Abstract

Increasing the overall efficiency of Li-ion batteries through control of the organization and spatial arrangement of component materials is a promising route for continued improvements in energy and power density. This approach explores particle morphology, electrode thickness, additive content, particle packing and tortuosity, and interfacial connectivity. Particle, electrode, and interface scale phenomena of Li-ion batteries were explored in various Li-ion systems.

 $MnCO_3$ coprecipitation was used as a platform to create shape controlled monodisperse $LiMn_2O_4$ active material. Particle size distributions are among the most monodisperse demonstrated in the literature, and the shape was shown to be independently tunable for large particles. The transition at higher reagent concentrations from rhombohedral crystals to cubes, rough spheres, and progressively smaller, smoother spheres was shown in great visual detail. Unlike similar coprecipitation systems, it was determined that interparticle mass transfers were not significant in affecting particle morphology, and that particle size and shape was controlled by the initial nucleation and growth process.

The interfacial reactivity during heat treatment of two promising materials for all-solidstate batteries, $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) active material and $Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ (LAGP) solid electrolyte, was studied through X-ray diffraction and SEM/EDS. Two products were identified – Li-ion active material LiMnPO₄ (LMP) and GeO₂. LMP was shown to form a continuous interfacial phase at the interface, showing some promise towards generating a Li⁺ conductive connection between LMNO and LAGP. The reaction as-used was not able to create a highperformance connection between electrode and electrolyte, however, likely due to disconnections in the form of void spaces and GeO₂ phases formed near the interface. Highly thick (>500 μ m) and dense (>62 % active) sintered electrodes which replace inactive additives with high temperature processing to form electronically conductive and mechanically robust interparticle bonds were investigated. Novel Li₄Ti₅O₁₂/LiCoO₂ full cell arrangements with high areal capacities were assembled and electrochemically characterized. The full cells were observed not to have the capacity fade issues seen in sintered electrode half cells. The full cells also have very good areal rate performance and capacities. A 2032 coin cell prototype using super thick electrodes with combined thickness 2.90 mm was shown to outperform commercial rechargeable 2032 cells in terms of energy and power.

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Chapter 1

Introduction

1.1 Motivation

Climate change caused by anthropogenic greenhouse gas emissions is a tremendous threat to human safety and prosperity.¹ Avoiding the most catastrophic impacts and restricting global average temperature change to 2°C will require immediate and steady reductions in greenhouse gas emissions, down to net-zero emissions during this century.² Meeting these goals will require a rapid shift in the global energy paradigm away from extraction and combustion of fossil fuels towards renewable forms of energy generation and transport.³ The development of inexpensive means of storing and transporting electricity generated by intermittent renewables is central to this overall shift. Thus energy applications such as grid storage and electric vehicles represent some of the most significant future applications of batteries.^{4,5}

Although existing in the modern form since the early 1990s, lithium-ion (Li-ion) batteries have continued to undergo steady, decade-over-decade growth in general performance, with a finite yet substantial capacity for further practical improvement.⁶ While development and modification of Li-ion material chemistries as well as chemical paradigms beyond Li-ion are major areas of research, a complementary approach to these methods is the control and understanding of electrode morphology.^{7–10} Electrode morphology depends on particle morphology,^{11,12} particle packing and arrangement,¹³ film thickness,^{14,15} interfacial

connectivity,¹⁶ and many other factors.¹⁷ Through this approach, this work contributes towards an understanding of these factors and how they may be tuned to create higher-performing batteries to address the energy needs of the 21st century.

1.2 Battery Fundamentals

Batteries consist of the following components: an anode which is oxidized during discharge, a cathode which is reduced during discharge, an electrolyte acting as a transfer medium for ions between anode and cathode, a separator which prevents direct contact and shorting between anode and cathode, and a current collector and external circuit acting as a transfer medium for electrons between anode and cathode. Figure 1.1 is a basic schematic of a Li-ion cell.



Figure 1.1. Li-ion electrochemical cell with a lithium metal oxide cathode and a carbon anode.¹⁸

Li-ion active materials, such as the carbon anode and lithium metal oxide cathode shown in Figure 1.1, have porous crystals that are able to reversibly intercalate and deintercalate Li^+ ions in and out of the structure during a charge or discharge cycle.³ During a discharge, the carbon deintercalates lithium ions, which travel initially out of the solid carbon particle, through the porous anode structure, across the separator, into the porous cathode, and finally into the metal oxide particle. Concurrently, electrons flow from anode to cathode through the metal current collector, generating an electric current that can be used to perform work. A cell with a lithium cobalt oxide, $LiCoO_2$ (LCO) cathode and a graphite anode would have the following reactions with discharge being shown as the forward direction:

Anode:
$$LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$$

$$Cathode: CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$$

The amount of energy stored by a battery is the product of two factors: capacity and voltage. Capacity refers to the quantity of charge transferred during a single charge or discharge cycle. Cell voltage is based on the difference in the redox potential of the electrochemical reactions in the anode and cathode material. Cycling data is most often expressed in the form of a voltage profile, an example of which is shown in Figure 1.2.



Figure 1.2. Voltage profile of one charge cycle and one discharge cycle of a Li/LCO half cell with a lithium metal anode and LCO cathode cycled at a constant current within a voltage window of 2.5 to 4.3 V.

The cell configuration in Figure 1.2 with one intercalation compound as a cathode and a lithium metal anode is commonly used for materials testing and is referred to as a half cell. Correspondingly, cells with two intercalation compounds are referred to as full cells. The increasing line in Figure 1.2 is the charge profile and the decreasing line is the discharge profile.

Capacity is often expressed in terms of how much charge a material is able to transfer per unit mass. For example, LCO has a theoretical capacity of 150 mAh/g when charged up to a potential of 4.3 V vs. Li/Li⁺. Operation of batteries at high rates (high magnitudes of current) typically results in reduced performance above a threshold determined by the kinetic parameters of the cell. Most commonly, rates are expressed on a gravimetric basis as C rates. A rate of 1C would correspond to a current sufficient to charge or discharge the cell in one hour. Therefore a rate of C/20 would correspond to a rate sufficient to charge or discharge the cell in twenty hours. A Li/LCO cell is shown discharging at various rates in Figure 1.3.



Figure 1.3. Discharge profiles Li/LCO half cell cycled at rates of C/20, C/5, and C within a voltage window of 2.5 to 4.3 V.

Cycling batteries at higher rates can reduce the performance of the cell as seen in Figure 1.3. This manifests as some combination of reduced capacity and higher polarization, the difference between the standard redox potential of the electrochemical reactions and the measured cell voltage due to kinetic factors. The general ability of a battery to maintain its ideal voltage and capacity at a high rate of charge or discharge is known as rate capability. Transport processes

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limiting the rate capability of batteries include the reaction rates of Li^+ intercalation and deintercalation at the active material interface (referred to as charge transfer reactions), Li^+ diffusion between sites within solid particles, Li^+ diffusion through the liquid electrolyte, and electronic transport through the electrodes.

1.3 Structure of Li-ion electrodes

1.3.1 Li-ion Electrode Structure and Assembly

Conventional Li-ion electrodes are composite materials consisting of a mixture of active material particles mixed with small quantities of conductive additive and polymeric binder to impart electronic conductivity and mechanical strength, respectively. The separator and any pore space within the electrodes are immersed in and wetted with a liquid electrolyte. Figure 1.4 shows the general arrangement of these components within a half cell configuration:



Figure 1.4. Diagram of Li-ion half cell with lithium metal anode and composite cathode. The cathode is comprised of relatively large active material particles mixed with small conductive additive particles and binder (not shown). Lithium and electron transport paths through the cell are shown as red and yellow lines.

In Figure 1.4, Li^+ is being electrochemically stripped from the lithium metal anode into the electrolyte, diffusing through the porous separator, then through the pore space within the electrode to the surface of an active material particle, and intercalating into the surface. Within the particle, lithium ions are redistributed through a process of solid diffusion between sites. Electrons flow through the external circuit, and through some combination of the conductive additive and active material to the active material's surface. The most typical limitations for composite electrodes are Li⁺ diffusion through the solid particle or through the porous electrolyte medium filling the electrodes and separator.¹⁹

Forming composite electrodes involves mixing the components into a slurry and casting them onto a sheet of current collector foil, then calendaring (compressing by passing through rollers) to increase packing density.²⁰ A scanning electron microscope (SEM) image of an uncompressed conventional Li-ion cathode with $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) active material is shown in cross section in Figure 1.5.



Figure 1.5. Micrograph of composite NMC cathode containing large NMC particles surrounded by small carbon particles and binder. It is shown in cross section with the current collector foil visible near the bottom of the image.²¹

The electrode shown in Figure 1.5 is typical for a commercial electrode in terms of thickness (70 μ m), large and dense particles (up to 25 μ m) and fraction of inactive conductive and

polymeric additives (5 wt%). Large particles, which have lower surface energies relative to their mass, are desired for their packing density in the initial casting step.²² The thickness of commercial electrodes varies by application, but is generally in the range of 50-100 μ m.^{5,14} Fractions of inactive material vary widely in both academic and commercial Li-ion cells. Electrodes made in an academic setting often have 20 wt% or more total additive content, while commercial cathodes can have additive contents as low as ~4%.^{5,23} It is worth noting that the volume fraction occupied by these components is higher than the weight fraction, since they are less dense than the active material. While these additives directly occlude space that could contain active material, the additives do impart sufficient elasticity to the electrodes to allow calendaring.

1.3.2 Design of Li-ion electrodes for High Energy Density

A major goal in most Li-ion battery research and design is to attain high energy density in terms of both weight and volume.¹⁵ This can generally be approached through active material selection, active material assembly into electrodes, electrode winding and assembly into cells, and the design of battery packs consisting of many cells. Most relevant to this work are the particle to electrode and electrode to cell levels of organization as shown in Figure 1.6 with the example of a cylindrical cell.



Figure 1.6. Organization of Li-ion active material particles into electrodes and cells. Energy density decreases with each step of higher organization. Cylindrical cell image from Panasonic Li-ion handbook.²⁴

Obtaining high energy density on the electrode level is done through achieving a high fraction of active material.²⁵ This can be accomplished through limiting the fraction of the electrode allocated to inactive carbon and polymer additives and calendaring to densify the electrode and reduce space allocated to the electrolyte. Although material and application dependent, commercial cells can obtain an active fraction of up to approximately 60% of the electrode volume, near the limits of random close packing for hard spherical particles.^{15,17,26}

Assembly of battery electrodes into cells results in a large proportion of mass and volume devoted to inactive support components including the current collectors, separators, gaskets, and casing all of which ultimately limit energy density on the cell level.^{15,17,27} The fraction of current collectors and separators in the electrode stack are a function of electrode thickness, as illustrated in Figure 1.7 with two hypothetical cell stacks – one with relatively thin 50 μ m electrodes and another with very thick 200 μ m electrodes.



Figure 1.7. Effect of electrode thickness on relative fraction of current collectors and separators at the cell level between 50 μ m electrodes (left) and 200 μ m electrodes (right). The cathode current collector (aluminum) and anode current collector (copper) were assumed to be 10 μ m thick, and the separator was assumed to be 25 μ m thick.

In the most energy dense configuration shown in Figure 1.7, current collectors are coated on both sides with electrodes. The cell stack with 50 μ m electrodes has 26% of its volume allocated to current collectors and separators, while the cell stack with 200 μ m electrodes has only 8% allocated to these components resulting in a 24% higher volumetric energy density on the stack level. Thus, using higher electrode thicknesses increases the energy density of Li-ion cells by allocating a higher proportion of the cell components to active material.

Thickness is also limited by processing. In cylindrical or prismatic cells, electrodes must reliably withstand winding radii of ~1mm at the center of the cell.¹⁴ Very thick electrodes are less likely to survive the stresses of high throughput industrial processing and winding into cells without cracking or becoming delaminated from the electrode.²⁸ Another issue is undesireable heterogeneity of additive content throughout the thickness of the electrode, which is exacerbated by high thickness.²⁹

1.4 Power Limitations in Li-ion Batteries

1.4.1 Particle Scale Power Limitations

The power capability of Li-ion electrodes is often limited by factors on the particle level.¹² Kinetic limitations on the particle level can generally be categorized as being related to either charge transfer at the interface or solid diffusion within the particle. While material choice obviously affects these properties, particle morphology also has a strong effect. Figure 1.8 demonstrates the spatial pattern of reaction for an electrode during cycling where charge transfer and/or solid diffusion are controlling the overall process.



Figure 1.8. Diagram of Li-ion half cell with lithium metal anode and composite cathode shown mid-cycle where cycling performance is being controlled by charge transfer or diffusion within the particle.

In Figure 1.8, the small and less spherical particles have fully reacted, while large highly spherical particles have reacted only partially. In the case of solid diffusion limitations the deepest interior regions of the particles have not been accessed, leading to a core-shell arrangement with reacted material near the exterior of the particle and unreacted material on the interior. At high rates, this interior material will be inaccessible and will manifest as reduced capacity. Smaller particles have shorter interior diffusion paths in general, and nonspherical particles have short dimensions through which faster diffusion to and from the interior of the particle can take place.

In the case of charge transfer limitations at the surface, particles with the highest surface area to volume ratios – those with smaller sizes as well as less spherical shape, will react at

relatively faster rates than particles with lower relative surface areas. In this case, lithium may be evenly distributed throughout sites within the largest particles. At high rates, a higher overpotential will be needed to overcome the high charge transfer resistance associated with a low surface area, and a higher polarization will be observed.

In the current paradigm of battery manufacturing, particles that are large and more spherical are desired for high energy density,²² while smaller and less spherical particles are desired for high power.¹⁹ Because of these inherent compromises between energy and power, it is beneficial to understand the magnitude of these effects, as well as to have the synthetic capability to manufacture particles of optimized size and shape for a given application.¹² Development of this synthetic capability is the motivation behind the work in Chapter 2.

1.4.2 Electrode Scale Power Limitations

Power is also limited by transport of lithium ions and electrons through the thickness of the electrode. These transport limitations are primarily related to electrode thickness, packing density, tortuosity, and additive content. Figure 1.9 demonstrates the pattern of reaction for an electrode during cycling where lithium diffusion in the liquid electrolyte is controlling the overall rate.



Figure 1.9. Diagram of Li-ion half cell with lithium metal anode and composite cathode shown mid-cycle where cycling performance is being controlled by lithium diffusion through the electrolyte.

In the limiting case shown in Figure 1.9, particles on the separator side of the cell have reacted fully. Particles near the current collector, subject to the longest Li^+ path length, have not reacted. At high rates, diffusion of Li^+ will not be fast enough to access this material, resulting in capacity loss. Calendaring to increase active fraction and decrease porosity directly reduces the volume of electrolyte available to conduct lithium, and further increases tortuosity which substantially increases the effective path length of Li^+ in the electrolyte necessitating a thinner electrode for adequate rate capability.³⁰ Tortuosity in this case includes factors such as indirect pathing around solid particles, varying cross sectional areas in the pores, and disconnected pore structures.³¹ Tortuosity also increases quickly when calendaring to very low porosities, making <25% porosity difficult to attain with reasonable rate capability.^{32,33}



The electron transport limited case is shown in Figure 1.10.



In Figure 1.10, particles near the current collector have reacted fully, while particles closest to the separator have not reacted. At high rates, the cell polarization will be higher due to the high electronic resistance associated with transferring high quantities of current through the ceramic active materials. Contrasting with Li⁺ transport in the electrolyte, a high overall solid content improves electronic conductivity by increasing contact between the solid carbon additives and active material. To make the scenario in Figure 1.10 more realistic, the pictured electrode contains no additives, which is the case for the sintered electrodes developed through the work in Chapter 4. Since sintered electrodes contain no additives, have high fractions of active material, and are generally prepared with a high thickness, both long-distance electronic and ionic transport are likely to have a significant effect on the rate capability of that system.³⁰

1.4.3 Interfacial Contact in All-Solid-State Li-ion Batteries

Typical lithium ion electrolytes consist of lithium salts with bulky non-intercalating anions, such as LiPF₆ in an organic solvent e.g. ethyl carbonate. Organic solvents are used due to their high electrochemical stability, which allow Li-ion batteries to realize very high cell voltages of >4 V.³⁴ However, there are some compromises that come with organic electrolytes. This high electrochemical stability relies to some degree on the irreversible formation of a passivating layer of byproducts known as the solid-electrolyte interphase (SEI). Over time, the continued growth of this layer consumes electrolyte and lithium within the cell, causing capacity loss.³⁵ Organic electrolytes are toxic and flammable,³⁶ creating major safety risks. Safety equipment such as temperature control systems and mechanical shielding is often required for large battery packs, resulting in added mass and volume at the pack level.²⁷

All-solid-state batteries represent an alternative paradigm to organic electrolyte cells through the use of highly conductive solid electrolytes such as Li_{1.4}Al_{0.4}Ge_{1.6}(PO₄)₃ (LAGP).³⁷ They are typically nonflammable and thus completely safe, and in some cases have greater electrochemical stability than organic electrolytes, allowing the use of even higher voltage cathode materials such as LiMn_{1.5}Ni_{0.5}O₄ (LMNO) spinel with a redox potential of 4.7 V vs. Li/Li⁺.¹⁶ Solid electrolytes typically have lower bulk diffusion rates than liquid electrolytes; however, this is usually not as great an issue as forming lithium conducting contacts between the electrolyte and active material phases, of which both are often hard ceramic materials.^{38,39} One approach is high-temperature reaction of compatible materials to form a conductive interface; this is the motivation for the work in Chapter 3.

1.5 Objectives

This dissertation explores multiple Li-ion battery systems focusing on the particle, electrode, and interfacial levels of transport that limit the performance of current Li-ion chemistries. While the system involved has varied, the framework with which these problems have been addressed has remained consistent in that it takes a morphological approach towards addressing transport limitations in Li-ion batteries. Each chapter provides insight into active fields of study within Li-ion battery engineering:

- Chapter 2 elucidates the relationship of reagent concentration and various nucleation and growth regimes leading to shape-controlled morphologies of highly monodisperse MnCO₃, which can be calcined to form LiMn₂O₄ while maintaining precursor shape. This is an example of developing fine control of particle morphology, and this work resulted in a publication in Powder Technology.
- Chapter 3 investigates the reactivity of two materials of common interest for all-solidstate batteries, LMNO and LAGP, and determines the product composition as well as the morphology of the interface formed between these materials. This is an example of a system controlled by limited by interfacial contact between solid phases, and this work resulted in a publication in the Journal of the American Ceramic Society.
- Chapter 4 describes the novel assembly of sintered electrode full cells with extremely high areal capacities and provides practical insights on the challenges in characterizing the rate capability of these electrodes. This is an example of a system controlled by electrode-level transport limitations and this work has been submitted for peer review.

By addressing these questions, this work contributes towards the development of Li-ion batteries that perform more closely to their full theoretical potential in terms of energy density, power density, and safety.

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Chapter 2

Tuning Solution Chemistry for Morphology Control of Lithium-Ion Battery Precursor Particles

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Abstract

Many battery materials are synthesized via calcination of precursor particle powders with a lithium source. The precursor particles frequently are made via coprecipitation reactions and a number of combinations of coprecipitation agents have been demonstrated previously. Detailed control over the morphology of precursor particles and the resulting final electrode materials would be highly desirable, but currently detailed understanding of the impact of synthesis conditions on precursor morphology are lacking. Herein, tunable monodisperse MnCO₃ particles for Li-ion battery precursors of varying size and shape were synthesized through batch coprecipitation. The effect of solution chemistry on final particle morphology was confirmed via scanning electron microscopy and considered in the context of solution equilibrium calculations and nucleation and growth of precipitate crystals. The tunability of MnCO₃ particle morphology with reagent concentration was demonstrated with transitions from rhombohedra to cubes to spheres to smaller spheres with regards to overall secondary particle structures. Other experimental factors were also examined to further understand the processes resulting in the

transitions in $MnCO_3$ morphology. Precursor particles were calcined to form $LiMn_2O_4$ to verify the ability to maintain the tunable morphology in the final battery materials and to confirm suitability for battery cathodes.

2.1 Introduction

Lithium-ion batteries have become the dominant technology for consumer electronics applications and are increasingly being developed for larger-scale applications such as electric vehicle batteries and stationary energy storage.¹ While historically battery progress has largely been tracked by adoption of chemistries and materials structures with higher energy densities,^{2,3,4} another important factor in battery performance is the morphology of the electrochemically active particles within the battery electrode as well as their organization and distribution within the composite structure. For example, the battery materials literature is full of the synthesis and characterization of materials with a wide variety of particle shapes and sizes, including rods,⁵⁶ cubes,⁷ spheres,^{8,9} urchins,¹⁰ plates,¹¹ and many others.^{12,13,14,15} In some cases, the morphology serves to provide preferential diffusion paths for lithium or conduction paths for electrons that improve rate capability or energy density of the battery material.¹¹ In other reports, the morphology is taken advantage of to organize the overall electrode structure to accommodate improvements in lithium-ion diffusion in and out of the electrode as a whole.¹⁶ One of the key factors in being able to take advantage of active particle morphology-dependent improvements in battery electrode performance is that the electrode particle morphology must be well-controlled.¹⁷ Thus, underlying mechanisms that result in the final particle morphology with regards to size, shape, porosity, surface roughness, and polydispersity are important to engineering particles for

battery electrodes. In addition, tunability of one or more of these morphology metrics would also be desirable. The study described herein focuses on efforts to control particle morphology in a battery electrode precursor particle system.

The chemistry employed to synthesize precursor particles in this study was coprecipitation of Mn^{2+} with carbonate salts to form MnCO₃. Coprecipitation was chosen as a method because it is highly tunable and easily scalable for particle synthesis,^{9,18,19,20,21,22} and MnCO₃ was chosen as a target precursor chemistry because it can be calcined with a lithium source to form the final battery material LiMn₂O₄.²³ Given the relatively lower complexity of only having one transition metal involved in the coprecipitation synthesis and the availability of data on LiMn₂O₄ in the battery literature,^{24,25,26,27} MnCO₃ serves as a model system for precursor morphology tunability. A number of reports have previously been published in the literature on synthesis of transition metal carbonates, including MnCO₃, and a variety of particle morphologies that may be achieved.^{13,28,29,30,31} Notably, the most commonly reported morphology for transition metal carbonates used for battery material templates is approximately spherical and has relatively high polydispersity.^{13,32,33} The extent of the tunability of the morphologies and polydispersity of transition metal carbonate template particles, however, is currently unknown. The ability to be predictive in the resultant morphology of these particles would in principle enable detailed studies of the influence of particle morphologies on lithiumion battery performance.

In general, the morphology of particles generated from coprecipitation reactions can be influenced by a variety of factors, including reagent concentrations, nucleation and growth rates, ripening, collisions with reactor walls and other particles, temperature, and chemical modifiers including chelating agents.^{18,34,19} Due to the high level of complexity for consideration of all of these factors, we have focused our initial study on the influence of solution chemistry on particle morphology. In this paper, we will demonstrate a variety of particle morphologies that are accessible via relatively modest changes in coprecipitation solution chemistry. These morphologies are likely not driven by ripening processes that have been demonstrated to influence morphologies for other coprecipitation processes for battery particles previously reported in the literature for hydroxide synthesis³⁴. The conversion of our precursor particles to lithiated battery electrode active materials was also performed to demonstrate that the tunable morphologies can be retained in the resulting final electrode materials. While our solution chemistry approach is an initial report of understanding the morphology tunability of this battery precursor system, we speculate a wide design space of size, shape, and surface roughness control will be accessible via detailed study of this synthesis platform.

2.2 Experimental

2.2.1 Preparation of MnCO₃ and LiMn₂O₄ Particles

MnCO₃ particles were prepared as follows: 1200 mL of 1.5-240 mM NH₄HCO₃ (Fischer) in deionized (DI) water was poured all at once into 1200 mL of 1.5-12 mM MnSO₄·H₂O (Fischer) in DI water solution in a 4 L beaker. Solutions were preheated to 50 °C prior to mixing and the temperature was maintained at 50 °C for the duration of the synthesis. The solution was stirred gently with an impeller at 500 rpm to prevent particle settling in solution and MnCO₃ particles were precipitated for 0.5 h. All syntheses were

done at a pH of ~7.5. Vacuum filtration was used to collect the particles, and the particle cake was rinsed with 2 L DI water before being vacuum dried at 80 °C overnight. MnCO₃ particles were converted to LiMn₂O₄ particles through calcination after mixing stoichiometric quantities of LiOH in a Carbolite CWF 1300 box furnace in an air atmosphere at 800 °C for 5 h.

2.2.2 Material Characterization

Powder X-ray diffraction was performed with a PANalytical X'Pert Pro MPD using CuKα radiation. Scanning electron microscopy (SEM) with an FEI Quanta 650 SEM was used to image all samples. Particle size distributions were obtained by analysis of SEM images with the program ImageJ³⁵.

2.2.3 Electrochemical Characterization

Electrochemical analysis was done using CR2032 coin cells with lithium metal anodes and cathodes containing the synthesized LiMn_2O_4 active material. The LiMn_2O_4 containing cathode was prepared by coating a slurry comprised of LiMn_2O_4 active material, carbon black conductive additive, and polyvinylidene diflouride binder in a weight ratio of 80:10:10 onto an aluminum current collector. The electrode slurry was dried in an 80 °C oven overnight and dried in an 80 °C vacuum oven for 3 h prior to punching out 14 mm electrode disks. The electrolyte used was 1.2 M LiPF₆ dissolved in a solution containing 3:7 ethylene carbonate:ethyl methyl carbonate. Cells were cycled between a voltage window of 3.4 to 4.2 V vs Li/Li⁺ using a MACCOR battery tester.
2.3 Results and Discussion

In this study we specifically focused on the influence of solution chemistry on $MnCO_3$ particle morphology. We designed our experiments to systematically vary both the total Mn^{2+} initially in solution (via total amount of $MnSO_4$ salt originally dissolved in DI water) as well as the ratio of the dissolved transition metal to the coprecipitation agent. In our case, coprecipitation was facilitated by the CO_3^{2-} from dissolved NH_4HCO_3 . A representative example of the dramatic changes in $MnCO_3$ particle morphology facilitated by changes in total initial Mn^{2+} concentration (with constant NH_4HCO_3 : $MnSO_4$ ratio of 40:1) can be found in the SEMs in Figure 2.1.



Figure 2.1. SEM images of MnCO₃ particles prepared with a 40:1 ratio of NH₄HCO₃ to MnSO₄ and ascending concentration of MnSO₄: (A) 1.5 mM MnSO₄, (B) 3 mM MnSO₄, (C) 4.5 mM MnSO₄, (D) 6 mM MnSO₄, (E) 7.5 mM MnSO₄, (F) 9 mM MnSO₄, (G) 10.5 mM MnSO₄. The particles from the 12 mM synthesis were not recoverable. Scale bars correspond to 20 μ m. (H) Illustration of general shape and size transition of MnCO₃ at progressively higher concentration.

At the lowest initial Mn^{2+} concentration (1.5 mM), particles were relatively large at just under 10 µm in average length of a particle side (Figure 2.1A). The particle surfaces appeared smooth and the overall shape was rhombohedral, with the wide angle measured to

be ~103° from SEM images. It should be noted that this was similar to the rhombohedral angles reported for single $MnCO_3$ crystals³⁶. We also note that these particles have a large degree of clustering relative to others from the synthesis series shown in Figure 2.1, with particles often fused together. A slight increase in concentration from 1.5 to 3 mM initial Mn^{2+} resulted in a transition from a rhombohedral morphology to a cubical morphology (Figure 2.1B). The cubical particles were approximately the same size and the surfaces were smooth, however all angles on the particles were now $\sim 90^{\circ}$ and it was rare to find the cubical particles attached or clustered together. An increase in Mn²⁺ concentration to 4.5 mM resulted in particles that are in a transition region between cubical and spherical particles (Figure 2.1C). The average particle size (an approximate diameter assuming they were spherical) is not significantly different from the rhombohedra or cubes, however, there were many edges and corners on the surfaces of the particles and there was a flaky, layered appearance to the surface resulting in a large degree of surface roughness. There was no longer an obvious 8 sharp corners on the particle surface. At 6 mM Mn²⁺, the resulting particles have transitioned to an approximately spherical morphology (Figure 2.1D). The diameters of the spherical particles were on approximately the same length scale as the particle length/diameters of the previously collected particles at lower Mn²⁺ concentrations. It was clear the overall spherical secondary particle morphology consisted of aggregates of smaller faceted particles that can be seen at the surfaces of the particles. A further increase in Mn^{2+} initial concentration to 7.5 mM resulted in spherical particles as well (Figure 2.1E). These particles were also clearly made up of smaller primary particle aggregates that have agglomerated into a secondary structure that was approximately spherical. Relative to the spherical particles at the slightly lower Mn²⁺ concentration (Figure 2.1D), the average particle size has dropped significantly with the diameters decreasing by almost a factor of 4 (Figure 2.1E). Subsequent increases in initial Mn^{2+} concentration to 9 mM (Figure 2.1F) and 10.5 mM (Figure 2.1G) resulted in particle morphologies that were approximately spherical and similar to those found at 7.5 mM (Figure 2.1E), although as the Mn^{2+} concentration was increased the average diameter of the particles decreased slightly. We note that a final synthesis was done at 12 mM initial Mn^{2+} concentration; however, the particles were not recoverable for SEM characterization. A cartoon illustrating the transition from rhombohedral to cubical to transitionary cubical/spherical to spherical to decreasing diameter spherical is shown in Figure 2.1H to highlight the morphology changes from Figures 2.1A-G.

To gain further insights into the influence of reagent concentrations and solution chemistry on final MnCO₃ precipitate particle morpohology, a series of experiments were conducted where the same sequence of increasing Mn^{2+} concentrations was used as described earlier (1.5 to 12 mM in 1.5 mM increments, as used in Figure 2.1), however, the NH₄HCO₃:MnSO₄ ratio was varied as well with ratios of 10:1, 5:1, and 1:1 in addition to the 40:1 sequence described above. The detailed SEMs of the resulting particle morphologies can be found in the Supplemental Material in Figure A.1 (10:1 reagent ratio), Figure A.2 (5:1 reagent ratio), and Figure A.3 (1:1 reagent ratio). The morphologies observed are summarized in the illustration in Figure 2.2A.



Figure 2.2. (A) Ilustrations of morphology of MnCO₃ particles at prescribed synthesis conditions. Squares represent primarily rhombohedral or cubical particles, jagged squares represent cubical/spherical transitional particles, circles represent primarily spherical particles, and small circles represent small spherical particles. Blank locations denote conditions where particles were not recoverable. (B) Volume weighted average particle size (characteristic length defined in text) at prescribed synthesis conditions. Standard deviations of particle sizes can be found in Supplemental Material Figure A.4.

At all NH₄HCO₃:MnSO₄ ratios the general trend for change in morphology was the same, where for increasing Mn^{2+} concentrations the particles transitioned from rhombohedral and/or cubical morphologies to a cubical/spherical transitional morphology to large spherical particles to decreasing sizes of spherical particles. Also, as the NH₄HCO₃:MnSO₄ ratio decreased, the location of the cubical-to-spherical transition moved to higher initial Mn²⁺ reagent concentrations. At the lower NH₄HCO₃:MnSO₄ ratios, samples

with the lowest concentrations of initial Mn^{2+} were unrecoverable likely due to the small amount of precipitate formed.

Figure 2.2B displays the average particle size at the variety of synthesis conditions explored. Size was defined as the characteristic length of the particles (edge length for cubical or rhombohedral particles and diameter for transitional particles and spherical particles). The results displayed in Figure 2.2 demonstrate the diversity of particle morphologies and sizes that were accessible from the solution chemistry conditions investigated. The size range for smooth cubical/rhombohedral particles was 6-12 μ m. Transitional cubical/spherical rough particles ranged in size from 8-12 μ m. Spheres were synthesized in sizes ranging from 1-15 μ m. We note that the polydispersity of these particles was very low compared to coprecipitation battery precursor synthesis typically reported in the literature, ^{13,32,33} with many of our synthesized particle population polydispersities <10% (see Supplemental Material Figure A.4 for polydispersity of all reported samples).

The morphology transitions observed in our solution synthesis were consistent with tuning the nucleation and growth of the MnCO₃ particles within the range of concentrations explored. At the lowest Mn^{2+} concentrations, the synthesis had the longest inoculation times (inoculation time being the time elapsed between mixing and visible precipitation in the beaker) indicating a slow growth of the precipitates. In this slow growth limit particles also had sharp angles that deviated from the 90° degree cubical particles and began to approach the wide rhombohedral angle of rhodochrosite (MnCO₃), which has been reported as 103° .³⁶ The slow growth of the particles and angles of the particles observed being around 103° was

consistent with the particles approaching the single crystal limit of $MnCO_3$ (Figure 2.1A), thus it was likely that these particles were single rhodochrosite crystals. At increasing Mn^{2+} concentrations, inoculation times were always observed to decrease. The decreased inoculation time would result in more small nuclei precipitates being formed. At the highest Mn^{2+} concentrations, this would be consistent with the decrease in spherical particle size observed for increasing Mn^{2+} concentrations (Figures 2.1D-G). With more nuclei being produced because of the high initial precipitate reagent concentration, there was less reagent available for growth on a per particle basis and thus the final resulting particles were smaller for higher reagent concentrations. Correlations between higher nuclei density and smaller final particle populations have previously been reported for MnCO₃ synthesis.³⁰ It is important to note, however, that our spherical particles were agglomerates of these smaller nuclei. The transitional particles were an intermediate zone between the slow growth rhombohedral/cubical particles and the agglomerated small nuclei spherical particles. We speculate the substantial roughness at the surface is due to the agglomeration of partially formed slower-growing particles. Also of note was that an increase in NH₄HCO₃:MnSO₄ ratio decreases inoculation time and shifts the particle morphology transitions to lower Mn²⁺ concentrations. This is also consistent with the interplay between the number of nuclei formed as the solubility of $MnCO_3$ is dependent on both the Mn^{2+} concentration and the CO₃²⁻ concentration, thus increasing the relative NH₄HCO₃:MnSO₄ ratio increases the nucleation rate by driving precipitation forward faster.

It is important to understand the morphologies we have reported in the context of typical carbonate battery precursors reported in the literature. First, all of our synthesis was at relatively low concentrations specifically such that we could assess the interplay between solution chemistry and morphology by accessing these different nucleation and growth regimes. While our synthesis does not exceed 12 mM Mn²⁺ concentration, 2 M concentrations of Mn²⁺ and other transition metal ions are not uncommon for carbonate battery precursors in the literature¹⁹. Our low concentrations allow us to access the diversity of morphologies reported, and also enable us to generate particle populations with relatively low polydispersity. Another important consideration in precursor synthesis that we were not explicitly investigating in this study was stir rate. Multiple coprecipitation battery precursor studies in the literature have investigated stir rate effects on morphology and/or final material performance.^{18,37} We will only comment here that changing stir rate also influenced our particle morphologies. An increase in impeller rpm from 500 to 4800 rpm resulted in particles that, though clefted, were spherical in overall morphology at synthesis conditions that would give cubical morphology particles at 500 rpm (see Supplemental Material, Figure A.5). The detailed origins of the mixing-induced morphology transitions are not yet completely understood and will be an area of future investigations.

The presence of an ammonium/ammonia source has previously been reported as being critical in morphology control of transition metal carbonate and hydroxide particles.^{19,34} We similarly found the presence of an ammonia source to be crucial. Replacement of our typical NH₄HCO₃ coprecipitation reagent with NaHCO₃ resulted in dramatically reduced inoculation times and rapid formation of polydisperse particles (see Supplemental Material, Figure A.6 for SEMs from a representative synthesis where NH₄HCO₃ was substituted for and equal concentration of NaHCO₃). Ammonia has been shown to play a role in the coprecipitation of a variety of transition metals due to its ability

to form aqueous soluble complexes with the transition metals.³⁴ These complexes have previously been reported to play a major role in the synthesis of transition metal hydroxide particles, in particular by enabling dissolution/recrystallization of the precipitates which facilitated ripening of particles into larger secondary particles³⁴. To understand whether ammonia complexation was facilitating dissolution/recrystallization in our system, we performed calculations of the equilibrium concentrations of the solution species found in our system using the Medusa solution chemistry diagrams software. The equilibrium constants and major reactions associated with our synthesis are listed in Table 1.

Table 2.1. Equilibrium and solubility product constants (K) for selected reactions involved in $MnCO_3$ coprecipitation.^{34,38}

Equilibrium Reaction	Log K
$Mn^{+2} + NH_3 \rightleftharpoons [Mn(NH_3)]^2$	1
$Mn^{+2} + 2NH_3 \rightleftharpoons [Mn(NH_3)_2]^2$	1.54
$Mn^{+2} + 3NH_3 \rightleftharpoons [Mn(NH_3)_3]^2$	1.70
$Mn^{+2} + 4NH_3 \rightleftharpoons [Mn(NH_3)_4]^2$	1.3
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	-4.8
$MnCO_3 \rightleftharpoons Mn^{2+} + CO_3^{-2}$	-10.6
$Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2OH^-$	-12.7
$H_2 0 \rightleftharpoons H^+ 0 H^-$	-14
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	-6.4
$HCO_3^- \rightleftharpoons CO_3^{-2} + H^+$	-10.3
$Mn^{+2} + HCO_3^- \rightleftharpoons MnHCO_3^+$	1.27

Figure 2.3 shows the calculated equilibrium concentration of aqueous manganese species for all coprecipitation conditions tested. The dissolved manganese species are presented both in terms of total Mn solution concentration (Figure 2.3A) and as a fraction of the Mn that was available in the reaction vessel (Figure 2.3B).



Figure 2.3. (A) Total calculated fraction of manganese that remains soluble at equilibrium as a function of total initial $MnSO_4$ concentration. Relative $NH_4HCO_3:MnSO_4$ ratios used in the calculations were 5:1 (top curve), 10:1 (middle curve), 40:1 (bottom curve) (B) Calculated fraction of all manganese available in solution which was soluble at equilibrium as a function of total initial $MnSO_4$ concentration. Relative $NH_4HCO_3:MnSO_4$ ratios used in the calculations were 5:1 (top curve), 10:1 (middle curve), 40:1 (bottom curve) (B) Calculated fraction of total initial $MnSO_4$ concentration. Relative $NH_4HCO_3:MnSO_4$ ratios used in the calculations were 5:1 (top curve), 10:1 (middle curve), 40:1 (bottom curve).

Total aqueous Mn species included were Mn^{+2} , $MnHCO_3^+$, $Mn(NH_3)^{+2}$, $Mn(NH_3)_2^{+2}$, and $MnOH^+$. The neutral pH (~7.5 for all synthesis conditions) normally results in minimal NH_3 , with NH_4^+ being the dominant ammonia species in solution. Thus, the calculated $Mn(NH_3)^{+2}$ concentration was low for all conditions synthesized. Regardless of conditions used, at equilibrium our calculations predicted that soluble manganese species make up no more than 0.1% of total manganese in solution. Therefore, we conclude that ripening through aqueous dissolution and recrystallization of $MnCO_3$ in our system was unlikely. The results of Figure 2.3 are also presented in table form in Table S1 and Table S2.

Further evidence that long-term dissolution and recrystallization does not play a major role in particle morphology for our system was provided through particle ripening experiments. We performed two coprecipitations using experimental conditions that gave us cubical and spherical particle morphologies, respectively (Figure 2.1B and Figure A.1D). In these experiments, however, the particles were allowed to age for 7 hours instead of being collected after 0.5 hours. SEMs from the long-time coprecipitations can be found in Supplemental Material Figure A.7. Over the 7 hour synthesis, the overall particle morphology does not change substantially relative to 0.5 hours. In the spherical particle case, only minor changes in surface roughness were observed, but there were no significant changes in overall particle size or shape. Cubical particles undergo no noticeable morphological changes.

While equilibrium calculations suggest ammonia-complex enabled dissolution/recrystallization does not facilitate long-term ripening and morphology changes, control experiments where ammonia was substituted with sodium (Figure A.6) suggest that ammonia does play a role controlling particle morphology. One possibility was that even though the ammonia provides a relatively small amount of complexation of the manganese in solution, it was sufficient to lower supersaturation of the MnCO₃ enough to influence the

nucleation and growth of $MnCO_3$ precipitates during the crucial early stages of the coprecipitation synthesis. We have qualitatively observed that the overall particle morphologies were frequently completed within the first few minutes of mixing of the reagent solutions. Detailed studies of the formation rates of $MnCO_3$ during the early stages of the coprecipitation will be necessary to ascertain the role that ammonia was playing at early synthesis stages to facilitate $MnCO_3$ final morphology.

The detailed MnCO₃ synthesis studies described above were undertaken in an effort to achieve control over a diversity of morphologies and sizes of lithium-ion battery precursor particles. For these precursors to be useful in providing lithium-ion battery final active materials of tunable morphology, they must be able to retain their morphology after calcination and lithiation to convert the precursors to lithium-ion battery final active material.^{3,9} To demonstrate that a variety of morphologies of active materials could be obtained via this route we chose two extremes in MnCO₃ precursor morphology, spherical and cubical, for conversion to LiMn₂O₄. As is shown in Figure 2.4, the spherical MnCO₃ (Figure 2.4A) was successfully converted to spherical LiMn₂O₄ (Figure 2.4B) while retaining its overall spherical morphology and without sintering together into larger aggregates. Similarly, the cubical MnCO₃ (Figure 2.4C) was converted to cubical LiMn₂O₄ without significant fusing of particles into larger aggregates and while retaining the overall cubical morphology. Powder X-ray diffraction confirmed the full conversion to spinel LiMn₂O₄ (Figure A.8).



Figure 2.4. SEM images of (A) spherical $MnCO_3$ precursor particles and (B) the same particles after calcination to spherical $LiMn_2O_4$; and (C) cubical $MnCO_3$ precursor particles and (D) the same particles after calcination to cubical $LiMn_2O_4$. Scale bars correspond to 20 µm.

As a final confirmation of our MnCO₃ carbonate precursors as templates for tunable morphology lithium-ion battery cathode materials, we fabricated coin cells with cathodes comprised of the spherical and cubical LiMn₂O₄ particles shown in Figures 2.4B and 2.4D. The Li/LiMn₂O₄ half cells were cycled at increasing rates of ~C/20, C/10, C/2, and 1C (the 1C rate used for cycling was determined from using 148.2 mA/g of active LiMn₂O₄ material, the same rate was used on charge and discharge) between 3.4 V (vs. Li) to 4.2 V (vs. Li). Figure 2.5 shows the second charge/discharge cycle at C/20 for cathodes comprised of the spherical (Figure 2.5A) and cubical (Figure 2.5B) particles.



Figure 2.5. Charge/discharge curves from the second cycle of Li/LiMn₂O₄ half cells with cathodes containing LiMn₂O₄ active material particles with morphologies which are predominantly (A) spherical and (B) cubical. The rate of charge/discharge for both cells was approximately C/20.

The discharge capacities at the various rates can be found in the Supplemental Material, Figure A.9. The charge/discharge characteristics of both the spherical (Figure 2.5A) and cubical (Figure 2.5B) LiMn2O4 active materials were consistent with those previously reported in the literature,25 with two voltage plateaus at roughly 4.0 V and 4.1 V. Both coulombic and round trip energy efficiency for the cells was very high (>98% coulombic efficiency and >97% round trip energy efficiency at C/20), and the initial capacity >115 mAh/g for both materials. The spherical particles had slightly better rate capability and the cubical particles had slightly higher initial and low rate gravimetric capacity, however, it would be premature to assign these observations at this point directly to the influences of particle morphology.

2.4 Conclusions

The influence of solution chemistry on resulting particle morphology during the synthesis of MnCO₃ precipitates was investigated in detail. It was found that moderate changes in reagent concentration could be used to tune the morphology and size of $MnCO_3$ particles, with shapes including rhombohedral, cubical, spherical, and cubical/spherical transitional and sizes ranging from 1 to 15 µm. These particles were very monodisperse relative to other common battery precursor particles reported in the literature. The resulting MnCO₃ morphologies were correlated with inoculation times and nucleation and growth of influenced initial long-period precipitates and appear to not be by dissolution/recrystallization processes, in contrast to processes that facilitate other precipitate systems in the literature. The controlled-morphology MnCO₃ precursors tuned via solution chemistry were used as templates to produce LiMn₂O₄, a lithium-ion battery cathode material. Synthesized $LiMn_2O_4$ particles retained the morphology of the MnCO₃ precursors, demonstrating that the described solution synthesis can be used to produce a diversity of controllable sizes and morphologies of lithium-ion battery active materials.

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Chapter 3

High Temperature Electrode-Electrolyte Interface Formation between LiMn_{1.5}Ni_{0.5}O₄ and Li_{1.4}Al_{0.4}Ge_{1.6}(PO₄)₃

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Abstract

All-solid-state lithium-ion electrolytes offer substantial safety benefits compared to flammable liquid organic electrolytes. However, a great challenge in solid electrolyte batteries is forming a stable and ion conducting interface between the electrolyte and active material. This study investigates and characterizes a possible solid-state electrode-electrolyte pair for the high voltage active cathode material LiMn_{1.5}Ni_{0.5}O₄ (LMNO) and electrolyte Li_{1+x}Al_xGe_{2-x}(PO₄)₃ (LAGP). Insitu x-ray diffraction measurements were done on pressed pellets comprised of a blend of LMNO and LAGP during exposure to elevated temperatures to determine the product materials that form at the interface of LMNO and LAGP and the temperatures at which they form. In particular, above 600°C a material consistent with LiMnPO₄ was formed. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to image the morphology and elemental compositions of product materials at the interface, and electrochemical characterization was

performed on LMNO coated LAGP electrolyte pellet half cells. Although the voltage of Li/LAGP/LMNO assembled batteries was promising, thick interfacial phases resulted in high electrochemical resistance, demonstrating the need for further understanding and control over material processing in the LAGP/LMNO system to reduce interfacial resistance and improve electrochemical performance.

3.1 Introduction

High energy density and long cycle life of lithium-ion (Li-ion) batteries have resulted in their dominance for providing energy storage in portable electronic devices. However, full utilization of these batteries is often limited by the risk of performance degradation and even fire. Hence, the safety is a major challenge faced by next generation Li-ion batteries for adoption in new applications such as electric vehicles, where overheating or mechanical damage to battery packs with flammable liquid organic electrolytes can result in fires.^{1–3} Enhanced safety in Li-ion batteries can be achieved by replacing the organic electrolyte with solid state inorganic electrolytes⁴ that have high thermal as well as mechanical stability and in some cases a large electrochemical stability window compared to conventional organic electrolytes.^{5,6} The high electrochemical stability of some solid inorganic electrolytes, beyond 5 V vs Li⁺, could allow for the use of higher voltage cathode materials with higher energy densities without the drawbacks of electrolyte and electrode decomposition reported in organic electrolyte cells operated at high voltage.⁷ High thermal stability also allows for the possibility of high temperature operation,⁸ and all-solid-state batteries have design advantages for battery miniaturization relative to conventional Li-ion cells.9

Compared to liquid electrolytes, solid electrolyte materials generally have lower Li⁺ conductivity, which limits the rate at which batteries with solid electrolytes can be charged and discharged.⁶ An additional and often more significant challenge with solid electrolytes in all-solid-state batteries is that Li⁺-conducting and mechanically robust contact must be made between individual grains of both the electrode and electrolyte phases during processing and operation of the cell.^{10,11,12} In some cases, this electrode-electrolyte interface can be achieved through high temperature sintering;¹³ however, forming a stable and conductive interface between dissimilar active electrode and electrolyte materials via thermal treatment can be difficult due to a variety of challenges including reactivity between materials, dissimilar thermal expansion coefficients, and nonuniform sintering rates.^{14,15} Thus, the design of all-solid-state batteries requires consideration of all of these factors.

Spinel phase lithium manganese nickel oxide (LiMn_{1.5}Ni_{0.5}O₄, LMNO) is a promising Liion cathode material with a relatively high operating voltage of 4.7 V vs Li/Li⁺, good rate capability, and containing earth abundant transition metals.¹⁶ While the high voltage of LMNO is desirable for high energy density, this potential is outside of the stability window of common Li-ion organic electrolytes which can lead to electrolyte decomposition and ultimately cell failure.¹⁷ One route to accommodate the high potential of LMNO is to use an electrolyte which is stable at high potentials, and a number of solid state electrolytes have reported stability windows suitable for LMNO.^{18,19,20} Relevant to the present study, researchers have previously reported that the solid electrolyte material lithium aluminum germanium phosphate (Li_{1+x}Al_xGe₂₋ $_x$ (PO₄)₃, LAGP) with a rhombohedral NASICON-type (Sodium (Na) Superionic Conductor,²¹ Space group R3c) structure is stable from >1 V vs Li/Li⁺, where it is electrochemically active, to up to 7 V (vs. Li/Li⁺).²² The NASICON family of materials is known for having relatively high ionic conductivity, and room temperature conductivity values for LAGP of up to $\sim 4*10^{-4}$ S cm⁻¹ have been reported.^{19,23,24} The high voltage stability of LAGP led us to investigate LAGP as an electrolyte for a solid-state battery paired with an LMNO cathode.

Herein, we report the characterization of LMNO and LAGP during thermal treatment towards processing the materials as a solid-state electrode-electrolyte pair. LMNO and LAGP materials were brought into contact both as blended powders and as monolithic pellets and heated to elevated temperatures. LMNO and LAGP formed an interfacial phase when heated to temperatures above 600°C. The resulting interfacial phase was consistent with the formation of a LiMnPO₄ (LMP)-like reaction product. Although the bulk conductivity of LMP is low, its reversible cyclability as a lithium-ion active material has been widely demonstrated, indicating that Li⁺ conduction through the interface should be possible.^{25,26,27} This interfacial phase, which forms in-situ during thermal processing of LAGP/LMNO, could in principle provide the mechanical and ionic connection necessary for a solid-state battery; however, initial electrochemical evaluation suggests the resistance in the LAGP/LMNO cells would require substantial reductions to facilitate full charge and discharge of the LMNO active material.

3.2 Experimental

3.2.1 Preparation of LMNO and LAGP Powders

A 500 mL solution of 0.75 M $MnSO_4 \cdot H_2O$ (Fisher) and 0.25 M $NiSO_4 \cdot 6H_2O$ (Fisher) in deionized water was poured all at once into a 3 L solution of 0.2 M NaC_2O_4 (Fisher) in deionized (DI) water in a 4 L beaker on a heater/stirrer plate. Solutions were preheated to 60°C prior to mixing and the temperature was maintained for the duration of the synthesis. The solution was stirred continuously and vigorously at 800 rpm with a magnetic stirrer until completion of the synthesis. After 30 minutes of precipitation, Mn_{0.75}Ni_{0.25}C₂O₄·2H₂O particles were collected through vacuum filtration, rinsed with 3 L of DI water, and vacuum dried overnight at 80°C. Structural water content was confirmed through thermogravimetric analysis measurements on a TA Instruments Q50 TGA. The oxalate precursor powder was mixed with Li₂CO₃ (Fisher) powder with 3% excess Li salt relative to stoichiometric quantities (target Li:transition metal stoichiometry of 1:2) in a mortar and pestle. The mixed powder was fired at 800°C for 5 hours in a Carbolite CWF 1300 box furnace in air with a 3°C per minute ramp rate for both heating and cooling.

LAGP powder was prepared by mixing Li₂CO₃, GeO₂ (Alfa Aesar 99.9999%), Al(OH)₃ (Acros), and NH₄H₂PO₄ (Acros 98%+) in a mortar and pestle for 30 minutes in stoichiometric amounts for a target elemental ratio of Li:Al:Ge:P of 1.4:0.4:1.6:3 (i.e.; Li_{1.4}Al_{0.4}Ge_{1.6}(PO₄)₃, referred to as LAGP in this manuscript). The well-mixed powder was then fired at 600°C for 6 hours in air with a heating rate of 1°C per minute and cooling rate of 3°C per minute. The degassed product was mixed and crushed in a Fritsch Pulverisette 7 planetary ball mill with 5 mm diameter zirconia beads for 5 hours at 300 rpm. This was followed by a second firing at 900°C for 24 hours with a heating rate of 2°C per minute and a cooling rate of 3°C per minute and a second grinding step in the planetary ball mill using the same procedure.

3.2.2 Preparation of Pellets for Li/LAGP/LMNO Cells

0.2 g LAGP powder was loaded into a 13 mm diameter Carver pellet die and pressed with 12,000 lb_f for 2 minutes in a Carver hydraulic press. This pellet was sintered at 850°C for 24

hours with a heating and cooling rate of 1°C per minute. The ionic conductivity of the pressed pellets was verified using electrochemical impedance spectroscopy with a Gamry potentiostat and galvanostatic cycling of sintered LAGP pellets in Li/PEO/LAGP/PEO/Li cells (PEO refers to polyethylene oxide with LiBF₄ polymer electrolyte) symmetric cells, and the ionic conductivity of LAGP was measured to be 5*10⁻⁴ S cm⁻¹ at 75°C which was within range of previous reports.^{24,28,29} 1.00 g LMNO particles were suspended in 50 mL butanol and soft milled on a roller. This LMNO suspension was added dropwise onto the LAGP pellet followed by firing in air at temperatures between 650°C and 800°C. Approximately 0.5 mg of LMNO were coated onto an LAGP pellet. Materials were imaged using scanning electron microscopy (SEM, FEI Quanta 650), and compositional analysis and mapping with the SEM was conducted using energy dispersive X-ray spectroscopy (EDS).

Powder X-ray diffraction (XRD) was used to determine the structure of the assynthesized LMNO and LAGP powders with a PANalytical X'Pert PRO diffractometer using Cu K α radiation. XRD patterns for the two materials can be found in Figures B1 and B2 in the Supplementary Materials. Using spinel cubic phase for the LMNO, the calculated lattice parameter *a* was 8.221 Å, a relatively high value compared to typical reports in the literature.^{30–32} This could indicate a more disordered structure in terms of cation arrangement and/or a high ratio of larger-radius Ni to smaller-radius Mn ions.³³ The calculated lattice parameters for LAGP using a rhombohedral symmetry were *a* = 8.282 Å and *c* = 20.511 Å, consistent with previous reported values in the literature.^{29,34,35} For XRD experiments with blends of LMNO and LAGP at elevated temperatures, equal quantities by mass of LMNO and LAGP powder were mixed in a mortar and pestle and pressed into a pellet with 12,000 lb_f for 2 minutes. The pellet was placed onto a heated stage under a graphite dome in a Bruker powder XRD instrument using Cu K α radiation, and in-situ XRD scans were done on the pellet as the stage was heated to progressively higher temperatures in air. The temperature profile and timing of XRD scans can be found in Figure B3 in the Supplementary Materials.

3.2.3 Electrochemical Characterization

Electrochemical analysis of the LMNO powder was first done using CR2032 coin cells. LMNO powder was mixed with a polyvinylidene difluoride (PVDF) binder and carbon black into an 80:10:10 LMNO:carbon:PVDF composite electrode slurry with N-methyl-2-pyrrolidone as solvent. The electrode slurry was blade coated onto an aluminum foil current collector, dried at 80°C overnight, and subsequently further dried at 80°C under vacuum for 3 hours. The composite LMNO electrode was punched out into 14 mm diameter disks and assembled into a CR2032 coin cell with a 1.2 M LiPF₆ in 3:7 (volume basis) ethylene carbonate:ethyl methyl carbonate electrolyte, a trilayer polypropylene/polyethylene/polypropylene separator, and a Li (thickness : 110 μ m) metal anode. Coin cells were cycled within a voltage window of 3.4 V to 5.0 V using a MACCOR battery tester. Where C rates are given, 1C was assumed to correspond to 7.4 mA g⁻¹ LMNO.

Li/LAGP/LMNO all-solid-state cells were also prepared. LMNO was coated dropwise from a suspension onto a LAGP pellet as described earlier. The LMNO side of the LAGP/LMNO pellet was coated with an approximately 100 nm thick AuPd conductive layer using a Technics sputter coater and attached to a steel coin cell spacer using conductive paste comprised of PVDF and carbon black with a 1:1 ratio by weight. Then, Li metal was directly pressed onto LAGP on the side opposite the coated LMNO. The final Li/LAGP/LMNO pellet was placed into a CR2032 coin cell and underwent galvanostatic cycling between 2.0 V and 5.0 V using a MACCOR battery cycler.

3.3 Results and Discussion

With the variety of elements present within the LMNO and LAGP materials, redistribution and/or conversion of the materials was a possible outcome at the interface of the synthesized phosphate and oxide phases. To probe the resulting phases that may form and the conditions that result in new phase formation, we performed in-situ powder XRD measurements at increasing temperatures on a pressed pellet comprised of equal masses of LMNO and LAGP powders. XRD measurements were conducted on the LAGP/LMNO pressed pellet at different hold temperatures between room temperature and 800°C in order to determine the temperatures at which new interfacial products begin to form, as well as the structure of the product phases. The full 20 range (14-45 degrees) can be found in Figure B4 in the Supplementary Materials; however, the subset of 20 between 18-28 degrees captures the major changes in the materials shown in Figure 3.1.



Figure 3.1. In-situ XRD scans of a pellet comprised of LAGP and LMNO powder at room temperature and after being heated to 450°C, 600°C, 700°C, and 800°C.

Analysis of the location and intensity of all peaks led to the identification of 6 materials: the initial spinel phase LMNO and rhombohedral NASICON LAGP (referred to as the "initial" phases); the resulting phases at elevated temperatures consistent with peak locations for hexagonal GeO₂ and olivine LMP (referred to as the "product" phases);^{27,36} and the graphite dome and α -Al₂O₃ plate which were part of the experimental apparatus. As the pellet was heated to 600°C, there were relatively small changes in peak intensity, though there were notable shifts in peak locations. For example, the LMNO (111) peak at 18.6° shifted to lower 20 values at higher temperatures, attributed to thermal expansion of the lattice. The Al₂O₃ peak initially at 25.3° was part of the experimental apparatus and does not take part in any reactions during the temperature elevation. This peak thus also shifts to lower 20 values at increasing temperatures due to thermal lattice expansion, and the linear increase in the d spacing and unit cell volume with temperature of the Al₂O₃ from this peak confirms the temperature ramps were consistent in

the system (See Supplementary Materials, Figure B.5, for a plot of the calculated cell volume of the Al₂O₃ as a function of temperature). At 600° C and above, the appearance of product peaks began to be observed in the XRD patterns. The product peaks coincided with the disappearance of the initial material peaks, indicating the LAGP and LMNO were reacting to form the new products and thus were diminishing in their relative amounts in the sample as the temperature increased. All peaks attributed to LAGP and LMNO (with the exception of a greatly diminished LMNO (111) peak) were no longer observable when the sample reached 800°C, and only peaks consistent with GeO₂ and LMP were identified in the sample at this temperature. The conversion of LMNO and LAGP was not reversible, and the GeO₂ and LMP remained after allowing the sample to cool back to room temperature. Unique nickel-containing compounds were not identified in the XRD analysis, but nickel was still identified in the interfacial product phase as discussed below. Nickel was still likely present in the diminished LMNO that remained, and nickel has been reported as miscible in olivine LMP,^{37,38,39} and thus it is likely that the Ni still remains distributed between the residual LMNO and the product LMP. Table S1 in the Supplementary Materials summarizes the XRD peaks observed and their material assignments before and after the firing procedure to 800°C.

Since the olivine LMP-like phase (identified in XRD) conducts Li⁺,²⁷ it is possible that a controlled reaction of LMNO and LAGP could lead to the formation of a conductive LMP interfacial phase allowing for a strong contact between the LAGP electrolyte and LMNO active material with good Li⁺ conductivity.¹¹ LAGP pellets were coated with LMNO and fired at 650°C, 700°C, 750°C, and 800°C. The 650°C, 700°C, and 750°C pellets appeared visibly unchanged by the heat treatment, although some sintering was observed within the LMNO layer, and the LMNO coating was confirmed by scratch testing to have hardened. The 800°C fired

pellet experienced a flaking away of the LMNO layer. The pellets were cracked in half to perform SEM imaging at the LAGP/LMNO interface. Pellets fired at temperatures below 800°C maintained good adhesion between the electrolyte and active material layer. SEM imaging of the LAGP/LMNO interface for the 700°C, 750°C, and 800°C pellets are shown in Figure 3.2.



Figure 3.2. SEM micrographs of the LAGP/LMNO interface after firing in air at (A) 700°C for 1 hour, (B) 750°C for 1 hour, and (C) 800°C for 5 hours with a ramping and cooling rate of 1°C per minute. The three phases identified were the (I) LMNO cathode material particles, (II) LAGP electrolyte, and (III) interface.

The samples heated to temperatures of 650°C and 700°C were indistinguishable in SEMs (see Figure 3.2A for 700°C). There was no clearly visible reaction at the interface between the deposited LMNO particles ("T" in Figure 3.2) and the sintered LAGP pellet ("II" in Figure 3.2), and the interface appeared identical to the unfired pellet. At 750°C, a thick ~5 μ m new interfacial layer ("III" in Figure 3.2) has formed between the two materials and appears to be directly bonded with both the LMNO and LAGP (Figure 3.2B). Small gaps have formed on the LAGP side of the reacted interface. At 800°C crack propagation on both sides of the interfacial layer (Figure 3.2C). Cleavage of the interfacial layer in the 800°C sample was observed to occur on both the LMNO and LAGP side of the interfacial layer.

Pellets prepared at 750°C had clear visible separation between material phases (LAGP, LMNO, and interfacial layer), and a sample prepared at this temperature was examined using EDS mapping to determine the location of the phases seen in XRD and the segregation of the different elemental species. The product phases identified in XRD analysis, LMP and GeO₂, contain elements that are absent in either the active material (Ge, P) or the electrolyte (Mn, Ni), allowing visualization of the interface through EDS. The elemental composition of the interfacial layers can be seen in Figure 3.3.



Figure 3.3. Interface of LAGP pellet (lower section of each image) and deposited LMNO powder (upper section of each image) after firing in air at 750°C for 1 hour shown as (A) secondary electron micrograph, (B) EDS map with manganese labeled orange, (C) EDS map with nickel labeled yellow, (D) EDS map with germanium labeled green. Also included are composite EDS maps with (E) manganese and phosphorous, and (F) manganese, phosphorous, and germanium.

EDS mapping revealed 4 distinct regions at or near the LAGP/LMNO interface: a layer of deposited and partially sintered LMNO active material, a continuous phase of up to a few µm in thickness consisting of the LMP-like material (identified due to the colocation of Mn and P), a thin submicron layer of GeO₂ grains, and finally the LAGP electrolyte. The secondary SEM micrograph, Figure 3.3A, shows the interfacial region examined in EDS and was similar to Figure 3.2B. Figure 3.3B and Figure 3.3C show the presence of manganese and nickel, respectively, in the interfacial region. Manganese and nickel can be seen to overlap at all points, with no divergence in the interfacial phase. This observation provides further evidence that the Ni distributes within both the original LMNO phase and the product LMP-like phase. Figure 3.3D shows the presence of germanium at the region of the LAGP/LMNO interfacial phase, including regions that do not coincide with phosphorous. The Ge does not appear to distribute into the LMP-like region, and thus does not overlap with manganese or nickel in the interfacial layer. Figure 3.3E shows the overlap of manganese (and nickel, implicitly) with phosphorous in the interfacial layer, suggesting that the phosphorous from the LAGP electrolyte distributes into the LMP-like layer, but that the Ge does not. It can be clearly seen that manganese and phosphorous overlap in a 2 µm thick band on the side of the interfacial layer adjacent to the deposited LMNO. This observation was consistent with the LMP-like phase identified in XRD. In Figure 3.3E there is a $\sim 1 \mu m$ region containing neither of the elements of Mn, Ni, or P which was immediately adjacent to the LMP-like interfacial layer on the LAGP side only. There are also large grains containing no phosphorous extending to a significant depth (around 10-15 μ m) into the LAGP layer. In Figure 3.3F, which adds the signal from germanium, it can be seen that these features were rich in germanium, which suggests that this region contained the GeO₂ phase identified in XRD. There was no detectable penetration of germanium into the LMP-like interfacial layer or active material layer.

The interfacial layer appeared strongly connected with the active material in both EDS and SEM; however, there were some regions on the electrolyte side of the interface that may inhibit Li^+ conduction. The SEM images, in particular Figure 3.2B, showed gaps forming on the electrolyte side of the interface, although it was unclear the extent to which the interfacial area was occupied by these gaps. Additionally, EDS showed the formation of a thin GeO₂ layer on the electrolyte side of the interface as well. Overall, this points to Li^+ conductivity at the interface likely being limited by features that developed on the LAGP side. Nickel clearly was present in both the LMP-like phase and the initial LMNO phase, though quantitative resolution was insufficient to determine the relative local stoichiometry of the nickel in the LMNO phase and LMP-like phase near the interface.

The previous results provided evidence that the formation of new phases at the interface may produce good contact between the LAGP electrolyte and LMNO active material and that the contact was formed through the Li-conductive LMP-like phase. To investigate the electrochemical performance of this sample, cells were constructed with LMNO coated LAGP pellets prepared under the firing conditions shown previously from 650-800°C. Li metal was directly pressed onto the LAGP pellet to serve as the anode. Pellets fired at 700°C and above such as the samples shown in Figures 3.2A, 3.2B, and 3.2C had very high impedance and were unsuccessful at being charged/discharged. The electrochemical evaluation of the sample prepared at 650°C will be described below. The extremely large resistance for the samples heated to 700-800°C suggested the thick interface formation seen in the more intensely fired samples did not

facilitate good electrochemical performance. We speculate that less aggressively fired samples (such as at 650°C) undergo the same interface formation at a length scale small enough to facilitate some Li transport at the interface, but too small to be clearly differentiated using SEM and EDS maps. The XRD data in Figure 3.1 suggested product formation at temperatures as low as 600°C. A charge/discharge cycle of the sample fired at 650°C is shown in Figure 3.4A.



Figure 3.4. (A) Charge/discharge cycle of Li/LAGP/LMNO all-solid-state cell. Charge and discharge were at 100 nA. (B) Charge/discharge cycle of the LMNO material in a composite electrode within a conventional Li-coin cell cycled at C/20. The voltage window was 2.0 V to 5.0 V for the pellet cell and 3.4 V to 5.0 V for the conventional cell.

The charge profile of the all-solid-state pellet half-cell shown in Figure 3.4A has some qualitative similarity to the charge profile of LMNO in the typical organic electrolyte half-cell

with a conventional composite LMNO cathode shown in Figure 3.4B, with most of the charge capacity being within a plateau at ~4.9 V. However, there was no high voltage discharge capacity in the all-solid-state cell. Although the shape of the LMNO charge curve shared some qualitative features with the composite electrode, the charge capacity of 2.5 mAh g⁻¹ shown in Figure 3.4A corresponds to less than 2% of the theoretical capacity for LMNO. In contrast, conventional organic electrolyte half cells with the same LMNO used in the all-solid-state cells had a discharge capacity of 128 mAh g⁻¹ at a charge/discharge rate of C/20 (Figure 3.4B). The capacity delivered on discharge was in the voltage region consistent with the low voltage reaction of LMNO.⁴⁰ This discharge capacity was also observed in fresh cells that were immediately discharged from OCV (~3.3 V) to 2.0 V. Therefore, the discharge capacity shown in Figure 3.4B does not appear to be electrochemical discharge of the high voltage reaction of LMNO with high polarization. A typical LAGP conductivity value of 10⁻⁴ S cm⁻¹ coupled with the LAGP dimensions would give a polarization of 0.63 mV at the current used for cycling the Li/LAGP/LMNO cell, thus the LAGP electrolyte ionic conductivity should not have limited the LMNO capacity. The LMNO electrode ionic conductivity for the coated films was not directly measured, but a literature value of the ionic conductivity of $5*10^{-10}$ S cm⁻¹ based from a report by Amin and Belharouk for sintered pellets would result in a maximum overpotential of ~0.26 V over the 10 µm cathode film thickness for the samples.⁴¹ It seems unlikely that LMNO ionic conductivity fully explains the low capacity observed in the pellet cells because the $\sim 2\%$ theoretical capacity would only correspond to $\sim 0.2 \ \mu m$ of the cathode film being electrochemically active. The electronic conductivity of LMNO is much higher than the ionic conductivity, thus LMNO electronic conductivity was not expected to have a major impact on electrochemical performance.⁴¹ Thus, the resistance of the LAGP/LMNO interface and the ionic conductivity within the LMNO cathode were likely the major causes of the low capacity observed for the Li/LAGP/LMNO cells. Mitigating the resistance of the LAGP/LMNO interface will require further optimization of processing conditions to minimize thickness while preserving contact and/or exploring alternative material systems.

3.4 Conclusions

The reaction of the Li-ion active material LMNO and the solid electrolyte LAGP was characterized in order to examine the compatibility of these materials for processing into allsolid-state Li-ion batteries. In-situ XRD on a reacting pellet of mixed LMNO and LAGP powder indicated the formation of new phases at temperatures of 600°C and above, and the phases were consistent with LMP and GeO₂. LMNO powder was deposited onto LAGP electrolyte pellets and thermally treated at temperatures ranging between 650-800°C. SEM imaging and EDS mapping of the interface revealed morphological progression at progressive extents of formation of new phases at the interface, as well as the change in distribution of the elemental components as a result of the thermal treatment and formation of new phases. Fired pellets were also paired with Li metal anodes and electrochemically evaluated in coin cells. While the charging profile had potentials consistent with LMNO active material, the capacity achieved was extremely low, and the high voltage reaction was not reversible on discharge. Sintering LMNO and LAGP in air resulted in a good mechanical connection between the materials, but not a high performance electrochemical connection despite the presence of the Li-ion conductive LMP-like interfacial phase. The resistance of the electrode-electrolyte interface is a general challenge for many allsolid-state battery systems, and the added complexity of the oxide-phosphate materials and conversion to new phases in the LAGP/LMNO system means that explicit control over the thickness and contact at the LAGP/LMNO interface is critical for reasonable electrochemical performance in this system.

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Chapter 4

Sintered Electrode Full Cells for High Energy Density Lithium-ion Batteries

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Abstract

Increasing the energy density of lithium-ion batteries at the electrode and cell level is necessary to continue the reductions in the size and weight of battery cells and packs. Energy density improvements can be accomplished through increasing active material loading in electrodes by decreasing porosity and removing inactive additives, as well as by using thicker electrodes that reduce the relative fraction of separators and current collectors in the cell. This paper will describe the fabrication of sintered electrodes comprised of only electroactive material towards the goal of thick electrodes free of binders and conductive additives. The electrodes reported herein have no inactive additives in the electrode, >62% active material volume fraction, and high thicknesses of >500 μ m. The high capacity of these electrodes presents challenges for material characterization and extended cycling. In particular, lithium metal anodes limit the performance of sintered electrode cells at >1 mA/cm², a relatively low rate for the thick

electrodes. In this work, full $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)/LiCoO₂ (LCO) sintered electrode cells with total anode and cathode thickness up to 2.90 mm have been successfully fabricated and electrochemically evaluated. These full cells have improved stability and high areal capacities, as high as 45 mAh/cm² capacity at 1.28 mA/cm².

4.1 Introduction

Continued growth in the number of battery-powered devices such as portable electronics and electric vehicles demands the development of higher energy density lithium-ion (Li-ion) batteries.¹ While development of new Li-ion chemistry and overall chemical paradigms for batteries is a major route forward,^{2,3} substantial improvements in energy density can be made with established materials through design of the electrode towards improved electrochemical performance.^{4,5} Higher energy electrodes can be accomplished by increasing the packing densities of active material, removing inactive additives, and/or increasing electrode thicknesses.

Designing electrodes for high total energy or energy density often results in compromises in the rate capability of the electrode. Removal of conductive additives and binders in composite electrodes can reduce the electrode electronic conductivity and mechanical integrity, making it difficult to calendar for high density.^{6,7} Calendaring can increase electronic conductivity, but reduces the volume of the electrode allocated to the electrolyte, creating limitations in Li⁺ transport.⁸ Also, thick and dense electrodes can be difficult to manufacture without cracking or delamination.⁹ Large particles, which pack well into composite electrodes, have longer internal diffusion paths and lower surface areas for intercalation reactions, further limiting rate capability.^{10,11} These factors lead to some natural limits for composite electrodes, and typically those reported have thicknesses below 250 μ m and active material volume fractions below 60%.^{2,12,13}

Sintered electrodes offer a new paradigm for electrode architectures with established Liion materials.⁴ These materials consist of close-packed (>60% solid by volume) pure active material porous films that form electronically conductive and mechanically strong connections between particles to replace the roles of inactive additives in composite electrodes. Using hydraulic pressing to fabricate the electrodes enables thicker electrodes than those typically achieved with calendared composites, and the pressing of a single component mitigates some electrode heterogeneity. Furthermore, the pressing step achieves random close packing regardless of particle morphology, facilitating the use of small, high-rate-capability active material particles without major sacrifices to electrode packing density.¹⁴ Sintered electrodes have higher energy densities on an areal basis than state-of-the-art composite electrodes,¹⁵ and the advantages could be even greater with stacked sintered electrodes compared to stacked or wound composite electrodes due to the lower volume fraction dedicated to inactive components including current collectors and separators enabled by the use of thick electrodes.¹⁶

Herein, we report fabrication of Li-ion full cells where both electrodes were comprised of only sintered active materials – free of binder and conductive additives. The coin cells reported in this study have extremely high areal capacities – 21.4 mAh/cm² and 45.2 mAh/cm². For perspective, commercial Li-ion electrode pairs have been reported in a range generally up to 25 mg active/cm² corresponding to a capacity of about 3.75 mAh/cm² for e.g. LiCoO₂ (LCO).^{2,17} While other reports have paired sintered electrodes with Li metal which results in the highest

energy density, we will demonstrate that Li metal thin film electrodes result in significant performance and cycle life limitations for these high capacity sintered electrode cells. These high energy density electrode architectures provide a promising route to high energy density Li-ion cells, and further improvements towards mitigating rate capability limitations in these cells would provide a promising strategy to designing high energy battery packs.

4.2 Results and Discussion

Sintered LCO electrodes have been demonstrated previously as an excellent candidate material for sintered electrodes, with high energy density, high electronic conductivity after slight delithiation, and modest intercalation strain.^{4,18} LCO powder was synthesized, pressed into 440 µm thick pellets (surface morphology can be seen in Figure C.1 in Supporting Information), sintered, and assembled into half cells with lithium metal anodes to evaluate their performance. The Li/LCO sintered electrodes are compared with 80:10:10 active material:carbon black:PVDF binder composites in Figure 4.1.



Figure 4.1. Voltage profiles during charge/discharge for the 2nd cycle of sintered electrode (solid lines) and composite electrode (dashed lines) Li/LCO cells plotted on a (A) gravimetric basis considering just the active material and (B) areal basis. Areal current densities were 1.15 mA/cm2 for the sintered electrode and 0.028 mA/cm2 for the composite electrode, which for both cells corresponds to C/20 using a mass of active material basis.

As shown in Figure 4.1, the sintered electrodes had only slightly lower capacity than the composites on a gravimetric basis but much higher capacity on an areal basis. At C/20, the capacity was 97% that of the composite cell on a gravimetric basis, but 4000% of the composite cell on an areal basis with a round trip energy efficiency of 93.4% for the sintered electrode vs 94.4% for the composite. With a 100 μ m lithium metal anode and 440 μ m LCO cathode packed at 68% solid density, the energy density of this cell is extremely high – 1435 mWh/cm³ discharged at 77.9 mW/cm³ (volume of electrodes plus separator). However, the cycle life for the Li/LCO cell with the sintered LCO electrode was limited (Figure 4.2A), with the cell undergoing abrupt capacity loss after 15 charge/discharge cycles at C/20.



Figure 4.2. Capacity retention during charge/discharge cycling of (A) Li/LCO and (B) Li/LTO cells containing sintered electrodes and (C) a Li/Li symmetric cell. The cells in (A) and (B) were cycled at rates corresponding to C/20 based on active material mass (areal current densities of 1.15 mA/cm^2 for LCO, 1.10 mA/cm^2 for LTO), while the cell in (C) was cycled using a 50 hour cutoff for each charge/discharge at a rate of 0.53 mA/cm^2 , which corresponded to C/50 for the sintered electrodes. Li mass for gravimetric basis in (C) corresponded to the mass of two layers of 100 µm Li foil.

The low cycle life of the half cells made it difficult or impossible to accurately test the rate capability of the electrode materials. This is likely due to the extremely deep lithium stripping and plating with each cycle – cycles shown in Figure 4.2 correspond to a depth of approximately 130 μ m of densely pressed lithium metal per cycle. This remodeling of the lithium anode with each cycle results in high quantities of solid electrolyte interphase (SEI) formation and thus electrolyte consumption as well as potential dendrite growth.¹⁹ In a previous report, lithium metal and electrolyte were replaced periodically to allow extended cycling with high capacity

lithium-ion cathodes.⁴ In this work, sintered LTO spinel was investigated as a counter electrode to replace lithium and allow extended cycling without opening the cell. LTO is an anode material known for its high cycle life and safety due to its 1.55 V redox potential vs. Li/Li⁺, which is within the stability window of the electrolyte and thus limits SEI formation. Also, LTO has very low strain during intercalation/deintercalation, suppressing particle fracture during cycling.^{20,21} Additionally, while LTO is electrically insulating, the Li₇Ti₅O₁₂ phase formed during lithiation is highly conductive has been shown to support cycling LTO without carbon additives in both composite and sintered electrodes.^{22–24}

Since LTO has a low strain and voltage within the electrolyte stability window, it is expected to have among the best capacity retention of sintered electrode materials by minimizing pulverization of interparticle connections and maintaining conductivity within the film. However, despite all of these stability advantages, sintered LTO half cells had even lower cycle life than LCO (Figure 4.2B). The Li/LTO cell with a sintered LTO electrode successfully completed one discharge/charge cycle at C/20 (see Figure C.2 in the Supporting Information for the voltage profiles), but lost over 90% of cell capacity with the second discharge cycle. Capacity losses were always seen following delithiation of LTO (plating of lithium) - there were not significant losses following a lithiation of LTO (stripping of lithium) discharge cycle. We note that the thickness of lithium was doubled for Li/LTO cells to compensate for the initial discharge/lithiation reaction of LTO, as opposed to LCO's initial charge/delithiation reaction (e.g.; LCO starts on charge and thus there is more total Li available for charge/discharge in a LCO vs. LTO electrode of equal capacity paired with an equivalent Li anode).

To further confirm the limitations of the lithium metal electrode in these high capacity cells, Li/Li symmetric cell were constructed using Li foils with thickness of 200 µm (two 100 µm Li foils pressed together for each electrode) and electrode areas of 1.60 cm². The Li/Li symmetric cell was unable to complete full 20 hour cycles at current densities of ~1.1 mA/cm², which corresponded to C/20 for the sintered electrodes, without hitting the 1 V upper voltage cutoff. To demonstrate cycling of the Li/Li cell, we used a current density of 0.53 mA/cm² (~C/50 for sintered electrodes) and completed each cycle with a 50 hour time cutoff (Figure 4.2C). Only three full "charge" and "discharge" cycles were achieved before loss of capacity in the Li/Li cell. The relatively large fraction of Li stripped and plated with each cycle (~70% of the initial Li in the cell) likely led to significant SEI formation and Li loss in the cell. A voltage profile of the Li/Li cell is available in Figure C.3 in the Supporting Information. While at 0.53 mA/cm^2 there was polarization in the Li/Li cell that increased with a function of time both on charge and discharge, cycling at higher rates of ~1.1 mA/cm² to ~4.4 mA/cm² (corresponding to C/20 and C/5 for the sintered electrodes) resulted in very high polarization and the cell reaching the voltage cutoff of 1.0 V. The inability of the Li metal to cycle at current densities that for the sintered electrodes corresponded to C/20 or higher presented a challenge in attempting to determine rate capability of the sintered electrode materials, at least when paired with Li metal dense thin film anodes.

Due to the cycle life, capacity, and rate limitations of the half cells, full cells were constructed to characterize these electrodes without the use of Li metal. LTO/LCO sintered electrode full cells of two different thicknesses were assembled and underwent galvanostatic cycling at various rates which are shown in Figure 4.3.



Figure 4.3.(A,C) Voltage profiles for the 2^{nd} charge/discharge cycle at C/20 and (B,D) rate capability of LTO/LCO cells where both the LTO and LCO are sintered electrodes. The cell in (A,B) contained a total anode and cathode thickness of 1.21 mm, while the cell in (C,D) contained a total anode and cathode electrode thickness of 2.90 mm. The profile in (A) had a voltage window of 1 to 2.8 V and areal current density of 1.15 mA/cm², while the cell in (C) had a voltage window of 1.5 to 3.0 V and areal current density of 1.36 mA/cm².

The 1.21 mm (0.75 mm LTO and 0.44 mm LCO) thick LTO/LCO cell shown in Figures 4.3A,B achieved a capacity of 12.5 mAh/cm² even at the high current density of 4.62 mA/cm², and a capacity of 21.4 mAh/cm² at a current density of 0.462 mA/cm². The active loading was 153 mg/cm² based on the LCO side - around six times higher than typical heavily loaded commercial composite electrodes.^{2,17} We note that the cell capacity was possibly limited by LTO rather than LCO based on the capacity of Li/LTO cells. Detailed investigations determining the rate capability limitations of the LTO/LCO cells will be the subject of future investigations, but the

thickness of these electrodes will likely lead to significant concentration polarization and Li⁺ diffusion limitations within the porous active material matrix, thus improvement of rate capability of these electrodes will require careful design of the constituent particles, the Li⁺ diffusion pathways, and the total electrode thickness.²⁵ Scanning electron micrographs of the films are available in Figure C.1 in the Supporting Information.

To test the limits of the thickness of these sintered electrode cells, a 2032-type coin cell was assembled with 2.90 mm total electrode and separator thickness shown in Figure 4.3C,D. In order to fit the 1.08 mm LCO and 1.79 mm LTO electrodes, it was necessary to remove the spacers and wave spring, with the cell crimping providing the pressure in the cell which kept the electrodes in contact with the cell casing. We also used a relatively high voltage cutoff of 3.0 V (cell, vs. LTO anode) to extract additional capacity relative to the other LTO/LCO sintered electrode full cells, although such a high potential for LTO/LCO cells negatively impacted capacity retention. As seen in Figure 4.3D, the cell delivered comparable gravimetric capacity on an LCO material basis to the 1.21 mm cell at low current densities. The theoretical capacity for this cell was 109 mAh (based on 150 mAh/g LCO), with the highest discharge capacity achieved being 83.4 mAh at 1.28 mA/cm², or C/100, the slowest rate used. With some optimization, a capacity of 120 mAh could feasibly be achieved in this cell geometry at the slower rates typical of many coin cell applications, and with an average voltage of around 2.5 V this design compares favorably in energy density to rechargeable commercial coin cells such as ML2032 cells with nominal voltage and capacity of 3 V and 65 mAh.²⁶ Furthermore, the cell still provides significant capacity even at 12.8 mA constant current, corresponding to the nominal C/10 discharges shown in Figure 4.3D.

The capacity retention and rate capability of the 1.21 mm LTO/LCO full cell was greater than that of either the Li/LCO or Li/LTO cells, providing additional evidence that that cycling and rate capability limitations in the Li/LTO and Li/LCO cells was likely due to the lithium electrode rather than the sintered electrodes. Sintered electrodes have a unique reliance on small interparticle connections for electronic conductivity and cohesion. Because of the well-known issue of lithium intercalation and deintercalation causing strain and pulverization of active materials, it is expected that sintered electrodes will likely be more vulnerable than composites to intercalation pulverization. The low strain and high anode-side voltage of LTO make it one of the most durable Li-ion materials in composite cells, and these properties are likely just as important for the sintered electrode architecture. The mechanisms of capacity loss in sintered electrodes will be a topic for future studies; however, the results presented here demonstrate that high energy densities are made possible by using sintered electrodes as the anode and cathode comprised of only lithium-ion battery active material.

4.3 Conclusions

Li/LCO, Li/LTO, and LTO/LCO cells with thick and dense sintered electrodes were fabricated and characterized through galvanostatic cycling. The half cells have very high energy density; however, the cycle life of those cells was limited to as little as 1 charge/discharge cycle for Li/LTO, and cycle life limitations were attributed to the Li metal anode for the high current densities and total capacities that result from using thick sintered electrodes. LTO/LCO full cells were assembled that had improved cycle life and rate capability than the Li/LCO and Li/LTO cells, demonstrating that the short cycle life of the half cells was likely due to the deep cycling of lithium as opposed to pulverization of interparticle connections and loss of electronic conductivity and cohesion from the sintered electrodes. Additionally, the performance of the full cell was demonstrated in a cell up to 2.90 mm, showing that extremely high areal loadings are possible with these electrodes. Further efforts will be needed to probe capacity loss mechanisms within the sintered electrode film, as well as further optimization of the sintered electrode particle constituents and microstructures to improve these unique battery electrode materials.

4.4 Experimental

4.4.1 Preparation of Active Material Powders

LCO was synthesized using an adapted method previously reported in the literature.²⁷ First, CoC₂O₄•2H₂O precipitate particles were synthesized by pouring all at once an 1800 mL solution of 62.8 mM Co(NO₃)₂·6H₂O (Fisher Reagent Grade) dissolved in deionized (DI) water into an 1800 mL solution of 87.9 mM (NH₄)₂C₂O₄·H₂O (Fisher Certified ACS) dissolved in DI water. Solutions were preheated to 50°C prior to mixing and the temperature was maintained at 50°C for the duration of the synthesis. The solution was stirred continuously and vigorously at 800 rpm with a magnetic stirrer. After 30 minutes of precipitation, CoC₂O₄•2H₂O particles were collected via vacuum filtration, rinsed with 4 L of DI water, and vacuum dried overnight at 80°C. CoC₂O₄•2H₂O powder was mixed with Li₂CO₃ (Fisher Certified ACS) powder with 2% excess Li salt relative to stoichiometric quantities (e.g.; Li:Co mixed at 1.02:1 molar ratio) in a mortar and pestle. The mixed powder was fired at a 1°C per minute ramp rate to 800°C with no hold time in a Carbolite CWF 1300 box furnace in air, and upon reaching 800°C the furnace was turned off and allowed to cool to ambient temperature without control over cooling rate. After firing, the resulting LCO powder was milled in a Fritsch Pulverisette 7 planetary ball mill with 5 mm diameter zirconia beads for 5 hours at 300 rpm.

The LTO powder used was NANOMYTE BE-10 purchased from NEI Corporation. Characterization of this material can be found in previous reports.²⁸

4.4.2 Electrode Preparation and Characterization

Active material powder was mixed with solution containing 1 wt% polyvinyl butyral dissolved in ethanol at a ratio of 0.2 mL binder solution/0.1 g active material powder using a mortar and pestle. After solvent evaporation by exposure to air, the active material and binder mixture was further ground in a mortar and pestle. Either 0.2 g LCO-binder mixture or 0.22 g LTO-binder mixture were loaded into a 13 mm diameter Carver pellet die and pressed with 12,000 lb_f for 2 minutes in a Carver hydraulic press. A 16 mm diameter pellet die was used for the very thick LCO and LTO electrodes (Figures 4.3C,D). After pressing, electrodes were sintered in a Carbolite CWF 1300 box furnace in air through heating to a peak temperature of 700°C and held for 1 hour with a 1°C per minute ramping and cooling rate. After cooling, electrodes were attached directly to stainless steel coin cell spacers using an N-methyl pyrrolidone (NMP) solvated binder slurry of 1:1 weight ratio Super P carbon black conductive additive to polyvinylidene difluoride (PVDF) binder and dried overnight in an 80°C oven. Composite electrodes were prepared by coating a slurry comprised of active material (for LTO directly as received, for LCO after ball milling), carbon black conductive additive, and PVDF binder in NMP solvent with a weight ratio of 80:10:10 active:carbon black:PVDF onto an aluminum foil current collector using a doctor blade with a gap of 200 µm. The electrode slurry was dried in an 80°C oven overnight and dried in an 80°C vacuum oven for 3 hours prior to punching out 14 mm diameter electrode disks.

Electrodes for all cells were assembled into CR2032 coin cells in an argon atmosphere glove box with a single trilayer polymer separator and an electrolyte comprised of 1.2 M LiPF₆ in 3:7 ethylene carbonate:ethyl methyl carbonate electrolyte. Cells were tested through constant current charge/discharge cycling on a MACCOR battery cycler. Where reported, C rates were based on assumed capacities of 150 mAh/g for LCO and 175 mAh/g for LTO. Voltage ranges and current densities used during cell cycling for different cell types (Li/LTO, Li/LCO, LTO/LCO with sintered or composite electrodes and different loadings) can be found in the text and figure captions for each cell discussed.

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Chapter 5

Future Directions and Conclusions

5.1 Future Directions

Future development of the sintered electrode system described in Chapter 4 will focus on gaining a more detailed understanding of the overall kinetics. It is likely that Li⁺ diffusion in the electrolyte is the greatest limitation to overall performance in the highly conductive materials LCO and LTO. Neutron diffraction experiments that can reveal the spatial distribution of Li⁺ throughout the electrode may provide a direct look into depletion or saturation of lithium in electrolyte diffusion limited cases. Particle optimization has not yet been pursued. Very small active material particles should reduce charge transfer resistance and solid diffusion limitations further, and small particles are possible to prepare into electrodes without sacrificing packing density due to the hydraulic press technique currently used to prepare sintered electrodes.

Another route towards better rate performance for sintered electrodes is ordered structures to reduce tortuosity. Our lab has pursued ice-templated electrodes formed by freeze-casting towards this end. The greatest challenge in working with ice-templated electrodes currently is the low density of the electrodes formed from that method – currently up to about 42% solid density for our materials even after aggressive sintering conditions at 950 or 1000°C, although much higher densities in the range of the >60% have been obtained for other ceramic materials, giving hope that we will be able to reduce film tortuosity without sacrificing the dense packing fraction that makes sintered electrodes desirable.

5.2 Conclusions

In Li-ion systems, energy density and power density are fungible on multiple scales, including the constituent materials, particles, electrode morphology, and even pack design. Because engineering in this system is so multidimensional, it is essential to look for opportunities that offer an asymmetric benefit towards improving the overall performance of the system without creating too great a sacrifice in any particular outcome. The beginnings of true improvement are in understanding the relative magnitude of effect that tunable parameters like electrode thickness or particle size have on the performance of a given battery, allowing for rational parameter choices that facilitate an overall best performance.

The work on particle synthesis described in Chapter 2 provided a substantial benefit in understanding the various regimes of nucleation and growth in coprecipitation of MnCO₃ particles of various sizes and shapes. The monodispersity achieved was amongst the highest in the academic literature, and the description of the shape transition was very detailed. Furthermore, it was shown that unlike similar coprecipitation systems, the process was not equilibrium driven and that there was no significant interparticle mass exchange - particle morphology was determined by the initial nucleation and growth steps.

As academic researchers, we have the opportunity and obligation to look for greater asymmetries by seeking out underdeveloped or new paradigms that have the potential to create significant long-term impacts. This kind of impact has been earnestly sought in the work laid out on solid-solid interfaces in Chapter 3 and sintered electrodes in chapter 4. All-solid-state Li-ion batteries have the potential to be completely transformative, especially with novel designs that utilize the unique strengths of these materials. In our case, we combined the high voltage spinel material LMNO with the highly electrochemically stable LAGP. X-ray diffraction and SEM/EDS results were clear on what chemical products formed, the range of temperatures over which the reaction takes place, and the morphology of the interfacial product phase, including a continuous Li⁺ conductive LMP layer. The reaction as-used did not facilitate the development of high-performing batteries, but could possibly be modified in future work through atmospheric control or applied pressure to the interface to create a strong connection.

Sintered electrodes have the capability to substantially raise the practical energy density of Li-ion batteries on multiple levels. The LTO/LCO full cell configuration does not show the strong capacity fade related to lithium metal. LCO and LTO were also demonstrated to have good rate performance even at very high areal current densities. The 2032 coin cell prototype with super thick electrodes was shown to outperform commercial rechargeable 2032 cells, at least in terms of energy and power capability, further underscoring the extreme density of these materials.

Li-ion batteries are an established technology, but not a mature one, with substantial capacity remaining for further improvement. A major pillar of these improvements will be the continued development of more efficient particle and electrode-level structures for higher energy and power densities. Optimism for future development is appropriate, because there are many exciting lines of research and competing designs in the field. The work laid forth in this dissertation has proudly contributed towards the goal of creating better batteries for the future.

Appendix A

Supplemental Information for Chapter 2



Figure A.1. SEM images of $MnCO_3$ particles prepared with a 10:1 ratio of NH_4HCO_3 to $MnSO_4$ and ascending concentration of $MnSO_4$: (A) 3 mM $MnSO_4$, (B) 4.5 mM $MnSO_4$, (C) 6 mM $MnSO_4$, (D) 7.5 mM $MnSO_4$, (E) 9 mM $MnSO_4$, (F) 10.5 mM $MnSO_4$, (G) 12 mM $MnSO_4$. A synthesis was performed at 1.5 mM $MnSO_4$; however, there were no recoverable particles. Scale bars correspond to 20 μ m.



Figure A.2. SEM images of $MnCO_3$ particles prepared with a 5:1 ratio of NH_4HCO_3 to $MnSO_4$ and ascending concentration of $MnSO_4$: (A) 3 mM $MnSO_4$, (B) 4.5 mM $MnSO_4$, (C) 6 mM $MnSO_4$, (D) 7.5 mM $MnSO_4$, (E) 9 mM $MnSO_4$, (F) 10.5 mM $MnSO_4$, (G) 12 mM $MnSO_4$. A synthesis was performed at 1.5 mM $MnSO_4$; however, there were no recoverable particles. Scale bars correspond to 20 μ m.



Figure A.3. SEM images of MnCO₃ particles prepared with a 1:1 ratio of NH₄HCO₃ to MnSO₄ and ascending concentration of MnSO₄: (A) 6 mM MnSO₄, (B) 7.5 mM MnSO₄, (C) 9 mM MnSO₄, (D) 10.5 mM MnSO₄, (E) 12 mM MnSO₄. Synthesis was also performed at 1.5 mM MnSO₄, 3 mM MnSO₄, and 4.5 mM MnSO₄, however, there were no recoverable particles at all of these conditions. Scale bars correspond to 20 μm.



Figure A.4. Standard deviation of volume weighted average particle size at prescribed synthesis conditions. The average particle sizes at these conditions can be found in Figure 2.2.



Figure A.5. SEM images of particles prepared at 3 mM $MnSO_4$ and 40:1 $NH_4HCO_3:MnSO_4$ ratio with a stirring speed of (A) 500 rpm and (B) 4800 rpm. Scale bars correspond to 20 μ m.



Figure A.6. SEM image of particles prepared at 3 mM MnSO₄ and (A) 40:1 NH₄HCO₃:MnSO₄ ratio and (B) 40:1 NaHCO₃:MnSO₄ ratio. Scale bars correspond to 20 μm.



Figure A.7. SEM image of cubical particles prepared with 3 mM MnSO₄ and a 40:1 NH₄HCO₃:MnSO₄ ratio and collected after (A) 30 minutes and (B) 7 hours. Spherical particles were prepared with 7.5 mM MnSO₄ and 10:1 NH₄HCO₃:MnSO₄ ratio and collected after (A) 30 minutes and (B) 7 hours. Scale bars correspond to 20 μm.



Figure A.8. XRD patterns of the synthesized (A) $MnCO_3$ (reference¹) and (B) $LiMn_2O_4$ (reference²) particles. The XRD patterns are from powders comprised of the particles found in Figure 2.4.



Figure A.9. Discharge capacity of Li/LiMn₂O₄ half cells at increasing rates of charge/discharge (C/20, C/10, C/2, C). The cathode active material was composed of (A) spherical and (B) cubical morphology particles. Electrode particles used are those depicted in Figure 2.4. The rate used was the same for charge and discharge.

	Initial MnSO ₄ Concentration (mM)									
	1.5	3	4.5	6	7.5	9	10.5	12		
40:1	0.034	0.016	0.011	0.008	0.006	0.005	0.004	0.004		
10:1	0.054	0.021	0.013	0.008	0.007	0.006	0.005	0.004		
5:1	0.088	0.030	0.016	0.011	0.008	0.006	0.005	0.004		
1:1	4.143	3.672	1.178	0.863	0.660	0.525	0.440	0.344		

Table A.1. Manganese in Solution as a % of Total Manganese

Table A.2. Total Concentration of Aqueous Manganese (10^{-5} M)

	Table A.2. Total Concentration of Aqueous Manganese (10 M)										
	Initial MnSO ₄ Concentration (mM)										
	1.5	3	4.5	6	7.5	9	10.5	12			
40:1	4143	3672	1178	863	660	525	440	344			
10:1	88	30	16	11	8	6	5	4			
5:1	54	21	13	8	7	6	5	4			
1:1	34	16	11	8	6	5	4	4			

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Appendix B

Supplementary Materials for Chapter 3



Figure B.1. XRD pattern for the $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) powder.



Figure B.2. XRD pattern for the Li_{1.4}Al_{0.4}Ge_{1.6}(PO₄)₃ (LAGP) powder.

Powder X-ray diffraction was used to determine the structure of the as-synthesized LMNO and LAGP powders in a PANalytical X'Pert PRO diffractometer using Cu K α radiation. For experiments investigating the formation of new phases when LMNO and LAGP were in contact and heated to elevated temperatures, equal masses of LMNO and LAGP powder were ground together thoroughly in a mortar and pestle and pressed into a pellet in order to maximize contact between the two separate reactant phases. The pellet was placed onto a heated stage under a graphite dome in a Bruker powder X-ray diffraction (XRD) instrument using Cu K α radiation, and in-situ XRD scans were done on the pellet as it was heated from room temperature to the progressively higher temperatures of 450, 600, 700, and 800°C. The temperature profile of the heated stage and timing of XRD scans are included as Figure B.3. Included below as Figure B.4 are the patterns for the full range of XRD analyzed between 14-45 °20 at the different temperatures; Figure 3.1 in the manuscript contains the data from Figure B.4 with a restricted range to focus the discussion. Peak locations and assignments for Figure B.4 can be found in Table B.1.


Figure B.3. Temperature profile for the in-situ XRD experiment. The red lines indicate times where XRD measurements were performed.



Figure B.4. In-situ XRD patterns for the pellet comprised of blended LAGP and LMNO powders at room temperature, after being heated up to 450, 600, 700, and 800°C, and after cooling to 30°C at the conclusion of the heating procedure. Also included is the XRD pattern for the experimental apparatus in the absence of the pellet sample, including the graphite dome and an alumina plate that supported the pellet.

Table B.1. List of XRD peak positions for the pellet comprised of an equal mass blend of LMNO and LAGP powders at room temperature before and after firing to 800° C. Phases were indexed using the following reference patterns: LAGP (Reference Code $00-041-0034^{1}$), LMNO (Reference Code $01-070-8650^{2}$), Al₂O₃(Reference Code $00-046-1212^{3}$), GeO₂(Reference Code $00-036-1463^{4}$), and LiMnPO₄ (Reference Code $01-072-7844^{5}$). Peaks labeled "Apparatus Component" were unidentified peaks that were due to materials in the apparatus used to control the temperature, and were present in the absence of any LMNO/LAGP sample and their intensity did not change during the course of heating or cooling. When more than one species is listed, the peak location was consistent with more than one material.

Pre Firing 25°C						Post Firing 30°C				
°20	Species 1	h k l	Species 2	hkl	_	°20	Species 1	h k l	Species 2	h k l
15.05	LAGP	012				17.08	LiMnPO ₄	200		
18.63	LMNO	111				18.32	LMNO	111		
21.27	LAGP	104				20.64	LiMnPO ₄	101	GeO ₂	100
21.41	LAGP	110				22.51	LiMnPO ₄	210		
25.10	LAGP	113				23.87	LiMnPO ₄	011		
25.34	AI_2O_3	012				25.35	LiMnPO ₄	111	AI_2O_3	012
26.01	LAGP	006				26.05	GeO ₂	101		
28.37	Graphite	002				28.36	Graphite	002		
30.38	LAGP	024				29.43	LiMnPO ₄	211		
32.46	Apparatus Component					30.11	Unidentified Product			
33.29	LAGP	211				32.05	LiMnPO ₄	301		
33.97	LAGP 116					32.46	Apparatus Component			
34.92	AI_2O_3	104				34.93	AI_2O_3	104		
35.28	Apparatus Component					35.35	LiMnPO ₄	311		
36.13	LMNO	311				36.15	LiMnPO ₄	121	GeO ₂	110
36.60	Apparatus Component					36.63	Apparatus Component			
37.18	Apparatus Component					37.16	Apparatus Component			
37.56	LAGP	300	AI_2O_3	110		37.56	LiMnPO ₄	410	AI_2O_3	110
43.13	AI_2O_3	113				38.23	GeO ₂	012		
43.92	LMNO	400				39.01	LiMnPO ₄	102	GeO ₂	221
						39.58	LiMnPO ₄	401	GeO ₂	111
						41.87	LiMnPO ₄	202	GeO ₂	200
						43.13	AI_2O_3	113		



Figure B.5. Calculated relative unit cell volume expansion based on refinement of (104) and (113) α -Al₂O₃ XRD peaks during in-situ XRD experiment. The calculated unit cell volume at 25 °C was 259.42 Å³. The measured expansion was consistent with the volumetric expansion of Al₂O₃ reported in the literature.⁶

References

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Appendix C

Supporting Information for Chapter 4



Figure C.1. SEM micrographs of (A) $LiCoO_2$ (LCO) and (B) $Li_4Ti_5O_{12}$ (LTO) sintered electrode surfaces. (C) LCO and (D) LTO cross-sectional SEMs at lower magnification that captured the full electrode thickness.

Figure C.1 contains SEMs of sintered electrode thin films of LCO and LTO at high magnification (Figure C.1A,B) to show the morphology of the particles that comprise the film and lower magnification (Figure C.1C,D) to show the relatively flat and uniform electrode at a more macroscopic length scale The sintering provides interparticle connections that enable both electronic conduction through the electrode and mechanical strength necessary for cell fabrication and withstanding the pressure that holds the coin cell electrodes in contact with current collectors. The average thickness of LCO electrodes, including those used for electrochemical cycling in the main text in Figures 4.1, 4.2A, and 4.3A,B was $439 \pm 16 \mu m$, and the electrodes had a solids volume of 67.9%. The average thickness of the LTO electrodes,

including those used for electrochemical cycling in the main text and Supporting Information in Figures 4.2B, 4.3A,B, and C.2A, was $750 \pm 8 \mu m$ with a solids volume of 62.0%. Standard deviations were the result of three measurements on each of three electrodes for both samples. The electrochemical cell with thicker electrodes used for the data shown in Figures 4.3C,D in the main text had an LCO electrode with thickness 1076 μm and LTO electrode with thickness 1794 μm (single thickness measurements taken on the center of each pellet).



Figure C.2. Voltage profiles during charge/discharge for the 1^{st} cycle of sintered electrode (solid lines) and composite electrode (dashed lines) Li/LTO cells plotted on a (A) gravimetric basis considering just the active material and (B) areal basis. Areal current densities were 1.10 mA/cm² for the sintered electrode and 0.059 mA/cm² for the composite electrode, which for both cells corresponds to C/20 using a mass of active material basis.

Figure C.2 depicts the first charge/discharge cycle for a Li/LTO cell with both sintered and composite LTO electrodes. Note that the sintered electrode cell is the same as that used for Figure 4.2B in the main text. The first discharge cycle of the sintered electrode had a capacity of 119 mAh/g LTO compared to 172 mAh/g LTO for the composite electrode. The sintered LTO electrode also has more polarization on charge and discharge than a conventional composite electrode, reflecting relatively higher resistance both of the LTO sintered electrode relative to the composite electrode and the limitations of Li electrodes at the total current densities and capacities for the sintered electrode LTO cell (1.10 mA/cm² and 20 mAh total cell capacity for discharge).



Figure C.3. Voltage profile for the 2^{nd} charge/discharge cycle of a Li/Li symmetric cell cycled at 0.53 mA/cm² within a voltage limit of -1 V to 1 V and with a time limit of 50 hours.

Figure C.3 shows the second charge/discharge cycle for a Li/Li cell cycled at a rate of 0.53 mA/cm^2 . This cell was the same as that used to provide the data for Figure 4.2C in the main text. The total current density and total current for the Li/Li cell were representative of the lowest rates for the sintered electrode cells (~C/50 for the sintered electrodes), and thus the time limit on the charge and discharge were limited to 50 hours. The time limit was reached for both charge and discharge. Higher rates (e.g.; >1.0 mA/cm²) for Li/Li coin cells led to increased polarization and a fluctuating voltage profile that would reach the 1.0 V voltage cutoff on the first charge/discharge cycle and stop cycling.