition by varying the reaction conditions (i.e., time, temperature, etc.). The enhanced performance of N- TiOF_2 suggests that starting from reduced or partially reduced precursors may result in higher performance, and more generally that a useful focus for research is to optimize the anion composition of precursor materials.

Conclusions

A new method for the synthesis of TiOF_2 nanoparticles has been demonstrated through the direct fluorination of TiO_2 or TiO_xN_y precursors in an FBR reactor system. Using the new method for the synthesis of TiOF_2 we have been able to synthesize nanoparticles of approximately 20-30 nm domain size that show battery cycling data comparable to that of other nanostructured TiOF_2 based materials in the literature. Fluorination of the TiO_xN_y precursor yields a single phase product of TiOF_2 , and shows no residual nitrogen by XPS. The N- TiOF_2 shows a second plateau in the initial discharge at 1.4 V which is not seen in the O-

TiOF₂ material. This plateau is related to an intercalation-based lithiation reaction, and there is evidence to suggest a slightly reduced, fluorine rich TiO_{1-x}F_{2+2x} phase may be involved in the N-TiOF₂ electrode material. The N-TiOF₂ also shows an increased capacity over the O-TiOF₂ by about 30%, which is likely related to partial reduction in the N-TiOF₂ leading to improved electrical conductivity and electrode utilization. Mixtures of TiO₂/TiOF₂ were synthesized using the FBR reactor system simply by adjusting the reaction temperature of the fluorination. The fluorination of TiO₂ nanoparticles to form mixed phase powders was shown to increase the capacity by over 50% and greatly improve the cycle stability of the starting TiO₂ material. Our results highlight the role that anion modification of precursor materials can play in producing high performance electrodes, rather than the typical focus on post-processing of electrode powders.

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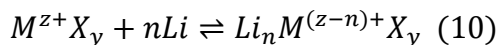
CHAPTER THREE

RUTHENIUM (III) CHLORIDE

Introduction

The best electrode material will be one that can be synthesized simply in large quantities and is a relatively small molecule, therefore, providing the best possible gravimetric capacity. There are several chemistries which are attractive for application to lithium ion batteries aside from traditional intercalation compounds. The conversion type electrode is one of these classes of materials and contains many compounds such as the metal oxides, nitrides, fluorides, and even chlorides. These materials have capacities that can reach $1,000 \text{ mAh g}^{-1}$, almost three times that of the standard graphite electrode,²⁷ due to the ability to access multiple oxidation states of the transition metal and follow the generalized reaction 7. Very little work has been done using metal chlorides as electrode materials in Li-ion batteries because of their high rate of material dissolution in non-aqueous electrolytes during cycling and because metal fluorides will provide higher voltages due to the stronger electronegativity of fluorine.^{15, 102, 104} There are, however, very few examples of attempts to use metal chlorides as electrode materials such as AgCl , CoCl_2 , and CuCl .¹⁰⁵⁻¹⁰⁷ Even when broadening the scope of research to composite electrodes of metal chlorides and other materials such

as carbons, graphenes and polymers, there is still only a small amount of literature in the area.^{105, 108-110} α -RuCl₃ has been studied as an interesting material in many areas of research due to its structure and unique magnetic and electronic properties. It is being studied as a model compound for the Kitaev spin model in which spin $\frac{1}{2}$ centers are arranged in a honeycomb lattice competing with exchange interactions as far as the third neighbor.¹¹¹⁻¹¹³ This material has also been researched for various reactions in the field of catalysis including aldol condensations and aminations.¹¹⁴⁻¹¹⁶ It has a layered honeycomb structure that is described as graphite like. With graphite being the commercially leading anode in Li-ion batteries, having a similar layered structure makes α -RuCl₃ a great candidate as a lithium intercalation type electrode which would follow the general reaction



where M is a cation with multiple oxidation states, and X is an anion such as oxygen. This general reaction illustrates a LiCoO₂ type compound undergoing intercalation. In addition being a metal halide means this material has good potential to be used as a conversion type electrode, therefore, with α -RuCl₃ we can expect both intercalation and conversion type reactions during the lithiation process. There are two structures for RuCl₃, the α form and the β form. Unlike

the β form, which is highly soluble in aqueous and non-aqueous solvents, the α form is nearly insoluble requiring high temperature acidic solvent stirring for weeks in order to achieve significant dissolution. This allows us to use bulk α - RuCl_3 as an electrode without the problems of serious dissolution in the electrolyte that is faced with many metal chlorides. This makes α - RuCl_3 a perfect candidate to be used to explore the chemistry of metal chlorides as electrodes in the field of batteries. Since this material is tested as both an intercalation and conversion type electrode, it is cycled as an anode down to low voltages vs Li/Li^+ .

Experimental

Synthesis of α - RuCl_3

Pure α - RuCl_3 was synthesized via direct chlorination of RuCl_3 powder (Sigma Aldrich) using HCl gas. This was necessary because the purchased powder was a mixture of chloride, oxychloride, and hydroxychloride phases. The purchased powder is first heated to $300\text{ }^\circ\text{C}$ under flowing HCl for 10 hours in order to remove any residual water from the material without forming a large amount of ruthenium oxide phase. The material is then quickly reground in order to achieve a uniform reaction before being placed back in the reaction tube. It is then heated to $375\text{ }^\circ\text{C}$ under flowing HCl for 24 hours to achieve full reaction to form pure RuCl_3 .

phase. After chlorination there is a mixture of both the alpha and beta phases. In order to achieve a pure product of only the alpha phase the product is heated in a sealed tube for 48 hours at 500 °C.

Structural analysis of α -RuCl₃

The powder and ex situ electrodes were characterized using a Panalytical Empyrean powder X-ray diffractometer employing Cu K α radiation. Data was collected within the 2 θ range of 10-90°, using a spinning reflection sample stage, and a Si zero background sample holder was used for the powder sample.

Crystal structures were refined using the Rietveld method in FullProf Suite.⁴⁷⁻⁴⁸

SEM measurements

The size and the morphology of the α -RuCl₃ product material particles were investigated using a JEOL JSM- 6060 scanning electron microscope. Images were taken while using an accelerating voltage between 7-10 kV and using the slowest scan speed.

XPS measurements

The surface chemistry of the precursor materials, electrode powders and cycled electrodes were investigated using a PHI 3056 XPS spectrometer equipped

with an Al K α source (1486.6) at a measurement pressure below 10⁻⁸ Torr. After electrochemical cycling the electrodes were immediately disassembled in an Ar filled glovebox and rinsed with anhydrous DMC (less than 0.5 mL - Aldrich). Samples were transferred to the XPS chamber using an air-tight vacuum transfer system. High resolution scans were acquired at 350 W with 23.5 eV pass energy and 0.05 eV energy step. Survey scans were measured at 350 W with 93.9 eV pass energy and 0.3 eV energy step. The binding energies were shifted by setting the adventitious carbon signal to 284.8 eV to account for charging (0.1 – 0.3 eV). The intensities of the presented spectra are not normalized and are simply shifted vertically for clarity. The spectra were deconvoluted using Gaussian-Lorentzian functions and a Shirley-type background.

Electrochemical measurements

The electrochemical measurements were carried out at room temperature using two electrode CR2032 type coin cells. The working electrodes were prepared from a slurry of active material (α -RuCl₃), conductive agent (carbon black), and a binder (poly(vinylidene difluoride)) at a ratio of 80:10:10 percent by weight. The mixture was cast onto copper foil using the slurry method and dried to form the electrode. All electrodes contained a mass loading of between 2.4-4.2 mg cm⁻² of active material. All coin cells were assembled in an argon filled glove box using pure lithium foil as the counter electrode and polypropylene as the

separator. The electrolyte solution consisted of 1M LiPF₆ in a 1:1:1 volume ratio of ethylene carbonate, dimethyl carbonate, and diethyl carbonate from Novolyte with water impurity < 20 ppm. The assembled cells were cycled galvanostatically using a LAND CT2001A battery testing system. The battery cells were tested galvanostatically, with a current constant of 38.7 mA g⁻¹ while cycling between 3.0 and 0.05 V, which corresponds to a C/10 rate relative to the maximum theoretical capacity of 387 mAh g⁻¹ for α -RuCl₃.

Results and Discussion

α -RuCl₃ characterization

After synthesis, the α -RuCl₃ was measured and indicated formation of pure α -RuCl₃ (ICSD 20717). α -RuCl₃ has a CrCl₃-type structure consisting of edge sharing octahedra forming a honeycomb network in the a-b plane and stacked honeycomb layers along the c axis. Refinement gives a lattice parameter of a= 5.98 Å and a chi2 of 3.20, as seen in Figure 14. The refinement shows significant deviations due to stacking faults and preferred orientation in the structure. Through SEM images, size, morphology, and the layered structure of the α -RuCl₃ can be seen. There are two morphologies of particles present throughout the sample. The first is a large particle with a diameter of ~5 μ m and the second

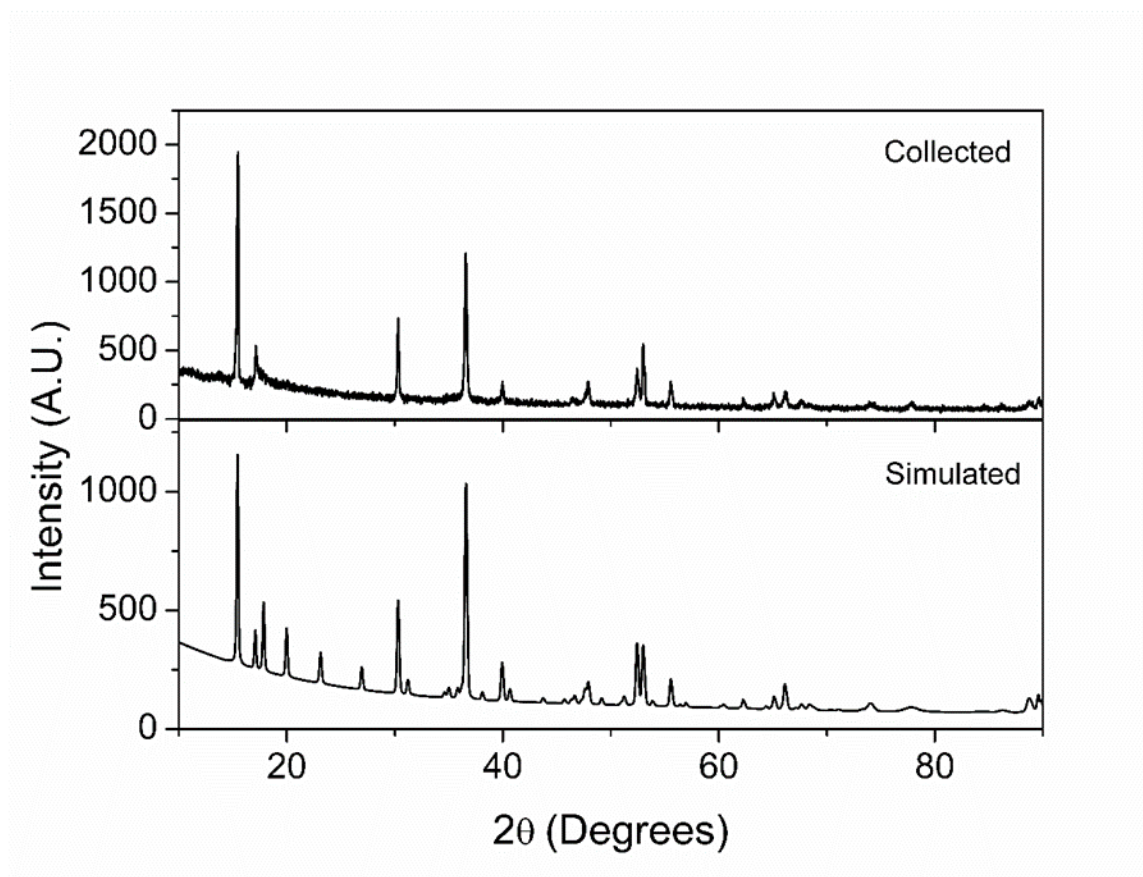
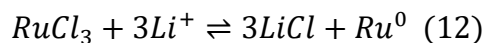
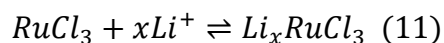


Figure 14: XRD spectra of α -RuCl₃ collected pattern compared to the refinement simulated pattern.

appears to be an agglomeration of smaller particles that are $\sim 1 \mu\text{m}$ or less in diameter, as seen in Figure 15.

Electrochemistry of $\alpha\text{-RuCl}_3$ formed through direct chlorination

In order to first confirm that no alloying side reactions would occur between the Li and the Ru, thin films of Ru were prepared as anodes for the Li battery testing. The Ru thin films showed no capacity, as seen in Figure 16, which means that LiRu alloying reactions do not need to be considered when analyzing the $\alpha\text{-RuCl}_3$ battery cycling data. What we do see in the voltage profile is a complex series of plateaus, indicating multiple single phase and two phase reactions occurring during the complete lithiation of $\alpha\text{-RuCl}_3$. As shown in Figure 17, distinct plateaus can be seen at ~ 2.7 and ~ 1.5 V, indicating that these are clearly regions in which two phase reactions are occurring. There are also several strong inflections seen at ~ 2.4 and ~ 1.2 V. These inflections are located in the sloping voltage regions of the profile, which indicate a single phase reaction system. It was thought that this system would contain two reactions; first, an intercalation given by reaction 11, and then a conversion given by reaction 12, but the voltage profile indicates that the system is more complex than this.



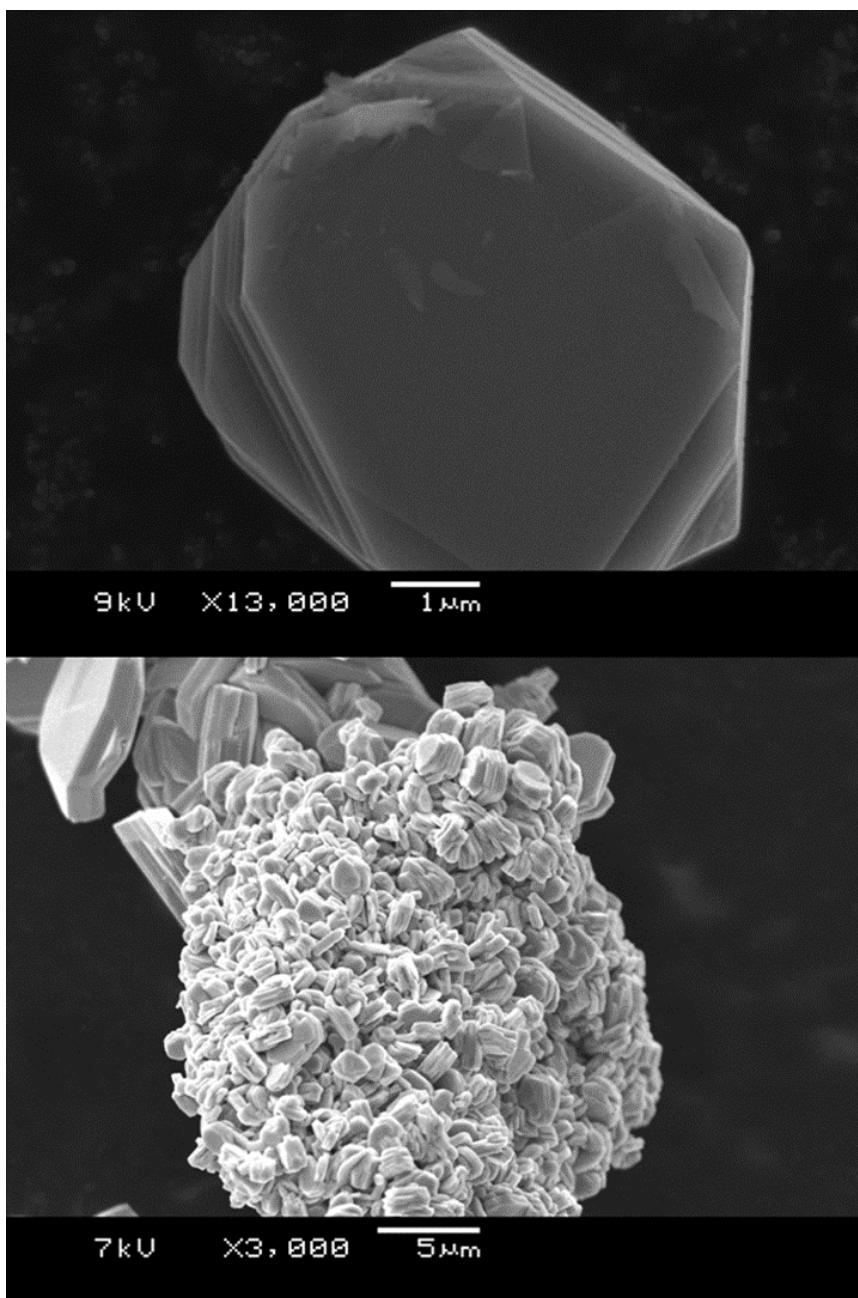


Figure 15: SEM images of α - RuCl_3 that show the layered structure as well as the two morphologies seen which are the larger $\sim 5 \mu\text{m}$ particles and the agglomeration of smaller $\sim 1 \mu\text{m}$ size particles.

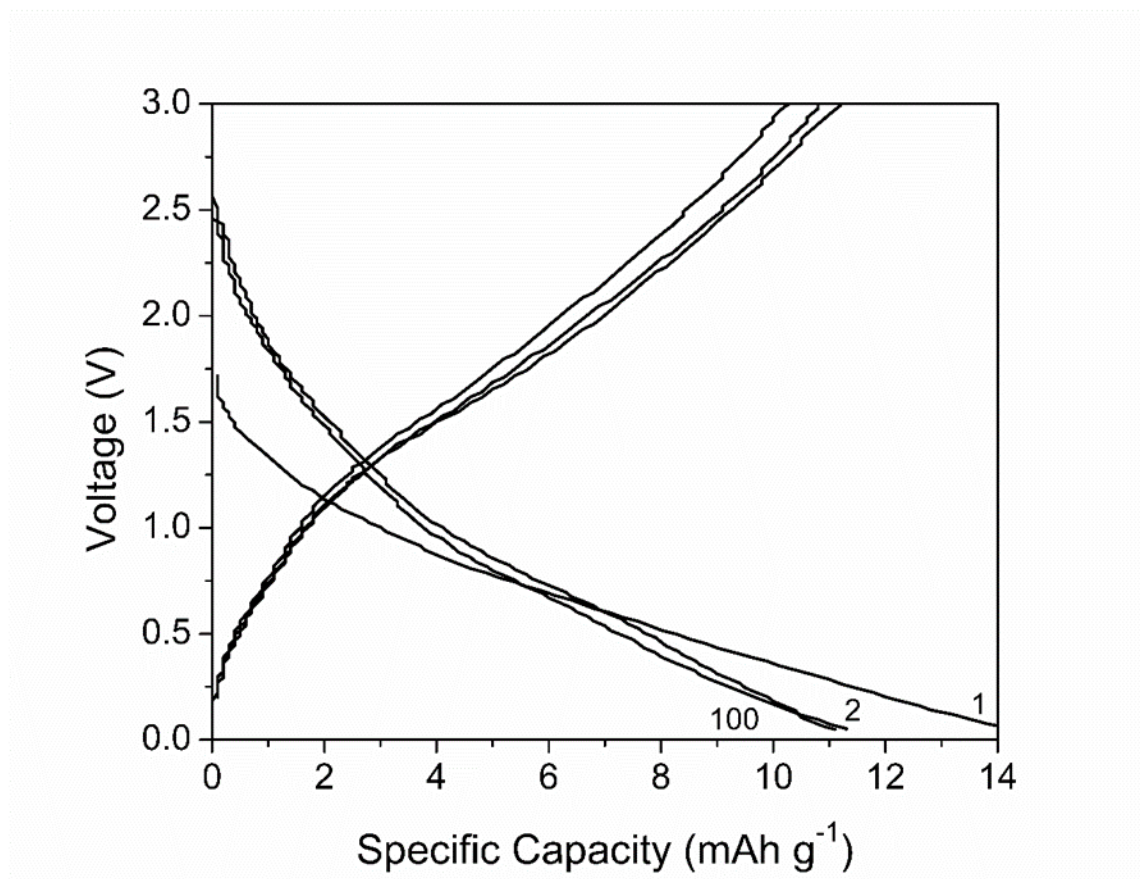


Figure 16: Ru thin film galvanostatic cycling showing no capacity, indicating that there is no alloy products of lithium and ruthenium that need to be considered.

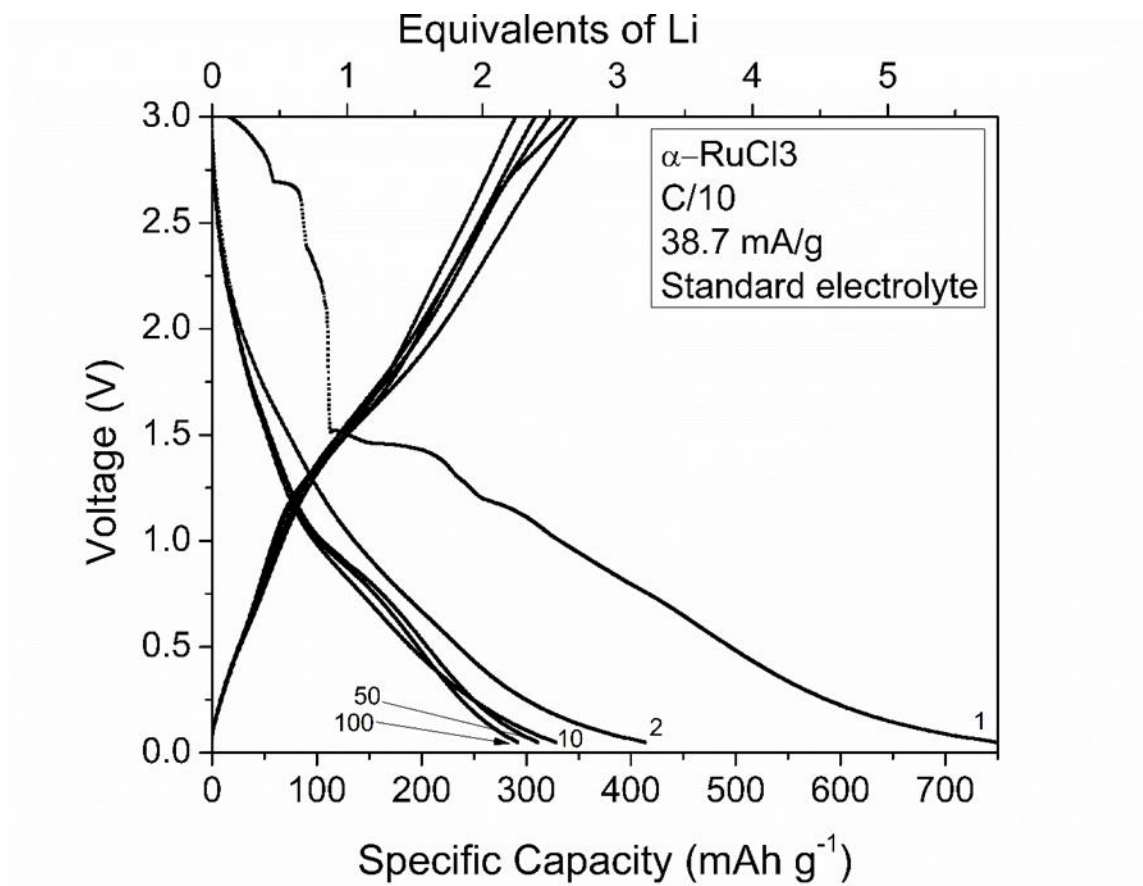


Figure 17: Galvanostatic cycling of α -RuCl₃ cycled between 3-0.05 V using standard electrolyte that consists of 1 M LiPF₆ in a 1:1:1 mixture of EC:DMC:DEC. A large capacity is seen in the first cycle due to SEI layer formation but the reversible specific capacity remains high at $\sim 300 \text{ mAh g}^{-1}$ at 100 cycles.

The intercalation of α - RuCl_3 is known to be possible with Li, as well as many other species including polymers.^{112, 117-118} The degree of Li^+ insertion in this type of system is however unreported. The total specific capacity seen for the first lithiation is 748.6 mAh g^{-1} , which is well over the theoretical capacity of 387 mAh g^{-1} indicating that a large SEI layer formation is occurring. Following the first lithiation, only a sloped voltage profile is seen, indicating that the initial crystalline phase is not reformed and that subsequent cycles are lithiated through only a single type of reaction. The second lithiation produced a specific capacity of 413.1 mAh g^{-1} , which indicates that much less SEI layer is being formed on the anode during this cycle, but since the produced capacity is still higher than the theoretical capacity it is likely that there is still some SEI layer being formed. After the electrode and SEI layer stabilize, a reversible specific capacity of 291.6 mAh g^{-1} can be seen at 100 cycles. Although it is difficult to assign distinct reactions to each region of the voltage profile, ex situ XRD attempts are made to illuminate this complex system.

XRD was performed ex situ in order to determine if any intermediate crystalline species were observed during the lithiation and delithiation process of α - RuCl_3 , as seen in Figure 18. An uncycled α - RuCl_3 electrode compared to the α - RuCl_3 powder used to form the electrodes matches the XRD pattern quite well, but there are two extra peaks, one at ~ 18.9 and the other at ~ 44.0 degrees, that appear in the uncycled electrode pattern. It is possible that these peaks arise from another

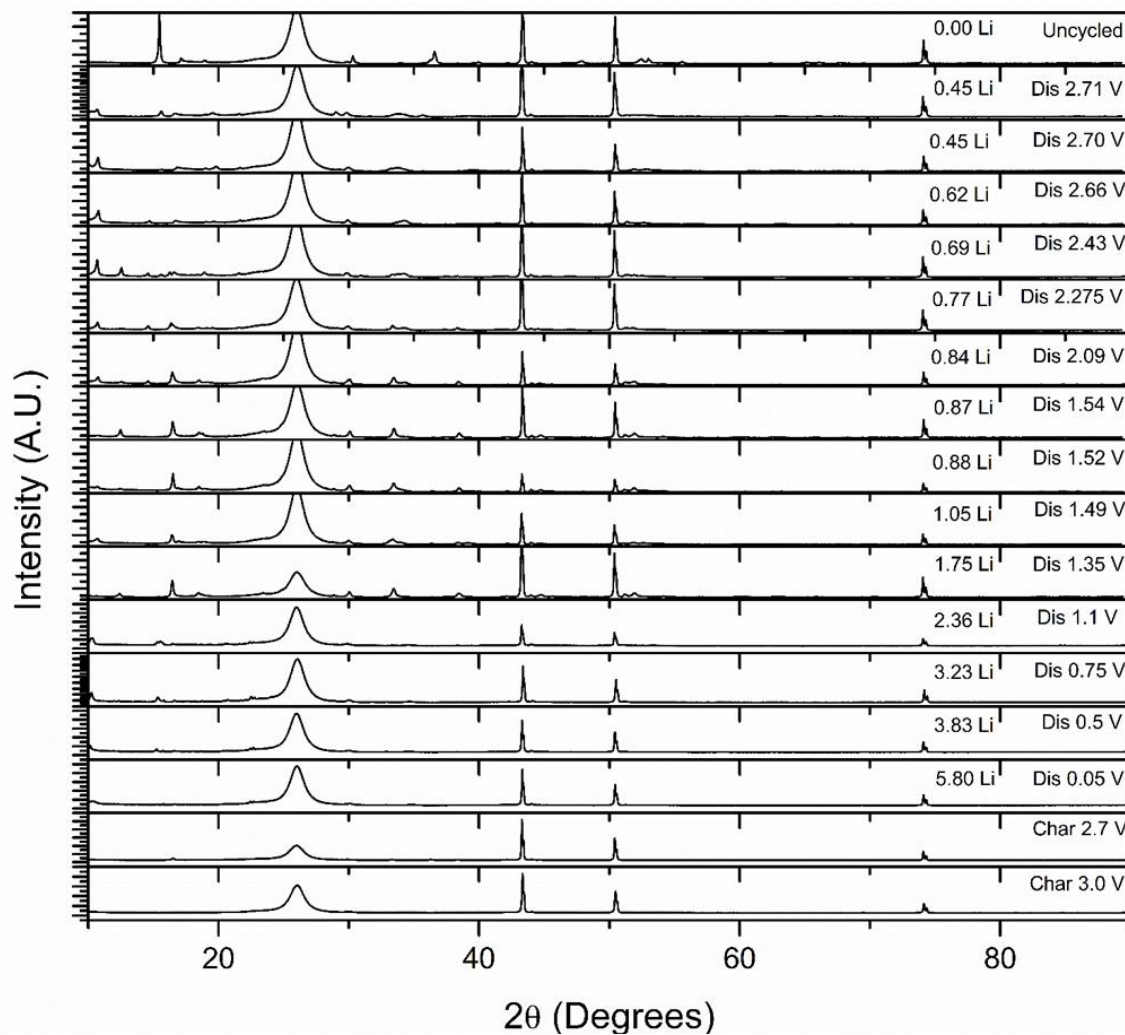


Figure 18: Ex situ XRD analysis of α - RuCl_3 at various degrees of lithiation. The large peak at $\sim 27^\circ$ is background due to the Mylar film. The peaks at $\sim 43^\circ$ and $\sim 51^\circ$ are from the copper current collector that the electrode was cast on. It can be seen that the pattern changes with regard to the degree of lithiation.

component of the electrode, such as the PVDF which shows its 020 peak in the ~18.6 degrees region.¹¹⁹ These peaks could be from an unindexed ruthenium oxide or oxychloride phase, since this material was cast in air the possibility of minimal surface formation of these species exists. After lithiation to 2.7 V there is a reduction in the main α - RuCl_3 peak at ~15.5 degrees and the clear emergence of a peak at ~10.8 degrees. Although the intercalation of Li into α - RuCl_3 is reported multiple times in the literature there is no published XRD pattern data to be found. The peak at ~10.8 degrees is what we believe is representative of the formation of a Li_xRuCl_3 phase, where x is ~0.4 Li. As lithiation increases we see a decrease in the intensity of this peak, which is what is expected if the Li_xRuCl_3 is further reacting with lithium to form LiCl and Ru metal. Then at lithiation to 2.43 V, which is where we see the large inflection in the voltage profile, a new peak at ~12.6 degrees appears. This peak then greatly decreases in intensity, becoming almost unnoticeable until reaching lithiation to 1.54 V and similarly to 1.35 V. We believe that these reappearing peaks are most likely due to a phase transition, based on their position in the voltage profile near sharp voltage drops.¹²⁰ Another possibility is that when a certain point of lithiation is reached, a bilayer or co-intercalated solvent species is formed.¹¹⁷ One other interesting point to be considered when looking at the ex situ XRD data is the phase that the RuCl_3 is in. The α - RuCl_3 peaks in the uncycled electrode at ~17.1 and ~36.6 degrees appear to shift to lower angles as lithiation occurs. As lithiation continues from 2.71 to 1.35 V new

peaks are seen increasing in intensity at ~ 16.5 and ~ 33.4 degrees. We believe that these peaks are not due lithiation of the original α - RuCl_3 structure but rather a change from the α phase to the β phase of RuCl_3 , because two of the major peaks for β - RuCl_3 are seen near these positions at ~ 16.7 and ~ 33.3 degrees (ICSD 414040). After full lithiation and delithiation up to 2.7 V a few small peaks can be seen in the spectra that seem to indicate the formation of a partially crystalline β - RuCl_3 phase, as well as some very small amounts of unreacted LiCl and Ru metal. The presence of the two side products would partially explain the capacity loss during the cycling of the α - RuCl_3 electrode material.

XPS was used in order to determine if there was reduction and oxidation of the ruthenium during lithiation and delithiation cycling. Unfortunately, as seen in Figure 19, the Ru $3d_{5/2}$ peak lies very close in proximity to the carbon peaks that are developed in the SEI layer as the battery is cycled, therefore we cannot fit the data of these peaks. The data can, however, be used qualitatively to give information on whether or not the Ru is being reduced during the process of lithiation, as shown in Figure 20. In the initial powder a peak at ~ 281.9 eV can be observed, which is in good agreement with the literature average value of 282.4 ± 0.45 eV.¹²¹⁻¹²² What appears to be partial reduction from the raw α - RuCl_3 powder to the electrode can be observed in the data. This is most likely not a reduction at all, but rather an oxidation forming RuO_2 which, based on the literature, has an average Ru $3d_{5/2}$ peak value at a lower binding energy of 281.4 ± 1.3 eV.¹²¹ During

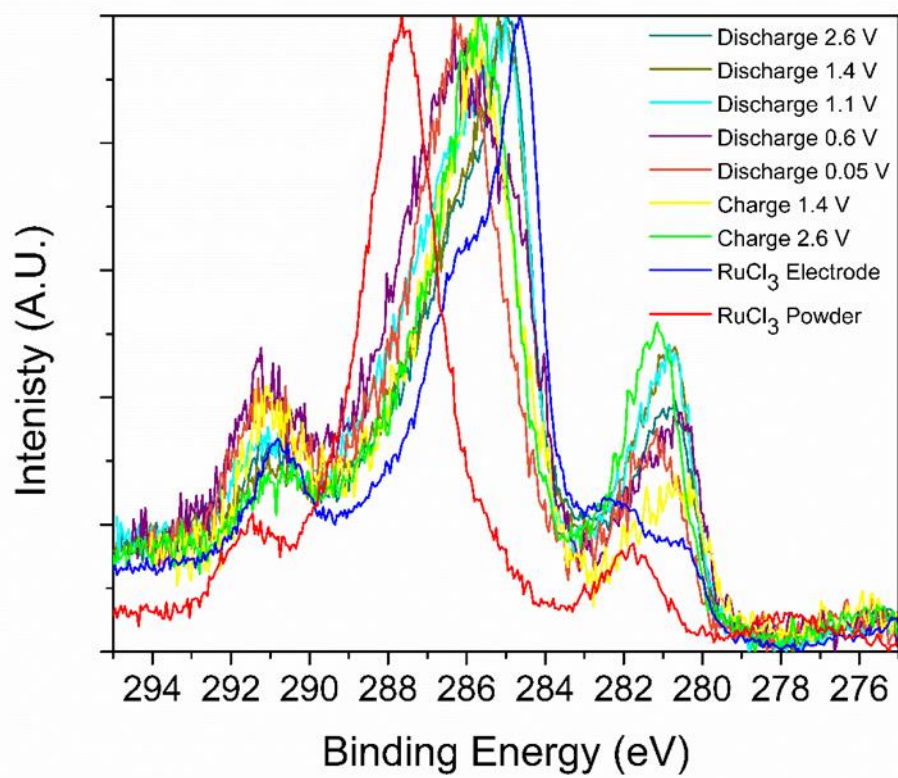


Figure 19: Ex situ XPS of α - RuCl_3 electrodes showing large carbon signal centered around 286 eV due to SEI layer formation which overlaps with the Ru $3d_{5/2}$ peak centered around 281 eV.

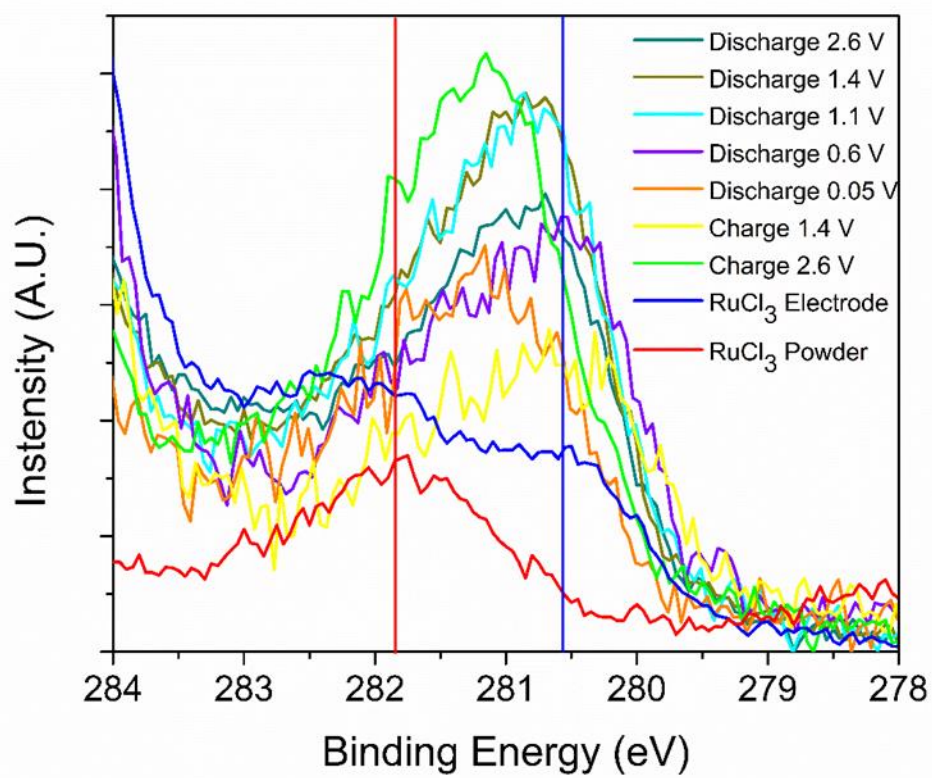


Figure 20: Ex situ XPS of α -RuCl₃ Ru 3d_{5/2} peak for the raw powder material, an uncycled electrode, and electrodes at various degrees of lithiation. Reduction of the ruthenium during discharge and oxidation of ruthenium during charge confirm that the material is reacting with lithium.

lithiation further reduction in the Ru is observed indicating that there is a reaction taking place between the Li and the α -RuCl₃ active material in the anode, and that the capacity observed in the electrochemical data is not just due to side reactions. Oxidation of the Ru can also be observed after the delithiation part of the cycle, indicating that Li is being removed and Ru is being oxidized by the Cl. Although it appears in the XPS data as though the Ru is not fully oxidized back to its original state, based on the capacity and the ex situ XRD data we can assume that the Ru is oxidized back to the 3+ state.

Other electrochemical tests were carried out in order to determine if cycling between different voltage ranges, which limits the amount of lithiation and avoids the SEI forming region, would provide better cycling stability results, as well as allow us to observe if intercalation is the only reaction occurring. The α -RuCl₃ was cycled between the voltages of 3 and 1.2 V and what was observed is that after lithiation to 1.2 V delithiation to 3 V could not be reached. During the delithiation part of the first cycle the voltage never increases above ~2.6 V, as seen in Figure 21. This test was run multiple times to ensure that the result was simply not due to cell failure. When the same cell that was discharged down to 1.2 V is discharged down to 1.0 V and then charged to 3 V, reversible cycling can again be seen. This indicates that the species formed above 1.2 V are formed irreversibly and that there is an important reaction that takes place between 1.2 and 1.0 V, which allows the α -RuCl₃ to be reversibly cycled, as seen in Figure 22.

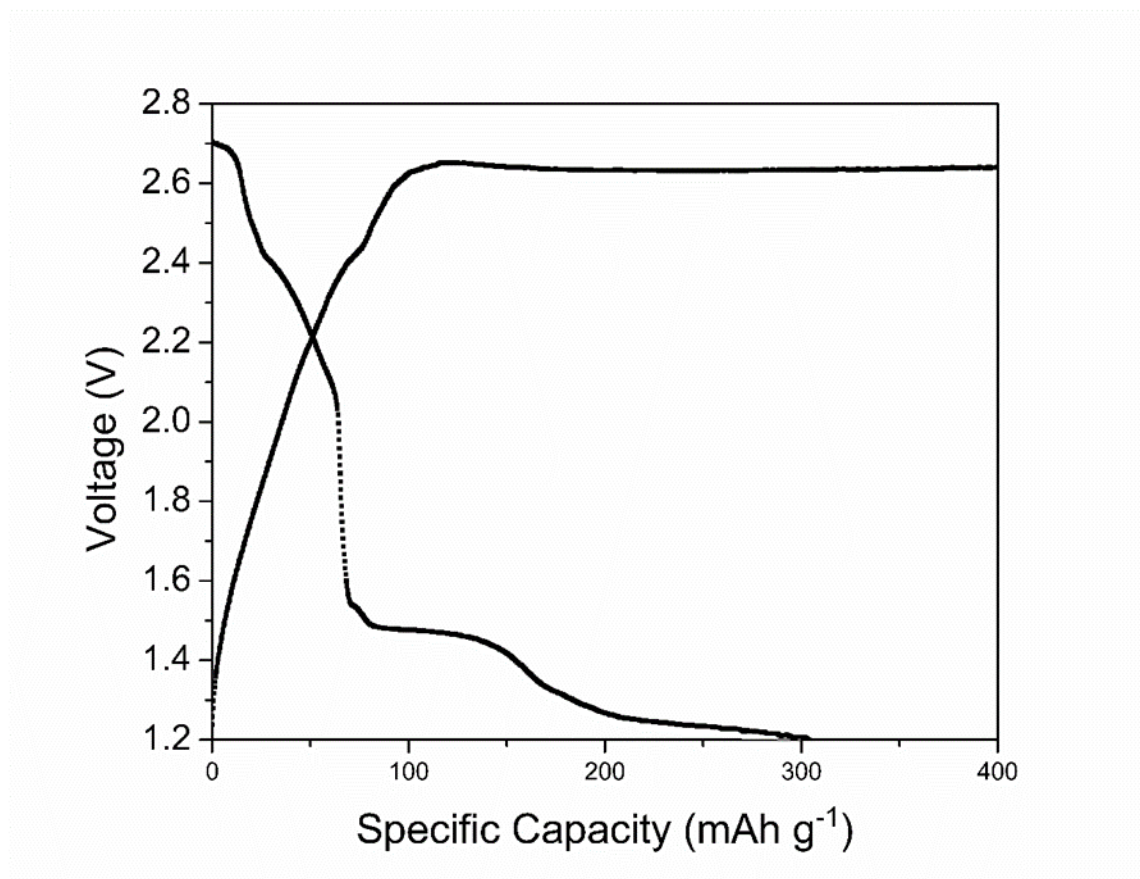


Figure 21: Galvanostatic cycling of α - RuCl_3 between 3 – 1.2 V showing that full delithiation to 3.0 V cannot be achieved when first lithiation is only down to 1.2 V.

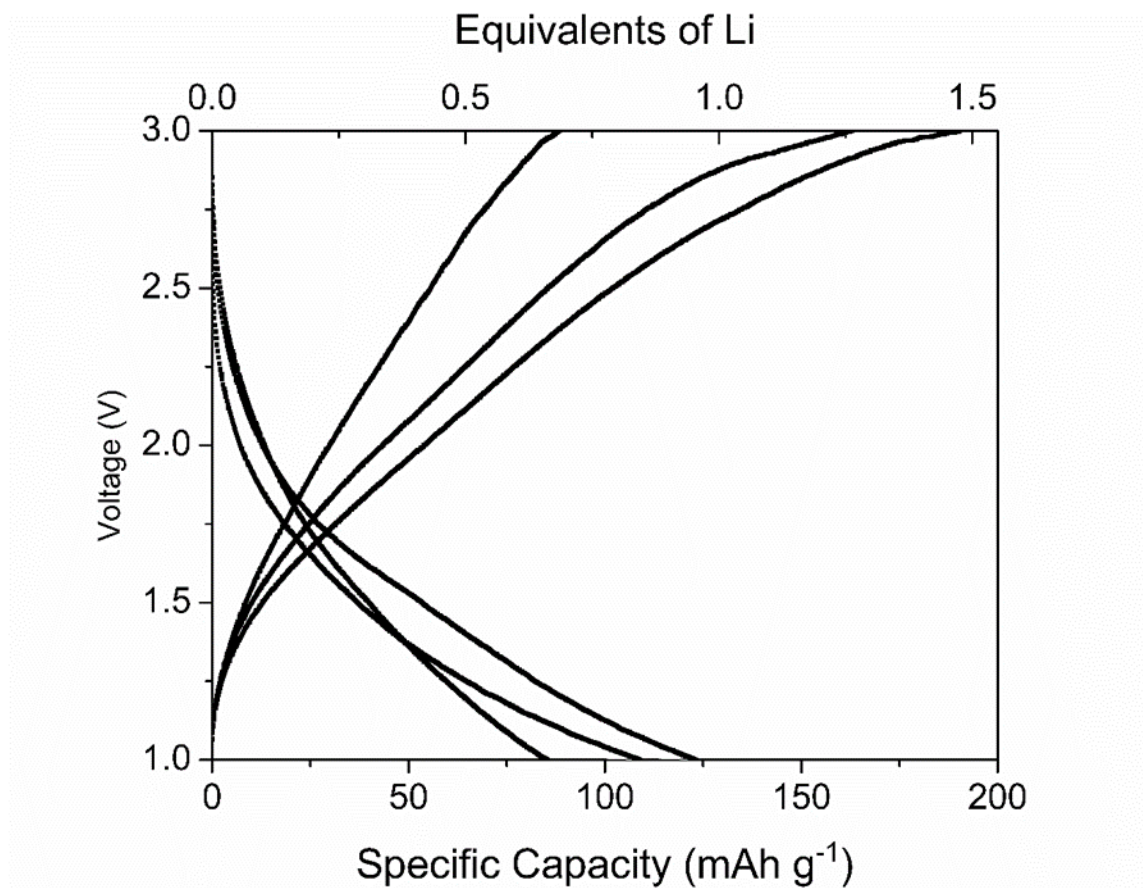


Figure 22: Galvanostatic cycling of $\alpha\text{-RuCl}_3$ between 3.0 – 1.0 V showing that reversible cycling can be achieved when the electrode is lithiated to 1.0 V.

A rate test was performed in order to determine the capacity of the electrode material at various rates of charging and discharging. The currents tested were at rates of C/10, C/5, C/2, C, 5C, 10C, 20C, and 50C, which correspond to values of 38.7, 77.4, 193.5, 387, 1935, 3870, 7740, and 19350 mA g⁻¹, respectively. As can be seen in Figure 23, the capacity quickly fades as the current is raised from C/10 to C. The capacity drops from its initial value of 509 mAh g⁻¹ to ~150 mAh g⁻¹ for the cycles performed at a current charge rate of C. When the current gets to a rate of 5C and above there is very little capacity. This decrease in capacity as the charge/discharge rate increases is due the slow kinetics as the diffusion of Li into the material becomes the limiting step. This is unfortunate, however, it is expected as poor high rate performance is common in the conversion type electrodes. This is the reason there is work going into making conversion materials like this into nanomaterials. With the reduced diffusion length of smaller particles it takes less time for the lithium to diffuse through the entire particle, allowing it to react more quickly. Considering that this is not a nanomaterial but rather a bulk powder material with particles having a size of ~5 microns, still having significant capacity at rate of C is fairly good. When the current is returned to a rate of C/10 the capacity increases, indicating that there is no damage done to the material by cycling at an increased current rate. It also appears that because the fast current rate cycles did not fully react with the material there was less breakdown or dissolution, which causes the decrease in capacity after many cycles.

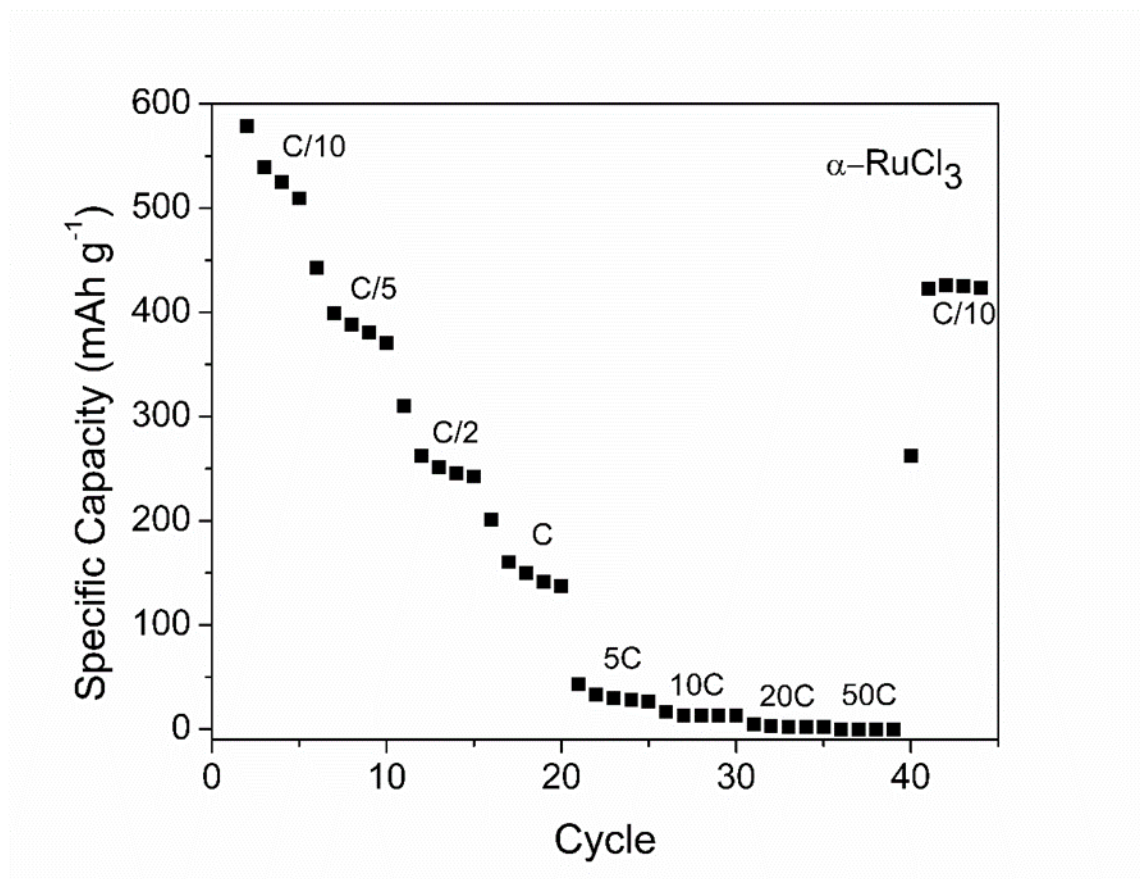


Figure 23: Rate capability test of $\alpha\text{-RuCl}_3$ showing that as the current increases the specific capacity of the material decreases rapidly due to large particle size and diffusion limitations of the material.

Conclusions

In conclusion, the unique α - RuCl_3 , with its low solubility and layered honeycomb structure, has been shown to work as a model compound for the reactions of Li with transition metal chlorides in a Li-ion battery. It is one of very few transition metal chlorides to be tested and show reversible cycling capacity in Li-ion batteries. The first discharge cycle of this material shows many plateaus and sloped regions in the voltage profile, indicating that there are several reactions taking place during the first lithiation. This interesting material has been shown through ex situ XRD to likely go through both intercalation and conversion type reactions during the first discharge/lithiation. Cycling α - RuCl_3 between different voltage ranges has shown that there is potential that must be reached in order for reversible cycling to occur. α - RuCl_3 shows a high specific capacity on its first discharge of 748.6 mAh g^{-1} and retains a reversible specific capacity of 291.6 mAh g^{-1} at 100 cycles, which is over 75% of its theoretical capacity of 387 mAh g^{-1} . This material shows good cycling stability and is the only metal chloride material to report reversible cycling with both this many cycles and significant capacity.

CHAPTER FOUR

IRON (III) OXYCHLORIDE

Introduction

Layered intercalation compounds have been greatly studied in the field of Li-ion batteries. This is because lithium can be intercalated into the van der Waals gap of such materials. A commonly investigated group of these materials include metal dichalcogenides.⁴ However, oxyhalides of transition metals, such as iron oxychloride (FeOCl) and vanadium oxychloride (VOCl), are also layered compounds. Using iron in cathode materials as opposed to using other metals has the advantage of reduced cost, which attracts much attention to iron based compounds. It is therefore understandable that FeOCl has drawn attention to the investigation of its intercalation by lithium.

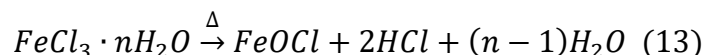
There is some debate, though, as to whether FeOCl can be reversibly intercalated by lithium ions. Some researchers have proposed that FeOCl cannot be used as a cathode material in secondary lithium ion batteries due to the fact that upon lithium intercalation an irreversible decomposition occurs forming α -Fe, LiCl, and Li₂O.¹²³⁻¹²⁶ It has been shown in other literature, however, that a stable structure of Li_xFeOCl, where $x < 0.5$, can be synthesized via chemical lithiation.¹²⁷ There is no literature support showing the reversible intercalation of lithium into

FeOCl as a cathode material. What has been shown is that FeOCl can be used successfully as a cathode in chlorine ion batteries, and derivatives of FeOCl, such as FeOOH intercalated with organic compounds, can be used as a cathode in lithium ion batteries.^{123, 128-130}

Experimental

Synthesis of FeOCl

The synthesis of FeOCl was carried out via thermal decomposition of iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$).¹³¹ We can see that the reaction produces FeOCl instead of anhydrous FeCl_3 , as shown by the reaction



This generic reaction shows that upon heating, the hydrated iron chloride will release water and hydrogen chloride resulting in a product of FeOCl. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to an alumina crucible and placed in a furnace tube. The sample was then heated to 200 °C at a rate of 10 °C per minute and held at that temperature for 48 hours in order to insure that the decomposition and removal of water was

complete. The product was a black solid that after being scraped from the crucible and ground by mortar and pestle produced a brown powder.

Structural analysis of FeOCl

The nanoparticles were characterized using a Panalytical Empyrian powder X-ray diffractometer employing Cu K α radiation. Data was collected within the 2 θ range of 10-90°, using a spinning reflection sample stage and Si zero background sample holder. Crystal structures were refined using the Rietveld method in FullProf Suite.⁴⁷⁻⁴⁸

Electrochemical measurements

The electrochemical measurements were carried out at room temperature using 2 electrode CR2032 type coin cells. The working electrodes were prepared from a slurry of active material (FeOCl), conductive agent (carbon black), and a binder (poly(vinylidene difluoride)) at a ratio of 80:10:10 percent by weight. The mixture was cast onto aluminum and copper foils using the slurry method and dried to form the electrodes. All electrodes contained a mass loading of between 2.3-2.8 mg cm⁻² of active material. All coin cells were assembled in an argon filled glove box using pure lithium foil as the counter electrode and polypropylene as the separator. The electrolyte solution consisted of 1M LiPF₆ in a 1:1:1 volume ratio

of ethylene carbonate, dimethyl carbonate, and diethyl carbonate from Novolyte with water impurity < 20 ppm. The ionic liquid electrolyte used consisted of 0.5 M LiTFSI.ppy. The assembled cells were cycled galvanostatically using a LAND CT2001A battery testing system. The battery cells were tested galvanostatically, with a current constant of 74.9 mA g^{-1} , while cycling between 3.0 and 0.05 V for anodes and between 4.5 and 1.5 V for cathodes, which corresponds to a C/10 rate relative to the maximum theoretical capacity of 749 mAh g^{-1} for FeOCl.

Results and Discussion

FeOCl characterization

After synthesis the FeOCl was measured and indicated formation of pure FeOCl (ICSD 16013), which has an orthorhombic structure that can be described as being bidimensional, built from a corrugated metal-oxygen plane that is sandwiched between two layers of halide ions. Refinement gives lattice parameters of $a = 3.77 \text{ \AA}$, $b = 7.90 \text{ \AA}$, $c = 3.29 \text{ \AA}$ and having a χ^2 of 3.22, as seen in Figure 24. Through SEM images, size, morphology, and the layered structure of the FeOCl can be seen. It can be seen that these are large particles of $\sim 25 \text{ }\mu\text{m}$ in size.

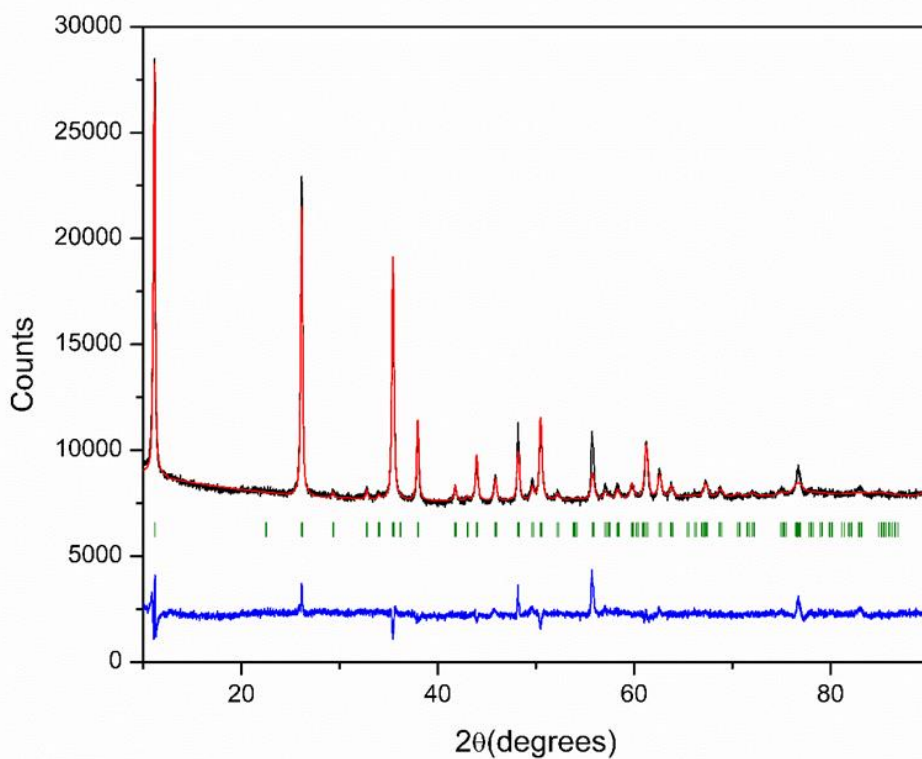


Figure 24: XRD Rietveld refinement of FeOCl showing the difference between the collected pattern and the calculated pattern where the black line is the collected data, the red line is the calculated pattern, and the blue line is the difference between them.

Electrochemistry of FeOCl

As mentioned previously it has been stated in the literature that FeOCl cannot be used as an electrode material in lithium ion batteries because of an irreversible decomposition that occurs.¹²³⁻¹²⁶ Here we provide the first evidence of FeOCl being able to be cycled reversibly as a cathode in Li-ion batteries. As seen in Figure 25, FeOCl as a cathode can be lithiated and delithiated reversibly at a rate of C/10 between 4.5 and 1.5 V. Using a standard electrolyte of 1 M LiPF₆ in a 1:1:1 mixture of EC:DEC:DMC it can be seen that the cathode of FeOCl can be reversibly cycled over 50 times. The first discharge shows an initial capacity of ~130 mAh g⁻¹. After the first ten cycles the capacity fades rapidly most likely due to material dissolution. FeOCl has a theoretical specific capacity of ~749 mAh g⁻¹, so even at the first lithiation of the cathode we see about 0.5 lithium reacting with the FeOCl. This is right at the 0.5 lithium maximum that was attributed to the Li_xFeOCl structure described using chemical lithiation methods.¹²⁷ Because of the poor cycle stability that is observed when using the standard electrolyte, an ionic liquid electrolyte was used in an attempt to increase cycle stability. When using the ionic liquid electrolyte, LiTFSI.ppy, cycle stability shows a dramatic increase during the first 50 cycles, as can be seen in Figure 26. Using the ionic liquid electrolyte, a similar initial lithiation specific capacity is seen at ~126 mAh g⁻¹, but after the 50th lithiation the specific capacity is still ~114 mAh g⁻¹. This is 90% capacity retention after 50 consecutive lithiation/delithiation cycles. We believe

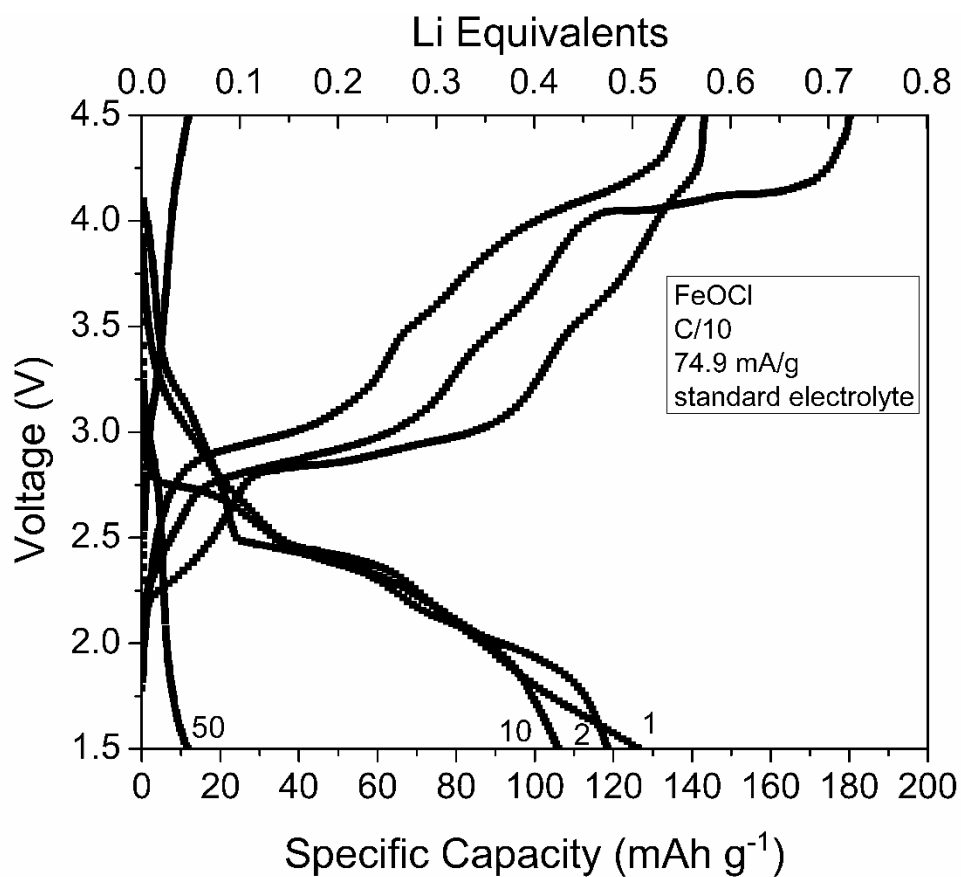


Figure 25: Galvanostatic cycling of FeOCl Between 4.5 – 1.5 V which was done using a standard electrolyte of 1 M LiPF_6 in a 1:1:1 EC:DEC:DMC solution.

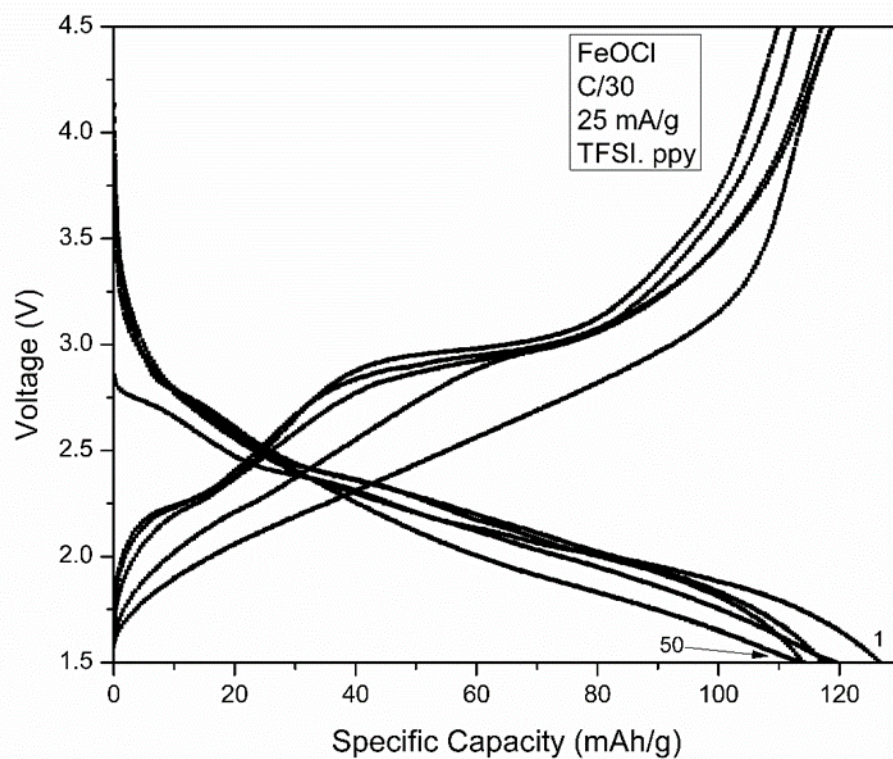
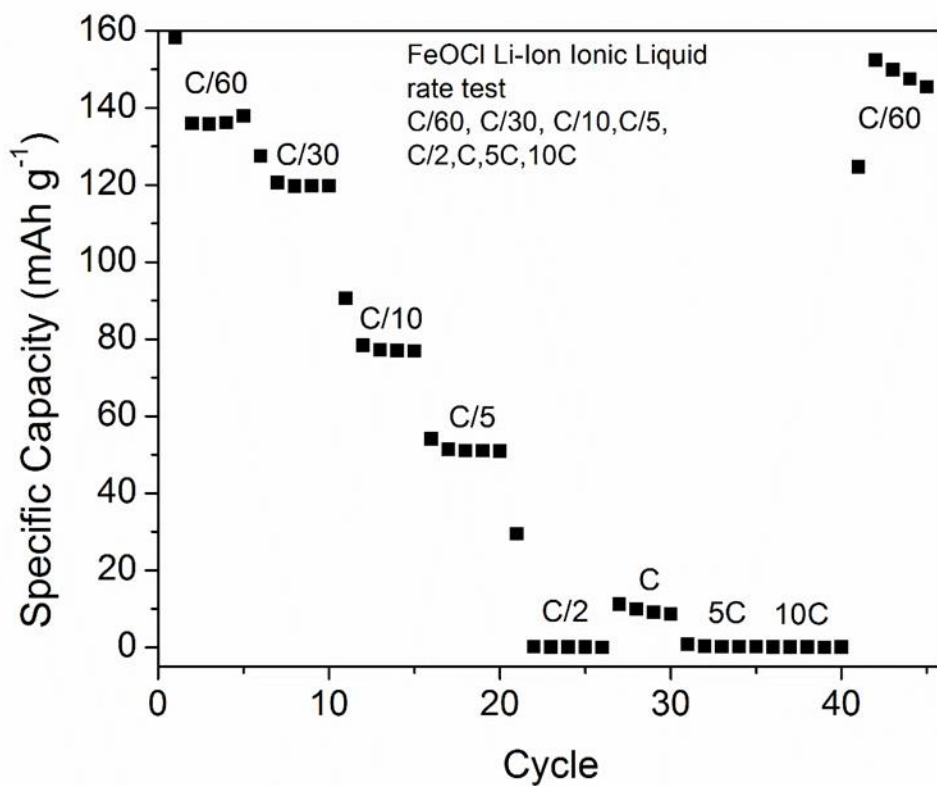


Figure 26: Galvanostatic cycling of FeOCl in an ionic liquid electrolyte . The ionic liquid used is 0.5 M LiTFSI.ppy which shows much greater cycle stability than the standard electrolyte.

that the increased cycle stability is due to some co-intercalation of the electrolyte ions which stabilizes the FeOCl structure.¹²⁸ A rate capability test was performed to determine if FeOCl in LiTFSI.ppy would make an acceptable fast cycling material. It can be seen in Figure 27 that the specific capacity decreases rapidly as the charge rate is increased, but the capacity increases again when returned to the original cycling rate. This indicates that the lithiation is limited by the rate of diffusion through the electrolyte.

Since the specific capacity of FeOCl as a cathode material is so low we wanted to see if more complete lithiation could be obtained by cycling the FeOCl as an anode material. As seen in Figure 28, the specific capacity is much higher in the anode than in the cathode counterpart. This is due to the fact that at lower potentials we are no longer simply reacting the lithium with FeOCl through intercalation, but also completely reducing the compound to iron metal and Li₂O and LiCl. The initial discharge capacity is over 1400 mAh g⁻¹ which shows that much more lithium is reacting with the FeOCl and also that a large SEI layer is forming, which accounts for the high capacity that is above the theoretical capacity of 749 mAh g⁻¹ for FeOCl. This also accounts for the large capacity drop between the first and second discharge cycles. The specific capacity drops rapidly, which is likely because the complete lithiation of FeOCl is not a fully reversible process, but even after 50 cycles a specific capacity of ~200 mAh g⁻¹ is still obtained.



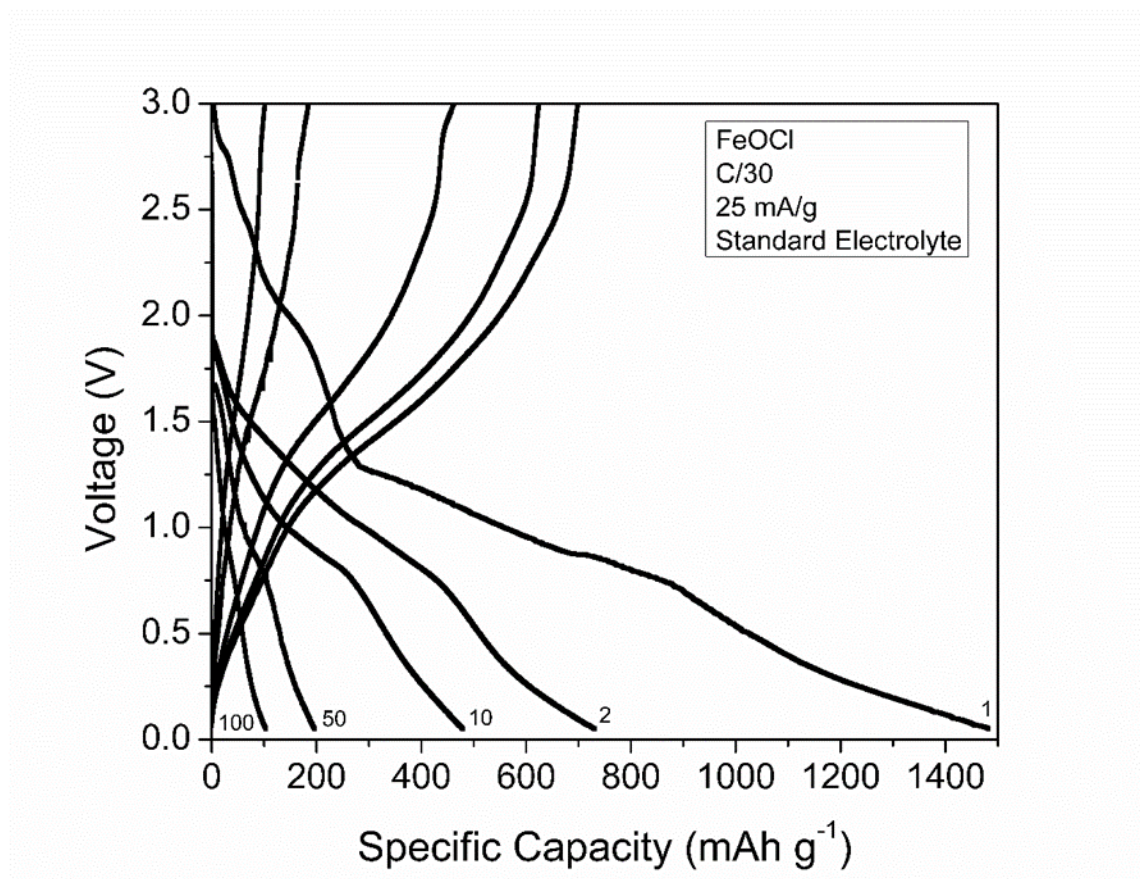


Figure 28: Galvanostatic cycling of FeOCl as an anode between the voltages of 3.0 – 0.05 V. Using the FeOCl as an anode material a much greater capacity can be seen as it is no longer simply going through an intercalation mechanism but rather a full conversion reaction.

Conclusions

In this work it has been shown that FeOCl can in fact be used as a cathode material for lithium ion batteries. FeOCl has been shown to be able to be reversibly cycled as both a cathode and anode in lithium half cells. As a cathode material FeOCl has been shown to have an initial specific capacity of $\sim 130 \text{ mAh g}^{-1}$ and even though the material shows poor cycle stability in a standard organic electrolyte, it can still be reversibly cycled for more than 50 cycles. If the standard electrolyte is exchanged for the ionic liquid electrolyte, lithium bis(trifluoromethane) sulfonimide polypyrrole (LiTFSI.ppy), the cycle stability can be greatly increased. Using the ionic liquid electrolyte a reversible specific capacity of 114 mAh g^{-1} can be observed after 50 cycles. This is a capacity retention of $\sim 90\%$ of the original specific capacity observed during the first discharge. FeOCl has also been shown to be cycled reversibly as an anode material in lithium ion batteries. The specific capacity fades during cycling, but after 50 cycles a specific capacity of $\sim 200 \text{ mAh g}^{-1}$ can still be obtained.

CHAPTER FIVE

FLUORINE DOPING USING DIRECT FLUORINATION

Introduction

Direct fluorination using the fluidized bed reactor system is a powerful tool not only for the synthesis of materials but also for the modification of materials. It can be used to modify the surfaces of polymers, such as the polymer separator in battery cells.¹³² Modifying the polymer separator with fluorine allows for new unique properties to be observed. It can also be used for many types of solid gas reactions, but can also be used in liquid gas reactions as well.¹³³⁻¹³⁴ This is important because it can be used to fluorinate the electrolyte used in the battery cells, which allows for different chemistries to occur. Most importantly, direct fluorination can be used to modify the active materials that are used in the electrodes of the battery cell.

Direct fluorination can be used to create mixtures of phases in compounds that more readily form a single anion phase as opposed to a mixed anion phase.¹³⁵ In this way small domains of fluoride material can be obtained while still maintaining domains of the original phase of the material. Therefore, you can achieve a mixed phase material that reacts in two different ways with Li-ions being exchanged in a Li-ion battery. Direct fluorination can also be used to dope fluorine

into the molecular structure by replacing a portion of the anions in the molecule with fluorine, creating a mixed anion phase.¹³⁶ The extreme of this is the synthesis of a pure new phase of mixed anion material, while doing this in minor amounts can lead to a nonstoichiometric fluorine doped system.¹³⁷⁻¹³⁹ A system such as this can show improved performance as an electrode active material through different mechanisms in which the replacement of one anion for fluorine plays a critical role. Although direct fluorination can be used in many ways it is a much under developed tool because of the hazards associated with elemental fluorine.

Focus is on the modification of electrode active materials through direct fluorination. The two test compounds that are modified are TiNb_2O_7 and MoO_3 , which have both been used as active materials in batteries. These materials were chosen because it is believed that through fluorination the battery properties can be enhanced. The fluorination of TiNb_2O_7 is done in order to increase the working voltage of the material. MoO_3 is fluorinated in order to enhance its intercalation properties, which has already been shown to work in magnesium ion batteries.¹³⁹ The goal is to introduce fluorine into the material without completely changing the structure of the material, since change in structure could result in the loss of ability to intercalate lithium.

Experimental

Synthesis of fluorinated TiNb_2O_7

Fluorinated TiNb_2O_7 was synthesized via the direct fluorination of synthesized TiNb_2O_7 in a fluidized bed reactor (FBR) system.¹⁴⁰ Before fluorination, the precursor was dried *in vacuo* for 24 hours at 150 °C using a hot oil bath. Drying is essential to remove any adsorbed water from the particles, which if present will react with fluorine gas to form hydrofluoric acid, which would alter the reaction mechanism of the fluorination. Powder samples of 0.5- 1.0 g size were loaded into the FBR within a nitrogen filled glovebox and sealed, then removed and weighed before being connected to the fluorination line. The FBR and sample were heated to 225 °C under flowing nitrogen, at which point a flow of 1.2 sccm fluorine/nitrogen mixture (Air Products) mixed with nitrogen carrier gas (12 sccm) was initiated. After 24 h the fluorine flow was shut off, and the system was allowed to cool to room temperature under nitrogen flow. The FBR was weighed again to determine any weight loss or gain that occurred during the reaction before collecting the sample in the glovebox. Before fluorination the TiNb_2O_7 was a white powder and after fluorination the product was also a white powder.

Synthesis of fluorinated MoO₃ nanoparticles

Fluorinated nanoparticles of MoO₃ were synthesized via the direct fluorination of MoO₃ nanoparticles in a FBR system. Before fluorination, the precursor was dried *in vacuo* for 24 hours at 150 °C using a hot oil bath. Powder samples of 0.5- 1.0 g size were loaded into the FBR within a nitrogen filled glovebox and sealed, then removed and weighed before being connected to the fluorination line. The FBR and sample were heated to 225 °C under flowing nitrogen, at which point a flow of 1.2 sccm fluorine/nitrogen mixture (Air Products) mixed with nitrogen carrier gas (12 sccm) was initiated. After 24 h the fluorine flow was shut off, and the system was allowed to cool to room temperature under nitrogen flow. The FBR was weighed again to determine any weight loss or gain that occurred during the reaction before collecting the sample in the glovebox. Before fluorination the MoO₃ nanoparticles were blue in color and after fluorination the nanoparticles were a pale green color.

Characterization of fluorine doped materials

The fluorine doped materials were characterized using a Panalytical Empyrian powder X-ray diffractometer employing Cu K_α radiation. Data was collected within the 2θ range of 10-90°, using a spinning reflection sample stage and Si zero background sample holder. Crystal structures were refined using the Rietveld method in FullProf Suite.⁴⁷⁻⁴⁸ X-ray diffraction data collected on silicon

powder standard under identical run conditions were used to obtain instrument profile parameters for microstructural analysis.

Results and Discussion

Fluorination of TiNb_2O_7

TiNb_2O_7 and the final fluorinated products were characterized by PXRD to determine any structural changes that occurred during the fluorination. The TiNb_2O_7 precursor was refined using the ICSD (15430) structure which has a space group $A12/m1$ and lattice parameters of $a=11.93 \text{ \AA}$, $b=3.81 \text{ \AA}$, $c=20.44 \text{ \AA}$, $\alpha=\gamma=90^\circ$ and $\beta=120.16^\circ$. As can be seen in Figure 29, the TiNb_2O_7 observed pattern matches the calculated pattern quite well, although it does appear that the material is not fully crystalline because the peaks are broad and not well defined. After fluorination, it can be seen that the PXRD pattern has been greatly altered. There are several intense, well resolved peaks that can be seen which indicates a new crystalline phase has been formed. There is a small peak at 25.6° which corresponds to the main peak in the TiNb_2O_7 , and the other main peak appears to be overlapping the main peak of the new phase, as can be seen in Figure 30. The new phase appears to be either TiOF_2 or $\text{NbO}_{1.95}\text{F}_{1.05}$ which both have a cubic ReO_3 type structure. The refinement of the new phase was performed using the

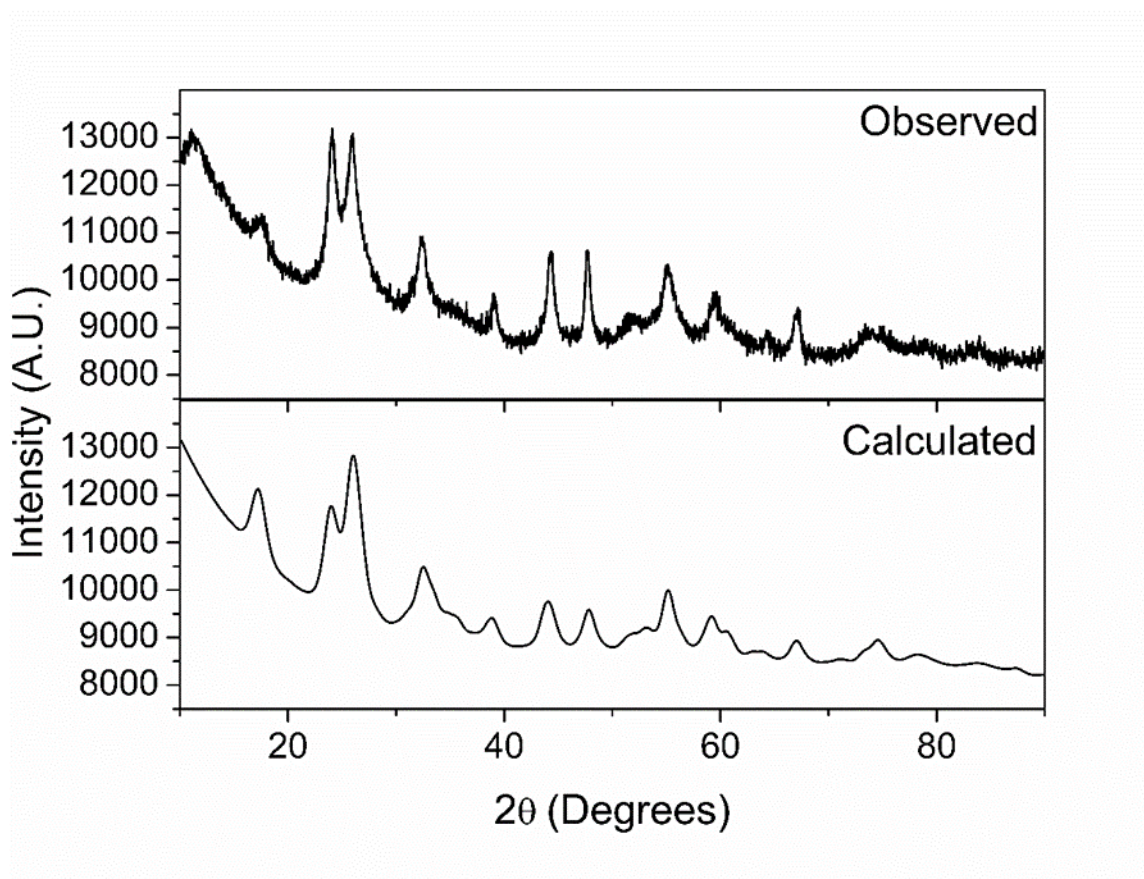


Figure 29: XRD of TiNb_2O_7 showing that the observed pattern matches very closely with the pattern calculated through the Rietveld refinement.

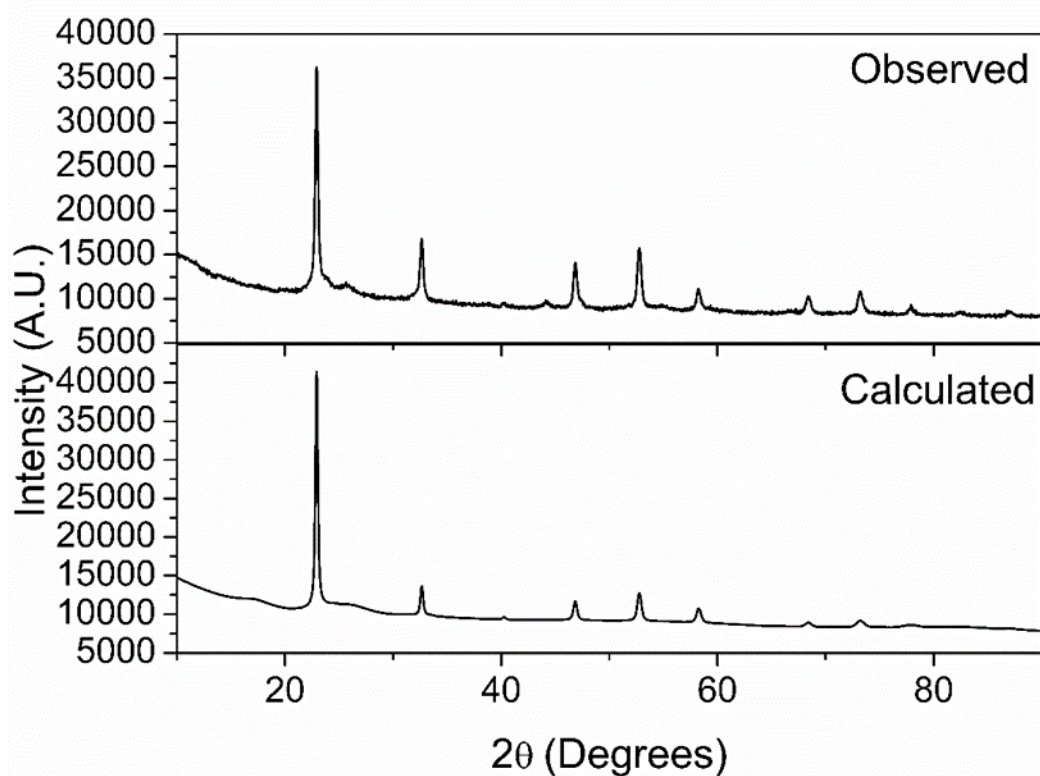


Figure 30: XRD of fluorinated TiNb_2O_7 which shows that the new observed pattern retains a small amount of the original pattern but contains peaks that match very closely with the calculated pattern for TiOF_2 . The broad peak at around 27 degrees in the calculated pattern is due to the inclusion of the original TiNb_2O_7 phase, which can still be observed in the collected data.

NbO_{1.95}F_{1.05} ICSD (160660) structure and yielded a lattice parameter of $a=3.878$ Å. This lattice parameter is slightly different from that of the NbO_{1.95}F_{1.05}, which is $a= 3.9059$ Å. It is also different from lattice parameter of TiOF₂ ICSD (38132), which is $a= 3.798$ Å. Because the refined lattice parameter is between the lattice parameters of the two structures it is possible that there is both some TiOF₂ and NbO_{1.95}F_{1.05} phases that were formed during the fluorination, but this would likely lead to two sets of peaks. Another possibility is the formation of a single phase with an intermediate ratio of oxygen to fluorine. This evidence shows that direct fluorination via fluidized bed reactor is a suitable method for the fluorination of TiNb₂O₇. It also shows that using this method we are able to fluorinate TiNb₂O₇ without complete elimination of the original structure, allowing for the formation of mixed phase species that may show enhanced properties as an anode in Li-ion batteries.

Fluorination of MoO₃

MoO₃ nanoparticles were fluorinated in order to achieve a MoO_{3-x}F_x type structure. These types of molybdenum oxyfluoride structures have been shown to function as cathode materials in Li-ion and magnesium batteries.¹³⁸⁻¹³⁹ Typical synthesis for these materials includes hydrothermal and solid state methods. The precursor MoO₃ nanoparticles and the fluorinated nanoparticles were analyzed using PXRD to determine if any change in phase occurs. As shown in Figure 31,

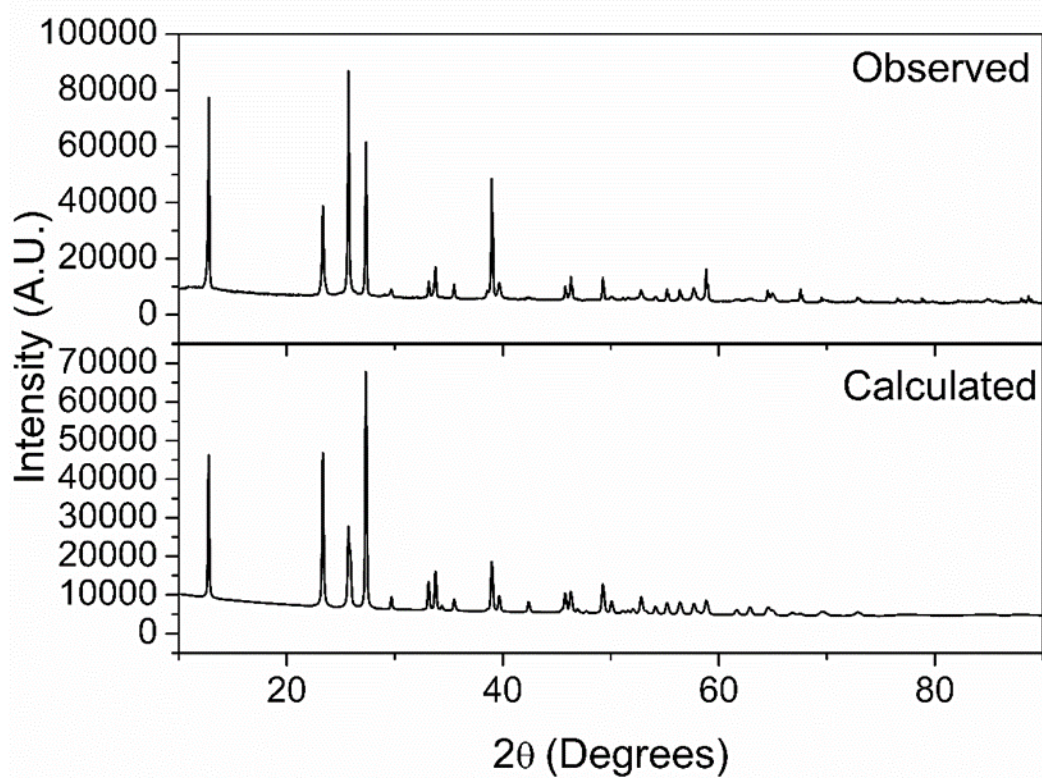


Figure 31: XRD of MoO₃ which shows that the observed pattern matches well to the pattern calculated by the Rietveld refinement.

no phase change is observed after fluorination. It is known from the literature that even phases with a fluorine content up to $x=0.2$ in the $\text{MoO}_{3-x}\text{F}_x$ type structure will produce the same pattern, only having slightly different lattice parameters.¹³⁸ As can be seen in Figure 32, the precursor and the fluorinated product have very similar spectra. It was certain that there had been some change during the fluorination, because the color of the powder material changed from blue to pale green. In order to investigate the presence of fluorine in the fluorinated material, XPS was used to characterize the surface of the material. Figure 33 shows a very small peak in the XPS spectrum which can be attributed to a very small amount of fluorine being added to the surface of the material. This result indicates that through direct fluorination the surface of MoO_3 is able to be modified by the addition of fluorine. Therefore, through changes in the reaction parameters, the degree of fluorination should be controllable, allowing the composition to be optimized for the best performance as a cathode material in battery systems.

Conclusions

In this work, it has been demonstrated that direct fluorination via fluidized bed reactor system can be used for the modification of metal oxide materials. TiNb_2O_7 and MoO_3 were both able to be doped with fluorine without eliminating the original structure. In the case of TiNb_2O_7 , it appears as though there is a

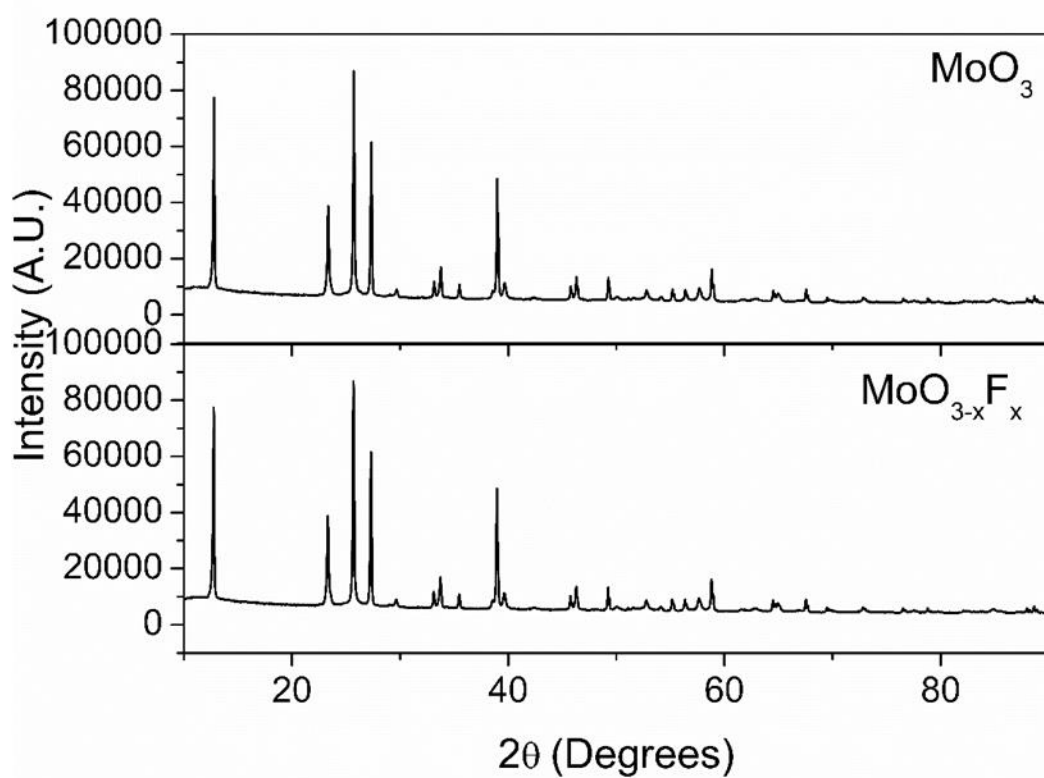


Figure 32: XRD of fluorinated MoO_3 which shows that the original pattern for the MoO_3 is retained after the fluorination takes.

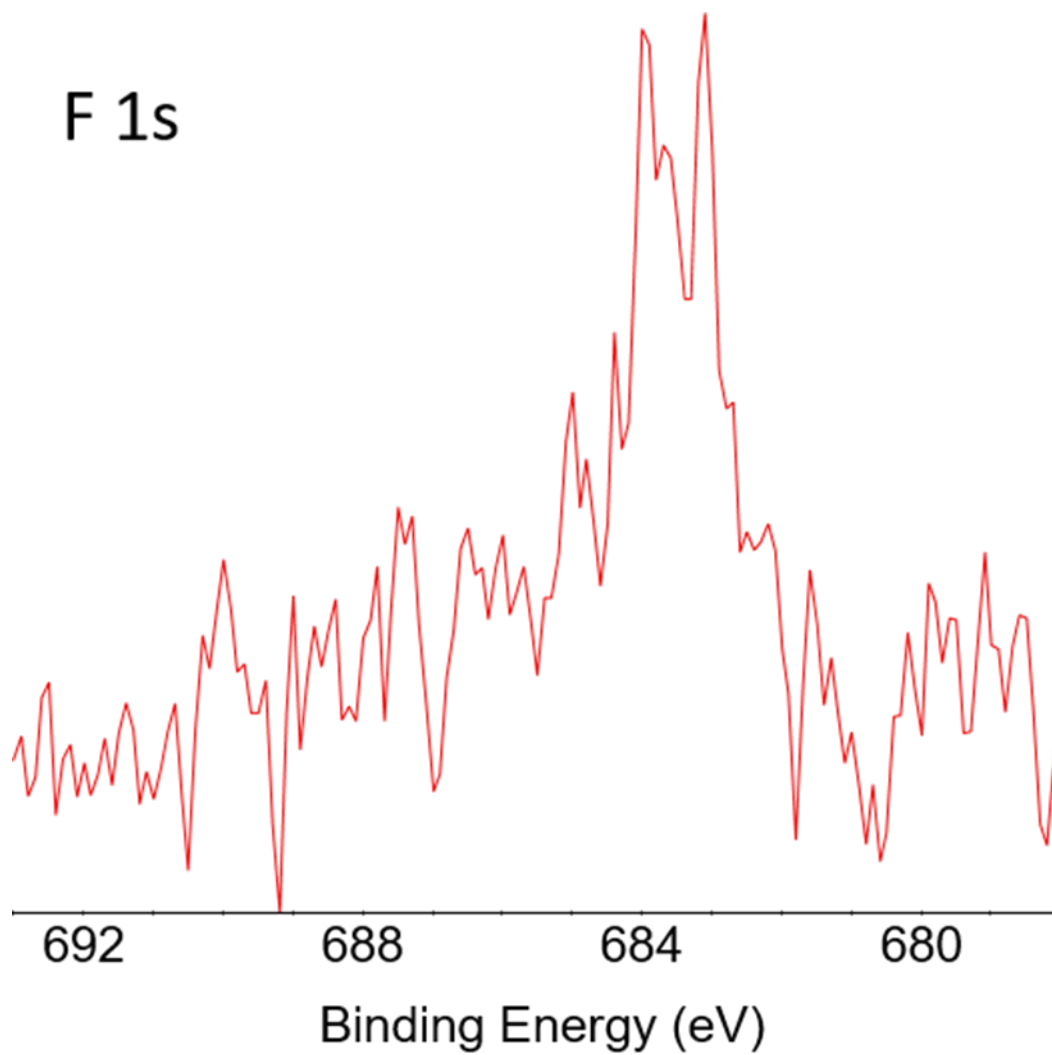


Figure 33: XPS of fluorinated MoO₃ showing that there is a small F 1s peak, indicating that there has been a small amount of fluorine added to the structure of the MoO₃.

modification to some of the material, most likely to the surface, yielding a mixed phase product. However, MoO_3 when fluorinated yields the same structural phase thus the addition of fluorine must be determined by other spectroscopic means. It was confirmed by XPS that there was a small amount of fluorine added to the structure of the MoO_3 . These two experiments show that fluorine doping of materials is possible using direct fluorination via FBR.

CHAPTER SIX

CONCLUSIONS

Metal halides and metal oxyhalides are shown to be excellent examples of conversion type electrodes. Direct fluorination is demonstrated to be an excellent method for the synthesis of metal oxyfluoride materials. TiOF_2 used as an anode material shows how a mixed anion species can outperform its single anion precursor, TiO_2 . It has been shown how the fluorination of a metal oxide to a metal oxyfluoride can drastically increase the battery properties of the materials. Evidence has been provided that the chemistry of the precursor can make critical differences in the battery properties. The titanium oxynitride and titanium dioxide precursors produce the same titanium oxyfluoride product based on PXRD, but some reduced species in the XPS data of the product of the TiO_xN_y precursor is shown. These reduced species, that are not in the XPS data for titanium oxyfluoride synthesized from the titanium dioxide precursor, are likely the reason that the capacity of the titanium oxyfluoride material is increased. Therefore, the composition of the precursor can have a dramatic effect on the properties of the final product, even if the final product has the same structure. This also provides more evidence that metal oxyfluorides can be excellent active materials in Li-ion batteries.

Metal fluorides are the most common metal halides used in battery electrodes because they provide the highest voltages but also have large

hysteresis between charge and discharge cycles. Metal chlorides are not commonly used in battery electrodes due to their high solubilities in common organic electrolytes. α - RuCl_3 was chosen as a model compound to investigate because of its low solubility and layered structure. It is unique in the fact that it appears to react through both intercalation and conversion type reactions during the first lithiation cycle. It was shown that α - RuCl_3 makes quite a good anode material for lithium ion batteries, providing many cycles while maintaining a high specific capacity. This provides some evidence that some metal chlorides may still be able to be used as electrode materials in Li-ion batteries.

There are some metal chlorides that cannot be used in Li-ion batteries with a standard organic electrolyte due to their high solubility. In this case, it may be beneficial to try a mixed anion metal oxychloride material that is less soluble. One such example is FeOCl , which is much less soluble than its iron (III) chloride (FeCl_3) metal chloride counterpart. Unfortunately, even though FeOCl is much less soluble than FeCl_3 it still does not have good cycle stability when using a standard organic electrolyte. However, if an ionic liquid electrolyte is used the cycle stability can be dramatically increased, possibly through the stabilization of the structure from the co-intercalation of electrolyte ions. This illustrates the fact that it is critically important to match the correct electrode material with the proper electrolyte in order to optimize the battery properties.

Direct fluorination via FBR has already been shown to be an effective method for synthesizing metal oxyfluoride materials, but it can also be a method used to dope materials with fluorine. Clear evidence has been provided that for two different materials direct fluorination can be used to introduce fluorine into the material without destroying the original chemical structure. This shows that direct fluorination is a versatile tool that can be used to synthesize new materials, as well as being able to dope fluorine into a chemical structure. By controlling the reaction parameters, it is possible that direct fluorination can provide a high degree of selectivity to the degree of fluorination.

This work has demonstrated that direct fluorination using a fluidized bed reactor system can be a tool for both the synthesis of oxyfluoride species, as well as an effective method for doping fluorine into specific materials. It has been shown that metal halides and metal oxyhalides can perform well as both cathode and anode materials in Li-ion batteries. Evidence has been provided that shows that metal halides and oxyhalides can overcome the issue of poor cyclability, providing many cycles while still maintaining significant specific capacity. In this work, it has been shown that metal halides and oxyhalides show rich and complex battery chemistries that require further investigation.

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