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Surface Engineering of Electrospun Fibers to Optimize Ion and Electron Transport in Li⁺ Battery Cathodes

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Abstract

This report documents research into the fabrication of Lithium Manganese Oxide (Spinel) (LMO) cathode material in the form of fibrous mats, the degradation process of this material in a battery electrolyte, the formation of core-shell coated fibers and the electrochemical properties of the active cathode core fiber. In practice, LMO experiences several degradation mechanisms ranging from capacity fading, the Jahn-Teller distortion phenomenon leading to dissolution in the electrolyte phase, and the formation of surface films by degradation of the electrolyte, and/or phase transitions at the surface to form Mn_2O_3 . Density Functional Theory (DFT) was applied to model from first principles the interactions between the electrolyte and the surface leading to Mn ion dissolution. Thermodynamic values of solvation energy were calculated and related to the applied potential on the material during electrochemical cycling. Direct *in situ* observation of the degradation process was conducted on fiber structures using AFM and coin cell measurements, showing the rapid formation of theorized surface films. This provides the first direct evidence of processes occurring at the interface, such as dissolution of the active material, facet development, decomposition of the electrolyte to form a surface electrolyte interface (SEI) layer, or the

formation of Li alcoxides/carboxylates. Methods for fabricating fiber structures of LMO were researched using two techniques; electrospinning and forcespinning. Chemical precursors were evaluated and optimized to lead to polycrystalline, hollow fibers of LMO, as well as tetragonal zirconia fiber mats. Sol-gel chemistries for the synthesis of LMO and zirconia have been implemented to generate these fiber morphologies. Core-shell methods were attempted using both techniques, proving partial success and insight into the physics of coherent core-shell fibers. The knowledge developed in this program has increased understanding of the degradation mechanisms of the active energy storage material, and aided development of a protective interface which resists these processes while permitting rapid Li^+ transport, good e^- conductivity, a stable interface, and prevention of the formation of a solid-electrolyte interphase (SEI) layer.

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Executive Summary

The purpose of this research is to understand and find a solution to degradation of a Li ion cathode material in order to improve lifetime cycling and reliability of batteries. We are investigating LiMn_2O_4 spinel (LMO); a commonly researched cathode material. In practice, this material experiences several degradation mechanisms ranging from capacity fading, the Jahn-Teller distortion phenomenon leading to dissolution in the electrolyte phase, and the formation of surface films by degradation of the electrolyte, and/or phase transitions at the surface to form Mn_2O_3 .

This program developed fiber synthesis techniques for the formation of the active material, and a continuous method for coating the core with a shell of protecting material to allow for structural and electrochemical properties to be stabilized. Sol-gel chemistries for the synthesis of LMO and zirconia have been implemented to generate these fiber morphologies. The electrospinning process and the new forcespinning process have been applied successfully to form these fibrous materials. Characterization of the cycling degradation of the core LMO phase has been studied using STM of these fibers on gold coated substrate in electrolyte. This provides the first direct evidence of processes occurring at the interface, such as dissolution of the active material, facet development, decomposition of the electrolyte to form a surface electrolyte interface (SEI) layer, or the formation of Li alcoxides/carboxylates. Computational modeling of the degradation of the battery electrolyte fluid over LMO surfaces has been conducted, and demonstrates the reaction pathway for degradation of the electrolyte and the thermodynamic stability of the cathode material during the cycling process.

The development of the knowledge of these materials allows for understanding of the degradation mechanisms of the active energy storage material, as well as a route to develop a protective interface to resist this process. Ultimately, this will lead to optimization of this cathode material to permit rapid Li^+ transport, good e- conductivity, a stable interface and prevention formation of the solid-electrolyte interphase (SEI) layer.

SECTION 1

Research Motivation

Energy storage technology is recognized as a critical need for maintaining the quality of life in developed and developing nations. Demand for lithium-ion batteries (LIB) are rapidly increasing due to its application in a wide range of devices such as cell phones, laptop computers, and camcorders, as well critical health applications such as a cardiac pacemaker where an energy source is required to regulate heart-rythms. Power needs are also critical for advanced military equipment, off-peak power for intermittent power generation sources including solar cells and wind generators, in electric vehicles, or space applications¹. The power source for these devices should possess high specific capacity (Ah/g) and density (Wh/g or Wh/l) that will make the batteries smaller and lighter, respectively².

The interfaces in cathode materials dictate numerous properties of electrode storage materials ranging from capacity loss, Li^+ transport activation energy cost, as well as electrolyte stability and degradation products. An optimized interfacial layer that creates a stable transport interface is critical to the effective application of energy storage materials. The formation of controlled interfacial layers has not been systematically examined due to the typical architecture of the cathode element in battery components, which consists of carbon black, binder and active material powders. Active materials research is directed to bulk modifications through doping during synthesis processes, and the formation of controlled interfaces has not been addressed. There are several cathode materials for lithium ion batteries known to have performance limits or progressive degradation due to reaction of the cathode material with the electrolyte to form a surface electrolyte interphase (SEI). Surface protection of nanoparticle cathode materials is used to improve overall battery performance, where the surface coatings are applied in a second synthesis step to the core particle synthesis. These coatings can be either organic (i.e. carbon) or inorganic ceramics (i.e. metal oxides).

Material Choice: Why investigate LiMn_2O_4 ?

In 1991, Sony commercialized the lithium rocking chair battery, which now is commonly known as a lithium ion battery. The pioneer introduction of LiCoO_2 cathode in rechargeable (secondary) cell had a very high voltage and energy density during that period. But LiCoO_2

batteries are expensive and are toxic. LiMn_2O_4 spinel is an excellent cathode material for the replacement of LiCoO_2 because it is cheap, environmentally benign, exhibits good thermal behavior and a fairly high discharge voltage. However, LiMn_2O_4 has several disadvantages such as capacity reduction during charge-discharge (CD) cycles due to phase transitions, and structural instability due to manganese (Mn) dissolution in the electrolyte by acid attack. Hydrofluoric acid (HF) generated by the fluorinated electrolyte salts is one such example for Mn dissolution and is given as below^{3,4} [3, 6],

Manganese (through MnO) and lithium (through Li_2O) dissolve into the electrolyte, which results in capacity fade at elevated temperature (40-50 °C). Therefore, coating the cathode material would be a great pathway to improve the cathode performance in LIB. Attempts have been made to coat the LiMn_2O_4 spinel cathode with ZrO_2 .^{5,6,7} The resulting basic surface of the coated cathode spinel helps in suppressing the Mn dissolution by scavenging unwanted HF from the electrolyte⁴. Also, the coating helped to reduce the cubic-tetragonal phase transition and improved the stability of the spinel structure⁸. Figure 1 shows the improved stability of the ZrO_2 coated LiMn_2O_4 spinel cathode particles at elevated temperature.

Figure 1. Comparison of electrochemical cycling stability of lithium cells with (a) uncoated LiMn_2O_4 and (b) ZrO_2 -coated LiMn_2O_4 electrode [from ref. 3].

Typical material science advances in cathode material synthesis involves reducing the size of the cathode particles toward or into nanomaterials. The small dimension allows for more rapid ion transport of the Li^+ charge carrier within the cathode material. An advantage can be developed over nanoparticle coated cathode materials by the use of a fiber based microstructure. A fibrous structure for the cathode maintains the short diffusion length for Li transport into/from the cathode, which is a primary advantage for nanomaterials. A fibrous structure also allows for the formation of passivating layers of a protecting inorganic ceramic material, sufficient for transport of Li ions but non-reactive to the degradation of the cathode material. Protective coatings are typically applied in a second step in powder cathode material synthesis, either by solution deposition routes or by high energy applications including laser ablation or magnetron sputtering. Further, the electrochemical properties depend on the morphology of cathode materials; higher surface area improves performance of LIB⁵. Cathode materials in the form of nanofibers have shown improved electrode properties^{9,10,11}

SECTION 2

Fiber Fabrication Methods – Electrospinning and Forcespinning

The Electrospinning Technique

Fibrous structures for materials production has been increasingly investigated using the technique of electrospinning. In this technique, a polar solvent is used to develop a sol-gel solution or a material precursor is dissolved in a polymer solution. The overall composition is pumped slowly out a nozzle or needle under a strong electric field. The electric field induces a counter force to surface tension, leading to the production of a fluid jet. The development of a jet is influenced by the local electrostatic field and surface tension, rather than the absolute size of the needle orifice, and in fact free surface electrospinning of a fluid phase can be demonstrated from a submerged point or asperity near the fluid-air interface. This jet dries rapidly in transit to a grounded target. Critical to the production of these materials using electrospinning are factors related to the ionic conductivity of the precursor solution, molecular weight of the polymer solution, field strength and distance to the grounded collector. It is often mentioned that limiting factors to the production of materials using electrospinning processes are the low production rates of the materials. Pumping rates for a single needle are on the order of 0.1 to 0.5 ml per hour. Multiple jets are proposed to alleviate the production rates, or other methods using various methods for raising asperities near the surface of a fluid bath to locally create bursts of electrospun materials.

Nanofibrous cathode material structures have recently been investigated using the electrospinning process. Electrospinning of ceramics is a scalable nano-fabrication technique that increasingly is applied to electrode manufacturing^{12,13}. Several cathode materials are being nanostructured using the process of electrospinning. Demonstration of electrospun cathode materials include: $\text{LiNi}_{0.5+\delta}\text{Mn}_{0.5-\delta}\text{O}_2$ ¹⁴, LiCoO_2 - MgO co-axial fibers¹⁵, cobalt oxide(CoO and Co_3O_4)¹⁶, LiCoO_2 ^{17,18}, $\text{Li}_{1+\alpha}\text{V}_3\text{O}_8$ ^{19,20,21}, nano-Vanadium pentoxide²², and LiMn_2O_4 ²³. Drawbacks to the electrospinning process lie in the production rate and the concentration limitations of conductive precursor solutions. The technique of electrospinning has a low production rate (0.1 to 1.5 ml/hr) of the precursor solution, and there can be limitations in the concentration of the inorganic precursors, related to the solution conductivity.^{24,25} Attempts to

increase rates for electrospinning generally focus on increasing the number of fiber spinning sources (i.e. nozzles)^{26,27,28,29,30,31,32} but the number and proximity of fiber jets is impacted by the electrostatic interaction between the jets. Increasing the synthesis rate of nanofibers remains a significant achievement for materials processing.

Electrospinning has been applied to the formation of core-shell materials by nesting one needle within a second needle, and controlling the flow rate of two polymer solutions with desired precursors to the fluid air interface. This method requires sensitive matching of the solutions and restricts the combination of materials that can be co-spun. The interface between two precursor solutions can lead to instability of either polymer or sol-gel or ionic precursors and the formation of an unspinnable gel phase at the needle tip. These restrictions can prevent the formation of core-shell fiber architectures.

The Forcespinning Technique

A novel technology for fiber production is applied which greatly increases the production rate and allows for the formation of core-shell materials using material chemistries which would be incompatible with electrospinning methods. The method is called Forcespinning, and it uses centrifugal force from a spinning needle to process a polymer/material precursor solution into a fibrous non-woven mat. The forcespinning approach differs from electrospinning in some critical aspects of formulation. In this technique, precursor solutions of metal salts, sol-gel or nanoparticles are developed in a dissolved polymer solution of high molecular weight, similar to the process for electrospinning. However, the concentration is typically much higher than in electrospinning. For example, electrospinning compositions typically have polymer concentrations between 2 and 5 %, whereas forcespinning is generally higher, such as 8 to 20 weight %. The solution is extruded from a spinnerette using fine nozzles (less than 200 microns) under high rotational speeds to form fibrous structures. In this method, electrostatic potentials are not applied, and the fiber jet is formed by the high rpm of the spinnerette (5000 to 10,000 rpm) and the inertial drag forces of the atmosphere as the polymer-precursor solution is ejected. The volume of solution is formed into nanofibers at a much higher rate than electrospinning; typically 1 ml of solution can be spun in minutes as opposed to the lower rates for electrospinning.

Fiber dimension is controlled by the rotational speed and distance to the collector structure, and by the drying rate, which is dependent upon the ambient humidity and solvent chemistry of the precursor solution. This fiber mat can be collected and heat treated in a furnace to react the inorganic precursors and remove the polymer fiber, leading to an oxide ceramic using similar chemistries to electrospinning or sol-gel fabrication of materials. Core-shell fibers of two oxide materials have not been demonstrated using forcespinning.

Table 1 shows compositions of polymer and solvent that exhibit the ranges needed for forcespinning compositions. The PEO sample at 8 wt% is the standard for testing the unit, and leads to opaque white webs of fibers over the collector posts. Polyvinyl alcohol (PVA) in water was not sufficient to form fibers, in contrast to PVA in electrospinning. However, addition of Polyvinyl pyrrolidone (PVP) to the composition with water was ultimately successful in forming fibers. The PVP performance in water solvent requires higher concentration to form fibers than in ethanol, and shows that below the ideal concentration, the fibers break up into droplets. As viscosity is increased, the droplets become larger and less breakup events occur. Fiber formation becomes a balance of drying, extensional forces in the strand, and sufficient viscosity in the initial condition. Use of ethanol allows for lower PVP concentration, and there are many examples of molecular precursor chemistry that are compatible with this environment. Even at 10 wt% in Ethanol, the PVP solution flows easily. The shear rate rheology of these compositions was measured using a Haake MARS rheometer with a 60 mm 1° angle cone plate sensor, and is presented as a record of the material properties in Figure 2. Under the centrifugation speeds used in forcespinning, (3,000-10,000 rpm), the shear rates likely exceed the capabilities of the instrument, but the high shear values of the polymer solutions give a measure of the solution properties. The drying rates are unknown, but must be very fast to form a fiber, as the entirety of a 1 ml test composition is spun in 30-90 seconds of centrifugal force.

Table 1. Experimental Results in survey of Forcespinning Compositions.

Polymer	Solvent	Molecular Weight (g/mol)	Concentration (wt%)	Results
Polyvinyl pyrrolidone	water	1.3 M	5	Wet Droplets
Polyvinyl pyrrolidone	water	1.3 M	10	Large Droplets, less frequent
Polyvinyl pyrrolidone	water	1.3 M	15	Very Large Droplets, frequency of impact reduced
Polyvinyl pyrrolidone	water	1.3 M	20	Fiber mat formation, larger fiber size
Polyvinyl pyrrolidone	water	1.3 M	25	Sparse fibers with large droplets/globs
Polyvinyl pyrrolidone	Ethanol	1.3 M	5	Droplets spray walls, isolated fibers
Polyvinyl pyrrolidone	Ethanol	1.3 M	10	Fine fiber web, continuous
Polyvinyl pyrrolidone	Ethanol	1.3 M	15	Fiber formation, tend to “bond” during cast
Polyvinyl pyrrolidone	Ethanol	1.3 M	20	No fibers, occasional droplet
Polyvinyl alcohol	water	84,000-124,000	8	No fibers formed, appears too wet
Polyethylene oxide (PEO)	water	900,000	8	300 nm fiber
QPAC 40	acetone	293,000	10	>1 μ m fiber

Figure 2. Shear Rheology of PVP solutions in Ethanol, used for forcespinning. Even high shear rate viscosity increases rapidly with drying, leading to stability of fiber structures.

SECTION 3

Chemical Precursors to Fibers

Fiber forming compositions must include the inorganic precursors to the desired phase (LMO), as well as a high molecular weight polymer to prevent breakup of the jet into droplets under the drying rate of the method. In this investigation, the initial technique studied was electrospinning. Yu et al. had a prior publication on the electrospinning of LMO materials, which was used as a baseline composition by including polyvinyl alcohol with LiCl and Mn(Acetate)₂. We performed experiments to determine if an alternate precursor would suffice for the phase pure formation. The investigation utilized Lithium and manganese nitrate and also lithium and manganese acetate systems as precursors.

The Yu et al. composition is as follows: A precursor solution for fiberspinning of LiMn₂O₄ was prepared as follows. manganese acetate tetrahydrate at 1.0 M concentration (12.2515 g) and LiCl at 0.5 M concentration (1.0598) was prepared in 50 ml of 10 wt% PVA solution (mol. Wt. ranging from 84,000 to 124,000 g/mol) predissolved in deionized water. The salts were mixed and agitated by hand, then sealed and placed in an oven at 65 °C overnight to dissolve and become homogenous. For the study performed here, the molar amounts of lithium and manganese precursors were substituted with either the nitrate or acetate salts at the same molarity.

Electrospinning was performed for all three systems. The typical parameters were 8 wt % PVA solution, with a pumping rate of 2.5 µl/min, 20 cm separation from the grounded target of Al foil, and applied voltage of 20 kV. SEM images of the fibers formed from the acetate system are presented in Figure 3. Image analysis shows the average fiber diameter ranged from 259 ± 14 nm before reducing to 164 ± 22 nm after annealing.

Thermal conversion reactions were studied using thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) ¹. Thermal conversion was performed in a box furnace with static air. The sample heating schedule was a one hour ramp to 100 °C with a hold for 1 hour, followed by heating at 4 °C/min to the desired calcination temperature, ranging from 550 °C to 700 °C. The dwell time at the reaction temperature was two hours for the study of the fiber morphology, and ten hours for studies of phase stability using X-ray diffraction (XRD). Scanning electron microscopy (SEM) was performed on both the precursor fibers and the calcined materials using a Zeiss Supra 55VP FESEM. ² X-ray diffraction (XRD) was performed using a Siemens D500 diffractometer employing a sealed tube X-ray source (Cu Kα radiation), fixed slits, a diffracted-beam graphite monochromator, and a scintillation detector. Typical scans were performed from 5 -80 degrees 2θ, 0.04° step size, and various count times. Crystallite-size estimates were derived via the Sherrer equation, employing the full-width-half-maximum (FWHM) method. Instrument broadening was derived using a LaB₆ standard (NIST 660c) and accounted for in the crystallite-size determination. The samples were assumed to have no significant strain broadening. Crystallite-size estimates derived via XRD were compared to SEM results for validation.

The acetate precursor was collected over a gold coated Si wafer for annealing and testing in AFM or SPM measurements. XRD was used to evaluate the phase formation as shown in

¹ Mettler-Toledo, Inc., 1900 Polaris Parkway, Columbus, OH, 43240.

² Carl Zeiss SMT Inc., One Corporation Way, Peabody, MA 01960.

Figure 4. The substrate creates significant peak contamination, but shows little LMO characteristics or other crystalline phase development.

The thermal analysis of the acetate and nitrate precursor PVA compositions are complimentary between the TGA/DTA and XRD hot stage investigations, in Figures 5, 6, and 7. The sample with nitrate precursors undergoes a direct transformation from the amorphous phase to lithium carbonate and MnO, at a temperature of ~ 200 °C. Further heating leads to LMO spinel formation at 600 °C. The acetate precursor completes degradation of PVA at ~ 470 °C, and again the lithium precursor forms carbonates and MnO is present at approximately 550 °C. The nitrates decompose rapidly at lower temperatures between 200 and 300 °C. In either composition, the incongruent reactions lead to side products and undesired phases, without the desired phase formation.

It is concluded in this work that the PVA system requires the LiCl precursor to give the desired LMO phase. The Cl^- anion may decompose at a higher temperature or participate as a transition species in the reaction with Mn acetate to affect the oxidation state and allow for the desired spinel phase to form. Figure 8 shows the TGA/DTA data for the decomposition of the LiCl-Mn(Ac)₂ PVA composition from Yu et al., and the following SEM of the fibers formed by electrospinning and then calcination in Figure 9. It appears that the LMO phase develops at temperatures above 500 °C, when the PVA polymer is fully combusted from the composition.

Figure 3. Electrospun PVA fibers of LMO acetate precursor composition. (a) As formed in the unfired state. (b) Post calcination over a gold coated wafer substrate at 700 °C with a 5 hour hold in air.

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Figure 4. XRD of calcined LMO acetate precursor sample, showing weak peaks for LMO and strong peaks for the Au coated Si wafer substrate.

LiMn₂O₄ from Acetate Precursors

Figure 5. TGA/DTA analysis of the PVA composition with lithium and manganese acetate precursors.

LiMn₂O₄ from Nitrate Precursors

Figure 6. TGA/DTA analysis of the PVA composition with lithium and manganese acetate precursors.

Figure 8. TGA shows temp must be greater than 500 °C for reaction to form material. Treatment temperature may need to be higher to develop grain structure.

Figure 9. SEM images of LiCl-Mn(Ac)₂ PVA fibers (a) pre-calcine, (b) post calcine at 650 °C, 10 hours.

Forcespinning of LiMn_2O_4 Cathode Nanostructures.

Forcespinning has a more rapid fabrication time than electrospinning, and altered rheological requirements in the formulation due to the variation in the forces acting upon the jet. Attempts with higher concentration of PVA polymer in the electrospinning composition did not successfully form many fibers. The materials produced appeared as large wet droplets and isolated fibers with “tacky or wet” surfaces, indicating that a fiber structure was not pulled by centrifugal and inertial forces. Another possibility is that the evaporation of the solvent was not occurring at the proper rate to stabilize a fiber. It is possible that the increased hydrogen bonding present in PVA polymers inhibits solvent loss by dehydration. An attempt was made to dilute the system with dimethyl formamide which made a successful web on the first attempt, but could not be repeated. A successful formula was developed by forming a composite with PVP.

A precursor solution for fiberspinning of LiMn_2O_4 was prepared as follows: manganese acetate tetrahydrate at 1.0 M concentration (12.2515 g) and LiCl at 0.5 M concentration (1.0598) was prepared in 50 ml of 10 wt% PVA solution (mol. Wt. ranging from 84,000 to 124,000 g/mol) predissolved in deionized water. The salts were mixed and agitated by hand, then sealed and placed in an oven at 65 °C overnight to dissolve and become homogenous. When dissolved, the PVA solution was mixed in a ratio of 2 parts to 1 part of a 20 wt% polyvinylpyrrolidone solution in water, creating a composite polymer solution with the dissolved salts. This leaves final concentrations of 0.667 M $\text{Mn}(\text{Ac})_2$, 0.333 M LiCl, with 6.67 wt% PVA and 3.33 wt% PVP.

Forcespinning was performed at speeds ranging at 6,000 rpm with a 30 gage needle, leading to fiber formation and collection on the vertical elements. SEM micrographs in Figure 10. show the spun fibers have smooth interfaces, and diameters ranging between 0.5 to 2 microns. Adhesion or bonding between adjacent fibers seems to be present. Calcination for conversion to the final oxide product was conducted in air at various temperatures. Figure 11 shows the morphology of the material after calcination to 650 °C for 2 hours. The fiber morphology is retained, and surface crystals are clearly visible across each fiber showing polycrystalline surfaces. There are broken fibers in the sample which exhibit a hollow cross section. The thermal reaction therefore appears to be leading to surface nucleation of the final product. The transfer rate of oxygen to the Li and Mn precursors must be limited, and the process must create sufficient mechanical stability at the surface to maintain the conversion during the loss of the polymeric components. The thermal conversion process was investigated further to examine this reaction process.

These fiber materials were converted in air to a black product, and studied using TGA/DTA, SEM and TEM. Figure 12 shows the TGA/DTA profiles at a ramp rate of 5 °C/min, in which mass loss and energetic events align well. The low temperature mass loss near 100 °C can be attributed to ambient or residual water, as these samples were not pre-dried. The mass loss between 200-250 °C with an exothermic event at ~230 °C was visually observed to be a combustion event, which likely relates to the PVP polymer. More exothermic events occur at 227.8 °C, 275 °C, 300 °C, 330 °C, 367.8 °C, a shoulder at 408 °C, 443 °C and 495 °C. All the mass loss appears to occur by 530 °C. The nature of all these events has not been identified, but the PVA polymer is expected to decompose at 350 °C (side chain) and 450 °C (main chain), which would account for two of the above seen events.

XRD measurements were performed upon fiber samples thermally converted at temperatures varying from 550 °C to 700 °C, with 10 hour periods at the conversion temperature,

presented in Figure 13. These show the formation of the LiMn_2O_4 phase without contamination as low as 550 °C. From the TGA/DTA data, we place the final thermal events as the crystallization process, occurring from 400 to 500 °C.

The XRD data was used to determine the average crystallite size using the Scherrer method. Figure 14. shows the values as a function of temperature. Grain growth is controllable across this range by control of thermal annealing point, ranging from crystallite sizes of 20 to 60 nm. Grain growth appears more rapid above temperatures of 650 °C. TEM images were used to compare with the values calculated from XRD. Figure 15 shows the hollow microstructure of the fibers produced in calcination, and Figure 16 shows TEM images of the fiber crystals after annealing at 600 and 725 °C. Those images show smaller crystal sizes than the values calculated by XRD peak broadening. The discrepancy may result from imaging only isolated areas of single fibers which would be non-representative of the sample as a whole, or reflect internal stress in the polycrystalline materials.

In conclusion, a formulation that allows for successful fiber formation by forcespinning was developed, that produces hollow fiber structures after calcination. Grain size can be controlled by choice of annealing temperature while maintaining the fibrous character of the derived materials.

Figure 10. Forcespun precursor fibers for Lithium Manganese Oxide Spinel.

Figure 11. Calcined microstructure of LMO fibers at 650 °C for 2 hours.

Figure 12. TGA/DSC data for the thermal conversion process. Heating rate is 5 °C/minute in air.

Figure 13. XRD 2θ characterization of LiMn₂O₄ fibers formed by 10 hour anneal periods at increasing temperatures.

Figure 14. Crystallite size as a function of conversion temperature. All runs performed in air with holds of 2 hours at annealing temperature. Crystallite size determined from the Full Width – Half Maximum of the (400) peak $\sim 48^\circ 2\theta$.

Figure 15. TEM images of LMO calcined fibers, showing hollow structure.

Figure 16. (a) TEM of samples fired at 600 °C. Particle size measured at near 15 nm. (b) TEM of samples fired at 725 °C. Particle size measured at near 35 nm.

Forcespinning of a Zirconia Shell Composition for LMO Cathode Fibers

Zirconium oxide ceramics are chosen for many diverse applications due to specific materials property advantages. Their high chemical resistance to alkali environments makes ZrO_2 suitable for protection of metal components or for filtration of corrosive fluids.³³ At high temperatures, cubic ZrO_2 exhibits high ionic conductivity and is applied as an oxygen sensor and as a solid electrolyte in solid-oxide fuel cells.³⁴ ZrO_2 is also applied in ceramic-ceramic composites and biocomposites based on the martensitic transformation from the tetragonal to the monoclinic phases, leading to a volume expansion which closes fracture crack tips or induces compressive stress to toughen the composite.^{35,36} In addition, tetragonal ZrO_2 is applied for catalysis and catalytic support for some gas phase reactions.^{37,38}

Chemical solution synthesis processes are often suitable for the production of conformal films and ceramic particles. These methods control grain size in the synthesis of tetragonal phase ZrO_2 .³⁹ The chemistry of tetra-alkoxy zirconium precursors is well documented. It is common to include organic chelate ligands such as acetic acid, acetylacetonate or ethylacetoacetonate to control the hydrolysis process of the Zr reactants.^{40,41,42,43} Stabilized solutions can thus be formed for powder precipitation, dip-coating, spin coating, and fiber drawing fabrication methods.⁴⁴ Electrospinning of chelate-Zr precursors has also demonstrated the capability to form porous fiber mats, which can be applied in membranes, sensors, photocatalysis, photovoltaics, insulation, or as scaffolds.^{45,46,47,48,49} The nanofibers produced by electrospinning are reported with diameters ranging from 50-200 nm under best case conditions after calcination to convert the precursor sol. Calcination temperatures are generally above 500 °C for the tetragonal phase and over 800 °C for the monoclinic phase. These routes are successful, but the technique of

electrospinning has a low production rate (0.1 to 1.5 mL/hr of the precursor solution), and there can be limitations in the concentration of the inorganic precursors, related to the solution conductivity.^{50,51} Attempts to increase rates for electrospinning generally focus on increasing the number of fiber spinning sources (i.e. nozzles)^{52,53,54,55,56,57,58} but the number and proximity of fiber jets is impacted by the electrostatic interaction between the jets. Increasing the synthesis rate of nanofibers remains a significant goal for materials processing.

In this work, a chelate precursor is applied to a novel nanofiber production technique called ForcespinningTM, in which centrifugal force is used to extrude polymer solutions. Fiber jets are formed by high rotational speeds of a spinnerette using fine nozzles (200 micron or less interior diameter). Reduction of fiber diameter occurs by the inertial drag between the fiber and the atmosphere as the polymer/sol-gel solution jet dries. The product is either collected between vertical posts or coated over a substrate. A significant advantage of this technique lies in the production rate. It is much more rapid than the electrospinning process, with a unit mL of solution becoming a fibrous mat in less than a minute as opposed to several hours for the same volume in electrospinning. It also has no electric field applied for fiber production, enabling solution systems that are not amenable to electrospinning to become fibrous products. In this study, we demonstrate the formation of zirconia fibers using this processing technique.

The zirconium complex was formed from Zr-butoxide (Sigma-Aldrich, 80 wt% in 1-butanol) and acetylacetonate (acac) (Sigma-Aldrich, ReagentPlus Grade, >99%) as a complexing agent. A chelated chemical solution of zirconium was prepared by reacting the zirconium butoxide with acac in a 1:2 molar ratio. The concentration of zirconium was 0.2 M in n-butanol solvent, and all ingredients were combined at room temperature and magnetically stirred for one hour to clarify. The solution was mixed with high molecular weight polyvinyl pyrrolidone (PVP)

polymer (Alfa Aesar, molecular weight 630,000 g/mol), and dissolved at 60 °C to achieve a uniform transparent solution. The polymer loading in the Zr(acac) solution was 20 weight %. No water was intentionally added to the solution to hydrolyze the precursor. All samples were prepared in ambient air and no moisture controls were used, therefore trace water can be expected in the solution.

The nanofibers were created using the ForcespinningTM method. This particular sample was amenable to form fiber mats under several processing conditions such as varying solvent-polymer concentration, nozzle diameter and rotational speed. Optimum parameters were observed with spinneret consisting of two nozzles with 140 µm diameter and 17.73 mm length and rotational speed of 7000 rpm for 45 seconds. Thick mats of nanofibers were formed into a free standing web supported over the vertical post of the collector located 10 cm away from the nozzle exits. These webs were collected by passing a glass slide through the net and wrapping the fibers by hand over the slide. Pellets of fiber precursors were prepared by collecting all the fibers produced from one mL of precursor solution by winding over a glass rod, followed by loading into a 0.5” steel die and manually pressing with the die plunger. A pellet was easily formed and stored under vacuum until thermal processing.

Pyrolysis of the precursor was studied by simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) ³. The data was collected at a ramp rate of 5 C/minute in air. A separate sample was calcined in air at a ramp rate of 4 C/minute to 650 °C, and held for 2 hours at temperature in a small laboratory furnace. Visual inspection of the calcination process was performed by collecting images using a video camera during thermal heating in a small tube furnace.⁴ The fiber pellet was cut into a rough square using a stainless

³ Netsche STA 409 PC. NETZSCH Instruments North America, LLC, 129 Middlesex Turnpike, Burlington, MA 01803 USA.

⁴ Control Vision, Inc., Sahuarita, AZ 85629

steel razor blade, allowing for observations of the temperature at which dimensional changes occurred. The fiber compact was supported over a sapphire plate, with a thermocouple located beneath the plate. The error in sample temperature is less than $\pm 3^{\circ}\text{C}$.

Scanning electron microscopy (SEM) was performed on both the precursor fibers and the calcined materials using a Zeiss Supra 55VP FESEM in secondary electron mode.⁵ Transmission Electron Microscopy images were taken using a Philips CM 30 TEM operating at 300 kV. Samples were examined by preparation of dilute suspensions of calcined fibers in ethanol, and evaporating a droplet onto a carbon TEM grid. Additional samples were fired at temperatures ranging from 550° to 700 C for dwell times of 10 hours and characterized for crystal phase and grain size. X-ray diffraction (XRD) was performed using a Siemens D500 diffractometer employing a sealed tube X-ray source (Cu K α radiation), fixed slits, a diffracted-beam graphite monochromator, and a scintillation detector. Typical scans were performed from 5 -80 degrees 2θ , 0.04° step size, and various count times. Crystallite-size estimates were derived via the Scherrer equation⁵⁹, employing the full-width-half-maximum (FWHM) of the Tetragonal ZrO₂ (101) peak. Instrument broadening was derived using a LaB₆ standard (NIST 660c) and accounted for in the crystallite-size determination. The samples were assumed to have no significant strain broadening. Crystallite-size estimates derived via XRD were compared to SEM results for validation.

The thermal decomposition of the precursor fibers was characterized by TGA/DSC, in air at a heating rate of 5 C/minute. Figure 17 shows weight loss initiating at low temperatures, which becomes more rapid in rate above approximately 200 C before ceasing at 500 C. There are small exothermic events with peaks located at 322 C, 402 C, and exothermic maximum at 445 C. In the

⁵ Carl Zeiss SMT Inc., One Corporation Way, Peabody, MA 01960.

constant mass region above 500 °C, the heat flow profile is also linear, indicating full reaction completion at 500 C. The total mass loss from the material is 85.7%.

Figure 17. TGA/DTA of PVP-Zr butoxide acetylacetonate precursor as forcespun fibers.

Figure 18 presents SEM and TEM images of the processed materials in the form of the (a) polymer/precursor fibers before calcination, (b) the morphology of the fibers post calcination for two hours at 650 C, (c) the cross-sectional view of broken fiber ends, and (d) the nanostructured size of the grains within the fiber. These images show straight fibers in the polymeric precursor, with diameters varying from the submicron to single digit micron sizes. These structures transition to the curved ceramic fibers upon calcination, with diameters between

200 to 600 nm. The SEM images show smooth surfaces on the fibers, and the TEM image shows that the grain structure of the fibers is in the nano regime, with sizes near 15nm. This nanosized grain structure exhibits the tetragonal phase as determined by XRD in Figure 19. This figure

Figure 18. SEM and TEM images of ZrO_2 fibers. TEM shows the nanostructured grain size of the converted product.

shows relatively broad, overlapping peaks, but is consistent with the tetragonal form of ZrO_2 . Although the peaks are broad, it is possible to see the peak shoulders forming on various hkl indexes, confirming the break in symmetry from cubic. This free-standing film-like specimen was not completely flat and uniform in height, which could cause some peak broadening due to smearing of the peak locations, but this would only tend to make the peaks uniformly broader

and not cause an error in symmetry assignment. There was also a trace peak from a possible 2nd phase of monoclinic ZrO₂ (appearing as a shoulder on the Tetragonal (101) peak). However, the dominant phase is tetragonal ZrO₂.

Figure 19. XRD characterization of the reacted ZrO₂.

Figure 18 presents the stages for processing the polymer sol-gel precursors into fiber materials. The forcespinning approach clearly processes the Zr(acac)-PVP polymer solution into a fibrous, non-woven network, as shown in Figure 18a, that exhibits an appearance similar to that of fibers produced by electrospinning of similar materials.¹²⁻¹⁷ The uncalcined fibers are

primarily composed of the PVP polymer, and are quite flexible and easily handled as might be expected. The calcination of the precursor leads to the formation of an all inorganic network. These results are not surprising, as chelate chemistries for forming ZrO_2 fibers have previously been employed with processing methods such as electrospinning, sol-gel spinning,^{60,61} and blow spinning.⁶² In comparison with these techniques, forcespinning of the solution leads to diameters slightly larger than that of the electrospinning process, yet at a much higher production rate. Methods for fiber drawing from sol-gel precursor solutions result in diameters varying from 3 microns to 10 or several 10s of microns.^{12,28,29, 32} Electrospinning can form reacted fiber diameters as low as 50 nm, but more commonly in the range of 100 to 400 nm, with a variation in diameter within the sample.^{4,12-17} It is possible that the fiber diameters produced with forcespinning could be reduced if a smaller spinning orifice is employed. Additional study of factors including rotational speed, ambient humidity and drying rate would also have to be considered, which is beyond the scope of this initial investigation.

One point to note in these materials is the formation of a curved and tortuous topology in these fibers post calcination. The mass lost in these materials is significant, and is near 85%. The curled profiles are an indication of the shrinkage stress present in the ceramic. Clearly the fiber structure is retained, indicating that the polymeric PVP does not melt or allow for viscous flow in the material during the calcination process. The reaction of the precursor species (acetylacetonate and perhaps PVP complexes) and the crystallization of the ZrO_2 will influence the development of the oxide ceramic, and affect the development of stress in the material. An investigation of the thermal reaction was conducted to understand the calcination process.

The dimensional change was characterized by pressing a fiber sample in a 0.5 inch steel die to form a pellet, which was then thermally converted. An approximately square cross section

was formed using a razor blade to cut the unreacted pellet, in order to observe the sample in the thermal reaction. Visual observations were used rather than standard dilatometry due to the mechanically fragile nature of the reacted material, which would not support an applied stress measurement. Figure 20 shows the dimensional transition of the compact of these fibers.

Figure 20. Dimensional shrinkage during thermal conversion of a fiber pellet. Temperatures for each stage are estimated (± 5 °C) as noted in each image.

The dimensional changes are an interesting contrast and compliment to the TGA/DSC data. Mass loss from the fibers is less than 10% below 200 °C, but the size of the fiber compact decreases by nearly half, and the sample becomes black and charred by decomposition of the organic components. The DSC values are negative up to this point, and an endothermic bond formation process rather than an exothermic combustion of the organic components appears

likely in this temperature region. In Figure 20a-e, the dimensional changes in the compact are evident. From a uniform looking surface, bubbles appear to create voids on the top surface, and shrinkage occurs. At 123 C (Figure 20c), it is clear that the free top surface has contracted significantly, whereas the lower surface has been bound to the sapphire plate supporting the sample. Image 20d shows additional contraction of the base, and overall further size reduction at 192 C in Figure 4e. Figure 4f shows that at 200 C, one of the top corners of the compact begins to change color from black to white, and soon the upper surface becomes white, leading to a full color change by 210°C in Figure 20h and 20i. This correlates with the initiation of rapid weight loss in the TGA curve beginning at 200 C and the development of the exothermic reaction in the DTA value, maximized at the first peak 322 C.

The components for reaction in the system include the PVP polymer, as well as the Zr-acac complexes and any hybrid complexes formed between the polymer and the molecular species. The TGA and DSC data profile the removal and conversion of these components. Prior studies have evaluated the reaction of zirconium chelate clusters and PVP degradation reactions during thermal processes. PVP degradation has been investigated previously by Silva *et al.*⁶³ For pure PVP reaction in air, mass loss is initiated at 250 C, with rapid degradation occurring between 370 and 430 C. This degradation is accompanied by an exothermic peak centered at 420 C. For compositions with metal complexes with PVP, Egger *et al.* state that PVP forms hydrogen bonds with the metal oxo-clusters in solution and in the dried gel.⁶⁴ Degradation (in the Zr acetate complex PVP system) starts below 240 °C, and the bonds related to C=O and C-N groups are reacted and eliminated at 300 °C. They are replaced by aliphatic compounds from 300°C and above, but no further information was given regarding the organic materials at 400°C. Emig *et al.* formed doped ZrO₂ fibers using acac and PVP polymers similar to our chemical

precursor.⁶⁵ Their work showed weight loss from 100 to 180 °C of 15% due to vaporization of their solvents of isopropanol and dimethylformamide. A broad exotherm ranging from 340 °C to 680 °C was attributed to burn out of acac, residual alkoxide groups, and their chlorides and polymers. The DSC data is made more complex with the energy of crystallization of the ZrO₂. Emig et al. report that ZrO₂ begins crystallization at 400 °C, a value also reported by Shukla et al.³⁶

The observations made here agree with past publication in many respects. The weight loss below 200 °C is due to reaction of the organic materials rather than solvent loss. The value of mass lost is similar to the value noted by Emig et al. but solvent loss is not believed to be the source of the mass loss. The pellets were held under vacuum before testing here and the charring was visible in the compact. Combustion of the organics was visible at 200 °C and initiated the weight loss process, with polymer degradation continuing to 500 °C. Much of the volume reduction in the compact occurs below the exothermic reaction and weight loss, suggestive of a densification of the organic precursor and polymer components prior to formation of the fully reacted tetragonal phase of zirconia. The exothermic peaks noted in the DSC curve can be attributed to the aliphatic compound formation at 322°C, the crystallization of ZrO₂ at 402 °C, and the final backbone degradation in the PVP polymer at 445 °C.

The development of the tetragonal phase of ZrO₂ in these fibers is notable, as there are no dopants to stabilize the tetragonal crystal structure. Shukla *et al.* noted some monoclinic phase for thermal processes at temperatures as low as 400 °C.⁶⁶ However, the tetragonal phase is stabilized for very small grain sizes in the undoped state. Theoretical treatments for the size related upper bound of the tetragonal phase have produced values as small as 6 nm⁶⁷ or 10 nm⁶⁸, but the formation of polycrystals tends to increase the critical size due to strain effects in the

volumetric transformation energy. In practice there are several examples of larger crystallite sizes in ZrO_2 materials which retain the tetragonal phase, and upper bound values near 30 nm are reported.^{69,70} Shukla et al. reported nanocrystallites within polycrystalline particles (diameter of 500-600 nm) that retain the tetragonal phase even at a crystallite size of 45 nm.³⁴ The nanocrystallites synthesized here are <20 nm, and should be stable in the tetragonal phase due to the small grain size thermodynamic stability effects.

Figure 21 presents XRD data for samples fired at temperatures ranging from 550 °C to 700 °C and held at temperature for ten hours, to determine if the fibers are stable against thermal changes in grain size and crystal phase. Liang et al. found that monoclinic phase transformation in zirconia nanofibers could occur as low as 650 °C.¹⁶ These fiber samples all remain as the tetragonal phase, although trace monoclinic peaks may be present. (Spectra taken for samples at 675 °C and 700 °C have an amorphous peak at low angle due to contamination from mounting grease in sample preparation). The inset figure shows the grain size as calculated using the Scherrer equation. If microstrain is present, these values are an underestimation of the true grain size, but this could not be definitively determined. The grain size ranges from 12 nm at 550 °C, to only 16 nm after firing at 700 °C for 10 hours. The tetragonal phase formed in these fibers appears robust, and the grain size remains under the value reported for stabilization of the tetragonal phase.

The formation of the tetragonal phase with low grain size is attributed to the chelation chemistry used in the zirconium precursor. It is common to use acac to complex the Zr alkoxide species. The acac acts with the Zr alkoxide to form a dimeric precursor, with the acac adsorbed to each Zr in the enol form.³⁰ There are two remaining alkoxide bonds available for hydrolysis

per Zr atom. Reaction of these to form ladder type polymers is considered to be the condensation mechanism for ZrO_2 ceramic formation. The molar ratio of acac to Zr species in this work is

Figure 21. Thermal annealing effects on ZrO_2 grain size. Inset figure shows the crystallite size as a function of temperature.

two, a value higher than values used in many other sol-gel fiber citations. Guinebretiere et al.⁴³ showed that molar ratios of acac to Zr as low as 0.4 led to stable transparent solutions. A ratio of two acetylacetonate molecules to each Zr cation is used to attempt to cap the remaining alkoxide bonds. Increasing the acac content inhibits hydrolysis, and leads to smaller nanoparticle size upon calcination above 500 °C. Nucleation of the tetragonal phase is high in order to form the nanosized grains observed here, in agreement with the exothermic peak at 402°C from the

TGA/DTA analysis. As our acac concentration forms a higher stability Zr precursor, we attribute the <20 nm grain size on calcination to the high nucleation density of the precursor.

In conclusion, phase pure tetragonal ZrO_2 non-woven fiber mat is rapidly formed using the forcespinning technique with calcination above 500 °C in air. The phase is retained without using any metal cation dopants. The retention of the tetragonal phase is attributed to the low particle size between 12-16 nm. The chelate to cation ratio is attributed to the high nucleation density leading to low grain size of the ZrO_2 tetragonal phase in these fibers. The width of the nanofibers range from 200-600 nm, in good comparison to prior work performed using the electrospinning technique. The fibers present a curved and tortuous profile after calcination. The ease and simplicity of the processing technique along with the higher volume production rate compared to electrospinning make this approach competitive for production applications of nanofiber mats.

Core-Shell Fiber Fabrication Efforts

In order to improve the stability and lifetime of the LMO cathode material, numerous attempts have been made to develop a protective coating over the active material.^{4-7,15} A goal of this work is to develop a continuous fiber coating process allowing for single step preparation of fibrous cathode materials. Such a method would have advantages in both performance and economics of energy storage materials. To that end, electrospinning and forcespinning were attempted.

Electrospinning was attempted using the formulations developed for the cathode core containing PVA polymer and the zirconium precursor shell material in PVP. Core shell electrospinning requires the nesting of one capillary within another larger capillary, and applying the electric field to the entire assembly, which can be performed by connection to just the outside shell capillary. A photo of the method used here is presented in Figure 22. A T junction is fitted with connections to allow for the passage of HPLC tubing through the horizontal top of the T, and for non-conductive tubing connection through the vertical axis of the T in which the shell material is pumped. The HPLC tubing is passed through a stainless steel flat tip needle (EFD Corporation) to create the core-shell extrusion passageway. (The photo shows the HPLC tubing extended far from the tip for illustrative purposes. In practice, the core is flush with the shell opening.) Individually controlled syringe pumps control flow rate of the core and shell polymer solutions to the jet creation zone. In this way, concentric flow of each material can be realized.

In testing this setup, it became apparent that the formulations made to this point were not likely to be successful in the electrospinning process. A rule learned from this method is that the solvent-polymer used in each system must be compatible. That is, the solvent in the shell must not destabilize the polymer in the core, and vice versa. Polyvinyl alcohol is not soluble in ethanol or other alcohols, which caused gelation upon mixing the two fluids at the tip of the needle. The gelled region stops the jet formation, which requires low viscosity. Formulations allowing for improved concentric flow of the precursors is needed to make this method successful.

Figure 22. Photograph of the core-shell electrospinning setup.

Forcespinning was investigated as an alternative, with the assistance of researchers Yatinkumar Rane and Karen Lozano at the University of Texas-Pan American. With the formulations developed for each core and shell, they developed a core shell forcespinning sample by nesting two syringes in a hand built configuration. A schematic is presented in Figure 23 for the type of setup required. The initial experiments were carried out using outer needle (shell material) of 21 gauge and inner needle (core material) of 30 gauge. At rotational speed of 4000 rpm uniform and even coaxial ultrathin fibers were prepared using Forcespinning. The fibers were then fired at 700 °C for 5 hrs. After the calcination, the fibers retain their morphology perfectly (Figure 24) and in addition with high surface area, fiber diameter in single digit micron scale.

Figure 23. Sketch of Coaxial setup spinneret for ForcespinningTM

Figure 24. Core/shell $\text{LiMn}_2\text{O}_4/\text{ZrO}_2$ ultrathin fibers.

As the image and inset figure show, the smooth shell of the material is morphologically similar to the smooth ZrO_2 fibers made independently by forcespinning. Also, the fibers in this figure all have a gap along the fiber showing the polycrystalline core material, similar to the LMO core fibers. These gaps are noticeable over the entire fiber length in some fashion, and the fibers also

are highly twisted and curving. There are several potential reasons for the conformations of the fibers seen here. One, the alignment of the needles is poorly controlled. Two, the density of the core and shell solutions are unequal, and the inertial forces during casting can lead to non-axial alignment. Third, the shrinkage stress in the fiber resulting from the calcination process can vary between the core and shell; a tensile stress in the shell composition due to contraction at lower temperature would be relieved by gap opening. Greater work is needed in understanding both the mechanical design of the concentric spinning head, as well as control over precursor formulation, including the development of congruent thermal reaction during the calcination process.

Solid Freeform Fabrication of Core-Shell Forcespinning Spinnerette

Efforts were made to develop concentric core-shell production capabilities using stereolithographic printing (Objet 30⁶, VeroWhitePlusFullCure 835 resin). Figure 25 shows the CAD diagram for a two chamber, symmetrical spinning head leading to a single needle capillary (EFD Products). There are dual loading openings allowing for equivalent capacity of spinning fluids (0.8 ml) in either chamber. The Luer lock fittings for the single component forcespinning spinnerette are attached to the ends of the core shell configuration, allowing for attachment of a single capillary. The component is fabricated in two halves, which are bonded together with cyanoacrylate glue to create the final part. A photograph of the components and assembled head is also shown in Figure 25. This design was tested in the forcespinning apparatus (Fiberio Instruments, Cyclone 2000), and the product was calcined and shown in Figure 26.

The result of these tests are mixed fibers of each composition, rather than concentric core-shell material. Clearly, one component of the core shell head preferentially was extruded before the other composition. Factors leading to this are the density and viscosity of each solution. The higher the density, the greater the centrifugal force acting upon the polymer solution. Likewise, a lower the viscosity has lower resistance to fluid transport. Another factor is the cylinder design. The flow pattern to a single needle requires concentric passage of each component. The center region can be envisioned to form a column equal to the diameter of the fluid opening. The shell material will have to wet the walls and deform to fill the chamber around the core. Fluid dynamics modeling of each system would be necessary to determine if a

⁶ Objet Geometries, Inc., 5 Fortune Drive, Billerica, MA 01821 USA

smooth transition could be made all the way to the single capillary head. A more facile route to a core shell design would require the development of a concentric or near concentric needle approach.

Figure 25. 3D Printed Core-shell forcespinning spinnerette, single capillary.

Figure 26. Calcined product of forcespinning tests with single capillary spinnerette.

SECTION 4

In-situ atomic force microscopic investigation of LiMn₂O₄ electrospun fibers

Although LiMn₂O₄ is a promising candidate for widespread use as a cathode in Li ion batteries^{71,72,73,74,75,76}, detrimental surface layers formed due to Mn dissolution and electrolyte oxidation during cycling can reduce its capacity and limit the Li ion transport rate^{77,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96}. X-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and Fourier transform infrared spectroscopy (FTIR) measurements on macroscopic electrodes have identified several possible components of the surface layer, including carbonates, fluorides and oxides^{97,98,99}. Even though these components have been identified, a detailed understanding of the surface layer nucleation and evolution is still lacking. One reason these studies are so challenging is due to the complexity of typical composite electrodes, containing cathode material powder, carbon black and binder.

Electrospinning offers the potential for simple, low-cost, and scalable synthesis of battery cathodes^{23,100,101,102,103,104,105,106,107,108,109,110,111,112,113}. The unique geometry of the fiber web with high surface area and small pore size allows the fabrication of electrodes without the addition of conductive carbon black and binder, as long as there remains an electrical path to the current collector. The nanometer-scale surface roughness of the bare fibers also provides an opportunity to observe the early stages of surface layer growth at small length scales and to gauge its stability during cycling.

In-situ, electrochemical scanning probe microscopy (EC-SPM) has been previously employed to study growth of the solid-electrolyte interphase (SEI) on graphite anodes^{114,115,116} and LiMn₂O₄ thin films¹¹⁷. The ability to control the electrode potential while simultaneously imaging in electrolytes of interest allows a direct measurement of changes in the surface morphology during cycling. In this work, we have used electrochemical atomic force microscopy (EC-AFM) to study surface layer formation on LiMn₂O₄ electrospun fibers. Our results clearly show that the surface layer forms after as few as five potential cycles, while selective dissolution of fiber grains can occur as the number of cycles increases.

The precursors for fiber synthesis were prepared using a sol-gel technique. Manganese acetate tetrahydrate and lithium chloride (Sigma-Aldrich) were dissolved in de-ionized water to obtain a stoichiometric molar ratio of Mn and Li cations²³. Poly-vinyl alcohol at 8 wt % was

added in order increase the viscosity and facilitate the electrospinning process. The solution was loaded into a syringe where the feed rate of was controlled at 1 $\mu\text{l}/\text{min}$. A DC voltage of 13 – 26 kV was applied to the syringe tip, while grounded Au-coated SiO_2/Si wafers were placed 15 cm from the syringe in order to collect the fibers. The substrates containing the fibers were then annealed in air, in a tube furnace, at $10^\circ\text{C}/\text{min}$ to 100°C , held for 1 hr, then the temperature was increased at $10^\circ\text{C}/\text{min}$ to the final temperature, followed by cooling at $\sim 3^\circ\text{C}/\text{min}$.

A variety of characterization techniques were employed in order to optimize annealing parameters to ensure spinel phase formation for in-situ AFM studies. Thermogravimetric analysis (Netzsch) was performed to monitor mass changes during annealing in air. X-ray diffraction (XRD) was used to investigate phase formation as a function of final annealing temperature. Theta two-theta scans were performed using a Philips X-pert MPD diffractometer with Cu $K\alpha$ radiation. Images of the fiber morphology before and after annealing were obtained with an FEI Nova Nano 230 field emission scanning electron microscope (SEM). The structure and morphology of the fiber grains was investigated using transmission electron microscopy (TEM) with a Philips CM30.

All electrochemical measurements were performed in an Ar-filled glovebox with less than 0.1 ppm H_2O and less than 5 ppm O_2 . Current-voltage (CV) characteristics were obtained as a function of scan rate in ethylene carbonate (EC), di-methyl carbonate (DMC) (1:1) 1 M LiPF_6 using an Autolab potentiostat. For these measurements the electrochemical cell consisted of an open teflon cup clamped against the working electrode of LiMn_2O_4 fibers on an Au-coated Si wafer, the reference electrode was a Li-coated Ni wire and the counter-electrode was a Li-coated Pt wire. A Veeco Multimode 8 mounted inside the Ar glovebox was used to perform electrochemical scanning tunneling microscopy (EC-STM) and electrochemical atomic force microscopy (EC-AFM) for in-situ studies of electronic conductivity and surface layer formation resulting from potential cycling at 5 mV/sec in EC:DMC 1:1, 1 M LiPF_6 . The EC-STM measurements used an etched Pt-Ir (80%-20%) tip coated in Apiezon wax to limit the Faradaic current, biased at 200 mV with a tunneling current of 1 nA. The reference and counter electrodes were Li foil cold-worked onto a Ni wire with the same Teflon cup containing the electrolyte as described above. EC-AFM measurements were performed in contact mode using a Au-coated Si cantilever with a force constant of 0.15N/m. In this case the closed cell was made of glass with a Viton o-ring providing the seal to the sample surface. The reference electrode was Li foil cold-

worked onto a Pt wire, while the counter electrode was a bare Pt wire. Electrochemical measurements were performed with the potentiostat supplied by Veeco.

The thermogravimetric analysis of mass changes during annealing are shown in Figure 8. At temperatures below 300 °C, endothermic peaks in the DTA curves indicate the evaporation of water and dehydration of PVA. The exothermic peaks at 250 °C and 325 °C result from the decomposition of manganese acetate and LiCl, while the peaks at 350 °C and above correspond to the decomposition of the PVA backbone and combustion of the decomposition products.¹¹⁸ Above 550 °C, there is no further mass change, indicating the formation of the inorganic oxide, in agreement with Yu et. al.²³

SEM images of the fibers before and after annealing are shown in Figure 27. Prior to annealing, the fibers have an average diameter of 200 nm, while after the oxide phase is formed on annealing above 600 °C, the diameter decreases and is composed of individual grains with sizes ranging from 10 to 100 nm.

Figure 27. (a) SEM image before annealing; (b) after annealing to 700 °C

The XRD theta two-theta scans in Figure 28 as a function of final annealing temperature show that the spinel phase starts to form at 600 °C. As the temperature increases up to 725 °C, the material becomes single phase, with the strongest intensity peaks at the highest temperature indicating an increasing grain size.

Figure 28: X-ray diffraction scans as a function of final annealing temperature

TEM studies at low and high annealing temperatures were used to investigate the fiber structure. Bright field imaging shows the polycrystalline grain structure in Figure 16. Fibers annealed to 600 °C have an average grain size of 25 nm which increases to an average grain size of 50 nm at 725 °C. Selected area diffraction along with the intensity profiles (Figure 29) performed at each temperature show a mixed oxide phase at 600 °C and a pure spinel phase at 725 °C. Fibers annealed at the higher temperatures where single-phase spinel was observed were used for the electrochemical and SPM studies described below.

Figure 29: Selected area diffraction images and line scans for (a) fiber annealed to 600°C; (b) fiber annealed to 725°C

The CV characteristics as a function of scan rate up to 10 mV/sec are shown in Figure 30. The two-step Li (de)intercalation peaks are evident. Higher currents are observed at higher scan rates since the diffusion is limited to the grain surface. A simple coin-cell battery containing a Li foil anode, Celgard 2325 separator, LiMn_2O_4 fibers on carbon-coated Al foil cathode and EC:EMC:1.2M LiPF_6 electrolyte is shown in Figure 31a. The voltage on charging and discharging between 3.0 and 4.1V was measured with a Maccor battery tester while applying constant currents of 2, 40, and 20 μA as shown in Figure 31b. The (dis)charging characteristics show a slope indicative of Li cycling with the decrease in the width of the plateau showing a loss in capacity as is expected for LiMn_2O_4 cathode materials.

Figure 30. Current-Voltage characteristic of fibers as a function of scan rate

Figure 31. (a) photo of coin cell batteries with fiber cathodes; (b) charge-discharge curves for constant current polarization

In-situ STM images of the fibers at the open circuit potential of 3.5V are shown in Figure 32. For SPM studies, a low density of fibers was deposited on the substrate to facilitate imaging. An optical video image of the surface clearly distinguished the individual fibers on the Au substrate and was used to navigate the piezoelectric scanner so the tip would be above a single fiber prior to imaging. Tunneling at the open circuit potential was typically quite stable, confirming the electronic conductivity of each of the grains within the fiber and their connection to the Au substrate. The individual grains along the length of the fiber are apparent and outlined for clarity. Unfortunately, the open cell design for STM imaging allowed a high evaporation rate of the electrolyte, limiting the time available for imaging, so that a thorough characterization following cycling was not possible.

Figure 32. In-situ STM images of fiber at open circuit potential

In order to investigate surface layer formation as a function of cycling, EC-AFM with a sealed cell was employed. The fibers were cycled five times at 5 mV/s between 3.7 V and 4.3 V as shown in Figure 33. The two-step Li (de)intercalation peaks are evident, and the integrated charge for each cycle did not change significantly upon cycling. The in-situ AFM images at the same location on the fiber before and after the five potential cycles are shown in Figure 34. The individual grain diameters are larger following potential cycling. A histogram of grain diameters before and after cycling is shown in Figure 35, where prior to cycling, the average grain diameter was 59 nm, while after cycling it was 72 nm. This increase in grain diameter is consistent with the growth of a surface layer on each individual grain as a result of oxidation and reaction of the electrolyte with the surface. After rinsing with DMC and drying with Ar in the glove-box, dry

imaging of the same area gave the same average grain diameter of 72 nm, as was seen in-situ, indicating that the surface layer is stable.

Figure 33. Five CV cycles at 5 mV/s prior to in-situ AFM imaging

Figure 34. EC-AFM images of fibers before cycling (a,b) and after cycling (c,d)

Figure 35. Histogram showing change in grain diameter from before cycling (blue) to after cycling (red)

The effects of ten potential cycles between 3.1 V and 4.2 V on another fiber sample are shown in Figure 36. The images from the same area of the fiber before and after cycling show that some of the fiber grains have undergone selective dissolution, as is especially evident when comparing Fig., 36c with 35f. This result suggests that the nanometer size grains making up the fibers can contain pre-existing defects that cause them to undergo dissolution upon potential cycling. Although Mn dissolution from LiMn_2O_4 during cycling is well known, the consequences of surface defects on the dissolution rate are currently not well understood.

Figure 36. EC-AFM image before cycling (a-c) and after cycling (d-f) showing selective dissolution of central fiber

Single phase, polycrystalline electrospun fibers of LiMn_2O_4 offer a unique geometry for in-situ scanning probe studies of nanoscale surface changes during potential cycling. EC-STM measurements show that each of the individual grains making up the fiber are electronically conducting and are electrically connected to the Au current collector, so that each grain is expected to (de)intercalate Li. The increase in average grain size after five potential cycles observed by EC-AFM provides the first evidence that the surface layer on LiMn_2O_4 forms during the very early stages of cycling. The selective dissolution of a small population of individual fiber grains, observed after ten potential cycles, indicates that surface defects may control fiber stability and that coatings or electrolyte additives may be required for implementation of LiMn_2O_4 electrospun fibers in battery cathodes.

SECTION 5

Computational studies of electrolyte and electrode degradation of spinel manganese oxide cathodes

Electrolyte oxidative decomposition

Oxidative decomposition of organic electrolytes on cathode surfaces and formation of surface films from electrolyte decomposition products occur as undesirable side reactions during power cycling in lithium ion batteries. This is an area less understood than electrolyte reduction on anode surfaces, especially at the atomic length scale. Electrolyte decomposition products such as LiF, acetone, aldehydes, carbon dioxide, organic radicals, and unidentified polymer, polyether, polycarbonate, and carboxylate species have been reported on the cathode or released as gas in oxidation reactions. One apparent paradox is that such reactions occur despite the fact that the intrinsic oxidation voltages of the key solvent and salt species, such as ethylene carbonate (EC) and PF_6^- , lie outside the normal operating voltages of undoped spinel LiMn_2O_4 oxide cathodes. In Ref. 119 and Fig. 37,¹¹⁹ we propose a resolution to this paradox, showing that the (100) oxide surface actively participates in EC oxidation. The oxide surface is strongly, chemically disrupted as a consequence. In particular, protons transferred from EC fragments to the oxide surface may lead to Mn dissolution (see below).

Figure 37. Both T=0 DFT calculations and finite temperature AIMD potential-of-mean-force simulations show that the spinel (100) surface actively participates in EC oxidation. EC physisorbs on a Mn ion on the surface (panel a), followed by two chemisorption steps, the last of which involves breaking an internal bond (panels b & c). In the final step, oxidation occurs via transfer of two electrons and a proton to the LiMn_2O_4 surface. The proton, now bonded to a surface O atom, may further enhance Mn(II) dissolution. Red, cyan, white, blue, and violet spheres represent O, C, H, Li, and Mn atoms, respectively.

Mn dissolution from the electrode

Introduction The electrode is also degraded by side reactions. After cycling power, spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ exhibits surface morphology changes and loss of Mn ions. It has been widely accepted that Mn(III) ions on spinel electrode surfaces disproportionate into Mn(IV) and Mn(II) via Hunter's reaction. Mn(II) then dissolves into the electrolyte. The presence of acid has been shown to facilitate dissolution and cathode degradation, both experimentally¹²⁰ and theoretically¹²¹. In organic solvents, acid has been speculated to come from reactions between PF_6^- and trace water, or alternatively from organic solvent decomposition products themselves. The identity of the counterion affects the extent of oxide dissolution. The mass loss associated with Mn(II) dissolution from the cathode accounts for a small fraction of the apparent cathode capacity loss. In addition, there is evidence that the emergence of proton-intercalated surface regions or other surface phases, not just the loss of Mn active mass, is involved in degradation of the cathode¹²². Dissolved Mn ions have been shown to diffuse to the anode, degrading the SEI there and weakening anode passivation. Thus, anode and cathode degradation are closely related. Despite these key insights from experimental studies, the free energy changes, activation barriers, specific surface configurations, and reaction pathways associated with Mn(II) dissolution have not been elucidated in organic electrolytes.

The trace water content in organic solvent electrolytes is small – about 10^{-12} M initially. It is therefore likely that some protons originate from the decomposed electrolyte. Within this assumption, the amount of H^+ inside the battery is difficult to gauge. Another explanation of capacity loss, the formation of Mn-deficient phases on the surface of the electrode, more readily lends itself to theoretical studies. The proposed surface oxide films contain no or a vastly reduced amount of Mn(III) and should be less susceptible to further disproportionation reactions and Mn loss¹²². In the last FY of the LDRD, our computational effort has focused on studying the feasibility of the formation of the simple, Mn(IV)-containing, Li_2MnO_3 rock salt compound. The proton inactivation route will be deferred to future studies.

We consider the reduction reaction

The parentheses denote whether the system is a solid or dissolved in EC liquid. The energy cost of the electron under spinel manganese oxide cathode operating conditions can be elucidated from the $\text{Li}^+ (\text{EC}) + \text{e}^- \rightarrow \text{Li}(\text{s})$ reduction half-cell reaction plus 4.0 eV. A more transparent formulation emerges when Eq. 1 is rewritten into a full cell reaction by subtracting the reference half-reaction. This eliminates the excess electron and yields

Alternatively, we could have subtracted from Eq. 1 any other half-cell reduction reaction associated with a reference potential of $X > 0$ volt. The Eq. 2' that is obtained would then become less exothermic by X eV, but a smaller post-processing value of $(4.0 - X)$ eV would need to be added. The final result will be the same, modulo DFT errors in estimating the reaction energies. Henceforth we concentrate on the standard state $\Delta G^{(0)}$ associated with Eq. 2, adding 4.0 eV post-processing to determine whether the reaction can occur during charge/discharge. We focus on bulk thermodynamics, neglecting for the time being interfacial effects and polaron dynamics which determine kinetics and dissolution barriers. We also consider the voltage independent reaction

As we do not have a structure for $\text{Li}_4\text{Mn}_3\text{O}_9$, we approximately rewrite Eq. 3 as

This is useful because the $3\text{Li}_2\text{MnO}_3$ rock salt structure is available.

Method Free energies of the solid state materials in Eq. 1 are approximated by their zero temperature energies and computed using VASP 5.2, with the PBE0 functional, PBE pseudopotentials, 500 eV wavefunction cutoffs, and the “normal precfok” setting. $2 \times 1 \times 2$, $1 \times 1 \times 1$, $8 \times 8 \times 8$, and $4 \times 4 \times 4$ Monkhorst-Pack Brillouin zone samplings are applied for the antiferromagnetic $\text{Li}_8\text{Mn}_{16}\text{O}_{32}$, ferromagnetic $\text{Li}_8\text{Mn}_4\text{O}_{12}$, paramagnetic Li_2 , and Li_2O unit cells. The $C2/m$ Li_2MnO_3 structure is taken from Koyama et al.¹²³.

The free energies of the solvated $\text{Li}^+(\text{EC})$ and $\text{Mn}(\text{II}) (\text{EC})$ species are more intricate; a mixture of g09 and VASP 5.2 calculations are used:

$$\Delta G^{(0)}(\text{Li}^+ (\text{EC})) = E_g(\text{Li}^+) + [E_g(\text{Li}^+\text{EC}_4) - E_g(\text{Li}^+) - 4 E_g(\text{EC})] + \Delta G^{(0)}_{\text{solv}}(\text{Li}^+\text{EC}_4) \quad (\text{Eq. 5})$$

$$\Delta G^{(0)}(\text{Mn}^{2+} (\text{EC})) = E_g(\text{Mn}^{2+}) + [E_g(\text{Mn}^{2+}\text{EC}_6) - E_g(\text{Li}^+) - 6 E_g(\text{EC})] + \Delta G^{(0)}_{\text{solv}}(\text{Mn}^{2+}\text{EC}_6) \quad (\text{Eq. 6})$$

The first term, a “gas phase” bare ion energy contribution (“ E_g ”), is computed using VASP 5.2 at $T=0$ K. The second term can be computed using g09 or VASP. The last quantity contains the net outershell solvation free energy of the Li^+EC_4 or $\text{Mn}^{2+}\text{EC}_6$ complexes with corrections for the 1M concentration standard state and net thermal corrections. It contains the entire net solvation free energy minus the gas phase cluster binding energy (the second term). In this report, both the second and third terms are computed using the g09 code and PBE0/TZVP level of theory, and there is no actual need to split them up (see, however, the next section). By “net contributions” we refer to properties of the ion-EC complex with isolated EC and $\text{Li}^+/\text{Mn(II)}$ contributions subtracted. The outershell electrostatic solvation energies are based on a dielectric continuum approximation and are computed using CHELPG-generated atomic charges.

A specialized free energy theory provides the framework for analyzing solvation in terms of an intermediate local solvation process, as written in Eqs. 5 and 6. Here, the intermediate step is based on the most probable ion-EC clusters occurring in solution (Li^+EC_4 and $\text{Mn}^{2+}\text{EC}_6$), shown in Figure 38. Also, the theoretical framework explicitly includes the experimental density of the EC solution, here incorporated into the net outershell solvation free energy. An advantage of this local free energy theory is that it facilitates using computationally expensive, but highly accurate, electronic structure methods. Susan Rempe’s research group, in collaboration with Lawrence Pratt of Tulane and others, have been pioneers in developing and applying this approach to a variety of solvation problems^{124,125}. In the results reported below, it is assumed that Li^+ exhibits ideal solution behavior (i.e., as though it is at infinite dilution). Taking into account non-ideal solution behavior destabilizes the Li_2MnO_3 rock salt compound by 0.234 eV. The non-ideal behavior is associated with dissolution of Li^+ into an EC solution that contains a background lithium ion concentration of 1 M concentration due to salt (e.g., LiPF_6).

We remove changes in zero point energy computed at $T=0$ K from Eq. 5 and Eq. 6. The energies of the solid state material computed using VASP do not contain ZPE; therefore including g09 ZPE values for solvated ions creates an imbalance. It will be shown that, in Eq. 2 (Eq. 4), the net ZPE for Li^+ and Mn(II) can amount to a sizable 0.224 eV (0.124 eV) that favors (disfavors) Li_2MnO_3 rock salt formation. The overall changes in ZPE mostly arise from the light Li^+ ion and the heavily charged Mn ions vibrating against O atoms in EC or the solid. The assumption here is that they cancel. Some imbalances in $T>0$ K vibrational energies remain in our treatment, but these contributions are much smaller -- less than $k_B T$ (0.026 eV) per degree of

freedom. Future explicit calculation of solid phonon spectra will be useful for validating our treatment of ZPE and vibrational free energies.

Figure 38. Geometries of the Li^+EC_4 and $\text{Mn}^{2+}\text{EC}_6$ clusters, optimized in the gas phase with the g09 suite of programs. Red, grey, white, and purple spheres represent O, C, H, and Li or Mn ions, respectively.

Results Table 2 lists the contributions from the five terms in Eq. 2. From the table, the dissolution reaction Eq. 2 is predicted to be endothermic by 3.57 eV at 4.0 V at standard state (i.e., when all solvated species are at 1.0 M concentration). Under these conditions, Eq. 2 is not favored unless the applied voltage is below 0.43 V, which is far below manganese oxide operating voltages. Note that the VASP energies listed are not absolute or even net cohesive energies. They are the energies of the simulation cell, and omit corrections associated with using the DFT/PBE0 functional in conjunction with PBE pseudopotentials. Such corrections rigorously cancel because of mass balance.

In contrast, Eq. 4, which does not involve reduction, is only endothermic by about 6 $k_{\text{B}}T$. This suggests Mn(II) dissolution can occur, especially because Mn(II) is continuously depleted by reduction at the anode (see the discussion section).

For future reference, Tables 3 and 4 list various contributions to Eq. 5 and Eq. 6, respectively. As in the published literature, the 2nd term in these equations, namely the gas phase binding energy of the first solvation shell cluster, is typically calculated using the Gaussian suite

species	LiMn ₂ O ₄ (s)	Li ⁺ (EC)	Li(s)	Li ₂ MnO ₃ (s)	Mn(II) (EC)	Li ₂ O(s)	Eq. 2	Eq. 4
Contrib.	-80.767	-0.141	-1.935	-57.929	-6.757	-18.880	-0.430	0.152

Table 2. Contributions to Eq. 2 and Eq. 4, in eV. 4.0 eV should be added to the final result in Eq. 2 to reflect the electron cost at the approximate spinel manganese oxide operating voltage.

Eq. 3	1 st term	2 nd term	3 rd term	-ZPE	total
Contrib.	5.188	-5.479	+0.324	-0.174	-0.141

Table 3. Contributions to Eq. 3, in eV. VASP values are energies of the simulation cell.

Eq. 4	1 st term	2 nd term	3 rd term	-ZPE	total
Contrib.	11.388	-16.467	-1.442	-0.236	-6.757

Table 4. Contributions to Eq. 4, in eV. VASP values are energies of the simulation cell.

of programs (or equivalent). However, for Li⁺(EC)₄ and Mn(II)(EC)₆ clusters, we observe some basis set dependence. Even using aug-cc-pvdz with basis set superposition error yields a value that differs from VASP results by -0.040 and +0.105 eV. For consistency, using VASP values throughout appears more reasonable. However, unlike VASP calculations with non-hybrid functionals, we observe a dependence on VASP energy cutoff that is on the order of 0.1 eV per metal ion complex. Systematic studies on this dependence have so far been hindered by memory overload problems in VASP 5.2 calculations, but will be re-examined in the near future.

Different choices of computational protocols, e.g., omitting ZPE in the solid but not liquid phase, or computing the 2nd term using VASP, can yield somewhat different estimates of Eq. 2. The discrepancy can be as large as 1 eV or more, suggesting the results reported herein are somewhat preliminary, and that further studies are needed. However, all calculations indicate that Eq. 2 is substantially endothermic at 4.0 V applied voltage. Eq. 4 is close to thermoneutrality, and the various numerical approximations used will affect the result quantitatively.

Conclusions and Discussions We predict a 3.57 eV standard state endothermicity at 4.0 V applied potential for Eq. 2 and a 0.152 eV for Eq. 4, which is voltage independent (although it

assumes the open circuit voltage of LiMn_2O_4). In battery electrolytes, $[\text{Li}^+]$ is roughly at 1.0 M concentration, i.e., it is almost at standard state. In contrast, dissolved Mn(II) is continuously reduced, plated, and depleted. Hence the thermodynamic driving force for dissolution and formation of the rocksalt phase should be larger than the +3.57 eV value reported in Eq. 2. Even accounting for such concentration effects, however, our predictions for Eq. 2 are consistent with infinitesimally small amount of dissolved $[\text{Mn(II)}]$ in the vicinity of the electrodes. The almost thermoneutral Eq. 4 is much more consistent with the significant Mn loss observed in cycling experiments by the Missert group and others. Note that the voltage-independent solid state version of Hunter's reaction, $2\text{LiMn}_2\text{O}_4 \rightarrow \text{Li}_2\text{O} + \text{MnO} + 3\text{Mn}_2\text{O}_4$, has also been predicted to be thermodynamically unfavorable¹²¹. However, one insight arising from our work is that replacing $\text{Li}_2\text{O} + \text{MnO}$ with the mixed oxide Li_2MnO_3 will substantially reduce the endothermicity.

Other factors may be responsible in Mn(II) dissolution from spinel lithium manganese oxide. Protons have been implicated in previous studies, especially in aqueous solutions. One future approach may be to quantify the amount of proton transfer arising from EC decomposition on LiMn_2O_4 surfaces¹¹⁹. Expanding the models to include counter ions like PF_6^- , which are present at high concentration in the electrolyte, may also lead to strong Mn(II) -anion interactions and help promote Mn(II) dissolution. Other, more complex models of surface oxide films containing Li and Mn(IV) , but no Mn(III) , like $\text{Li}_4\text{Mn}_3\text{O}_8$, will be considered. Currently we have approximated that phase with $3 \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{O}$; the quantitative error made there is currently unknown. These future research directions will apply techniques developed in this report. In that sense, this work lays the foundation for future computational work.

Finally, we have also conducted investigations of the redox potentials of Mn in its various charge states and possible EC reductive decomposition that may accompany solvation of Mn(0) and Mn(I) monoatomic species in EC liquid. These results will be reported elsewhere.

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