Title
Development of Pseudocapacitive Properties in Nanostructured LiMn2O4 as a Fast Charging Cathode for Lithium Ion Batteries

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Development of Pseudocapacitive Properties in Nanostructured LiMn$_2$O$_4$ as a Fast Charging Cathode for Lithium Ion Batteries

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Chemistry

by

Benjamin Lesel

2017
ABSTRACT OF THE DISSERTATION

Development of Pseudocapacitive Properties in Nanostructured LiMn$_2$O$_4$ as a Fast Charging Cathode for Lithium Ion Batteries

by

Benjamin Lesel

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2017

Professor Sarah H. Tolbert, Chair

Pseudocapacitive materials provide a high energy density solution to fast charging, long cycle life energy storage. This work explores the pseudocapacitive characteristics and attempts to optimize nanostructured LiMn$_2$O$_4$ for use as a cathode material in fast charging, long cycle lifetime lithium ion batteries. Because slow kinetics in traditional batteries is linked to long lithium ion diffusion lengths through micron sized grains, the key to achieving pseudocapacitance in most materials is through nanostructuring to reduced diffusion distance. One of the most effective methods for producing nanostructures is through nanocrystal/polymer templating, which produces a porous structure with interconnected nanoscale walls capable of intercalating lithium ions at pseudocapactive rates. To make a full pseudocapacitive lithium ion battery a
reality, however, a pseudocapacitive material of each electrode type, anode and cathode, must be paired. To date, many pseudocapacitive materials have been identified, but nearly all of them are redox active in a voltage range more suitable for anode materials. Recently, we identified a pseudocapacitive cathode material, nanostructured LiMn$_2$O$_4$ which shows impressive rate capabilities. Unfortunately, the improvements came at the cost of energy density, which decreased significantly with decreasing crystallite size. Kinetics for different crystallite sizes, however, increased suddenly below a certain critical crystallite size. We found that this critical crystallite size, below which pseudocapacitance occurred, was linked to a suppression of phase transition in nanoscale LiMn$_2$O$_4$. To address the capacity loss due to dissolution in high surface area nanostructured LiMn$_2$O$_4$ powders, a sol-gel templating method which formed dissolution resistant surfaces was employed. The resulting materials had long needle-like morphology and showed higher capacity and less dissolution than a similarly sized material synthesized with a different structure. It was concluded that the needles of the higher capacity structure were dissolution resistant surfaces along their lengths and therefore maintained higher energy density. In another approach, higher capacity was achieved in nanostructured LiMn$_2$O$_4$ with the addition of magnesium into the crystal structure. It was theorized that the increased capacity came from the magnesium ions stabilizing the surface from dissolution, therefore increasing capacity. This understanding and optimization of nanostructured LiMn$_2$O$_4$ has led to the first scalable pseudocapacitive cathode material that can be effectively used in fast charging, long cycle lifetime lithium ion batteries.
The dissertation of Benjamin Lesel is approved.

Richard B. Kaner

Bruce Dunn

Sarah H. Tolbert, Committee Chair

University of California, Los Angeles

2017
This manuscript is dedicated to my supportive and loving friends and family.

Particularly, my father and mother, Dov and Helene Lesel.
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Previous Publications and Contributions of Co-Authors:

**Chapter 2** is a version of Benjamin K. Lesel, Jesse S. Ko, Bruce Dunn and Sarah H. Tolbert, “Mesoporous LiMn2O4 Thin Film Cathodes for Lithium Ion Pseudocapacitors.” Jesse S. Ko helped with electrochemical measurements and writing of the discussion. I wrote the manuscript and Bruce Dunn and Sarah H. Tolbert helped edit. This manuscript has been published in *ACS Nano*, 2016.

**Chapter 3** is a version of Benjamin K. Lesel, John B. Cook, Yan Yan, Terri C. Lin and Sarah H. Tolbert, “Using Nanoscale Domain Size to Control Charge Storage Kinetics in Pseudocapacitive Nanoporous LiMn2O4 Powders.” John B. Cook helped with electrochemical measurements.
Yan Yan help with porosimetry and kinetic analysis. Terri C. Lin helped with porosimetry. I wrote the manuscript and Sarah H. Tolbert helped edit. This manuscript has been submitted for publication in *ACS Energy Letters*.

**Chapter 4** is a version of Benjamin K. Lesel, Terri C. Lin, Victoria M. Basile, Yan Yan and Sarah H. Tolbert, “Suppression of Phase Transition in Nanoporous LiMn2O4 during Electrochemical Cycling.” Terri C. Lin helped with sample preparation, electrochemical measurements, *in-situ* data collection at the Standford Synchrotron Radiation Laboratory (SSRL) and data processing. Victoria M. Basile helped with sample preparation for the *in-situ* experiments and data processing. Yan Yan synthesized the polymer used in the material synthesis. I wrote the manuscript and Sarah H. Tolbert helped edit. This manuscript will be submitted for publication shortly after this dissertation is filed.

**Chapter 5** is a version of Benjamin K. Lesel, Yan Yan, Nathaniel Szeto, Jiaming Chen, Shauna Robbennolt and Sarah H. Tolbert, “Increasing the Capacity of Nano-Structured LiMn2O4 by Selective Crystallization of Dissolution Resistant Surface Sites.” Nathaniel Szeto and Jiaming Chen synthesized the nanostructured LiMn₂O₄ materials. Shauna Robbennolt helped with transition electron microscopy (TEM) measurements. Yan Yan and I wrote the manuscript and Sarah H. Tolbert helped edit. This manuscript will be submitted for publication shortly after this dissertation is filed.

**Chapter 6** is a version of Benjamin K. Lesel, Jiaming Chen, Nathaniel Szeto, Yan Yan and Sarah H. Tolbert, “The Effects of Mg and Ru Doping on Nanostructured LiMn2O4.” Nathaniel Szeto and Jiaming Chen helped synthesized the material, XRD measurements, and prepare electrodes. Yan Yan synthesized the polymer used in the material synthesis and helped with XPS measurements. I wrote the manuscript and Sarah H. Tolbert helped edit. This manuscript will be submitted for publication shortly after this dissertation is filed.
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PUBLICATIONS AND PRESENTATIONS

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Lesel, B. K.; Ko, J.; Dunn, B.; Tolbert, S. H. “Mesoporous LiMn2O4 Thin Film Cathodes for Lithium-Ion Pseudocapacitors.” *ACS Nano*, **2016**, DOI: 10.1021/acsnano.6b02608

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CHAPTER 1

Introduction

With the increasing global awareness of greenhouse gas effects on the planet, interest in zero emission electric vehicles is becoming more widespread. One major factor hindering the hastened adoption of these vehicles is their low energy density and long charging down times. In an effort to remedy this problem, fast charging electrical energy storage devices have been researched in recent years. There are two common ways electrochemical energy is stored: through double layer capacitance in a capacitor or electrochemically in batteries. Typically, capacitors can charge very quickly but have low energy density, whereas batteries have high energy density but charge slowly. Efforts to increase the energy density of capacitors have been largely concentrated in increasing the surface area of these materials to produce supercapacitors.¹

Unfortunately, however, these supercapacitors can only reach at most 10% of the energy density of lithium ion batteries and thus still require major improvements before they can be used for most mobile applications. An alternative approach to having high energy density and fast charging is to identify and improve the rate limiting step in lithium ion battery charging. In fact, the root cause for slow charging in commercial lithium ion batteries is the slow solid state lithium ion diffusion through the electrode materials. To improve upon battery charge times, reducing the grain size of the electrode materials to decrease solid state diffusion distance is perhaps the best route. As it turns out, by reducing the grain size of most electrochemically active materials below a certain point, new characteristics arise such as increased redox kinetics and improved reversibility of the process. These improvements in material
characteristics lead to improved charge/discharge rates and cyclability of the resulting electrodes. In literature, the term pseudocapacitance is used to describe fast redox processes in electrochemically active materials. Although many accounts of pseudocapacitance occurs primarily on the surface of these materials, intercalation pseudocapacitance has also been identified where ions are transported quickly into and out of the “near surface”. When a materials grain size is small enough, typically in the tens of nanometers regime, the entire material can be considered “near surface”. In order for pseudocapacitance to occur, several conditions must exist including small diffusion distances compared to the diffusion constant of the material; interconnectivity between the grains for easy electron transport; sufficient space between grains to allows for ample surface access for the electrolyte; and a suppression of the typical phase transition that occurs in bulk systems during redox processes. Indeed, a structure that satisfies these parameters is one that is nanostructured and porous; a nanoporous structure.

Synthesizing nanoporous structures generally requires mixing active material precursors or nanocrystals with a soluble template, typically an organic polymer, in a solution phase process that leads to self-assembly upon evaporation of the solvent. Heating the assembled material allows for fusion of the active material into a continuous matrix with pores left behind by the removal of the template. Many examples of materials with nanoporous structures showing these characteristics exist in the literature, such as α-MoO₃, MoS₂ and T-Nb₂O₅, however, all these materials have redox activity versus lithium metal at voltages more suitable for anode materials. To create a full cell battery capable of pseudocapacitive kinetics, pseudocapacitive cathode materials must be discovered to pair with the anodes. Unfortunately, nanostructured cathode materials capable of achieving pseudocapacitance are rare since most require high temperatures (700 °C+) to form the proper crystalline phase, and high temperatures coarsen and destroy fine nanostructure. One outlier as far as crystallization temperature is the cathode
material LiMn$_2$O$_4$, which forms as low as 550 °C, and therefore makes an adequate candidate for forming the necessary nanostructures for pseudocapacity. In fact, many nanostructured LiMn$_2$O$_4$ materials have been fabricated, often by solid state conversion of nanostructured manganese oxides formed by templating and lithium salts. Many of these nanostructured LiMn$_2$O$_4$ materials show effective fast charge/discharge but an in-depth study of the kinetics was never done.

In chapter 2 of this dissertation, we synthesized ~10 nm nanoporous LiMn$_2$O$_4$ via a Mn$_3$O$_4$ nanocrystal/polymer templating method followed by a solid state reaction with lithium salt. Resulting materials had impressive kinetics retaining capacity at charge times into the seconds regime, and improved cyclability compared to bulk. Unfortunately, the capacity of this nanostructured LiMn$_2$O$_4$ was about half that of bulk systems. This low capacity comes from two surface factors that are over expressed in high surface area nanomaterials; one is that the surface is electrochemically inactive and the other is that these surfaces are typically prone to dissolution in standard battery electrolytes when charged. The inactivity is due to Mn$^{2+}$ in surface tetrahedral sites where Li$^+$ sits in the materials interior; because the number of Li$^+$ in tetrahedral sites dictates the materials capacity, having these sites taken by non-Li$^+$ atoms effectively reduces the capacity. The surface dissolution primarily occurs on charge where the inactive portion of the surface dissolves, leaving the uncovered layer to spontaneously reform into the inactive Mn$^{2+}$ rich surface. After a few charges, the electrolyte decomposes into a polymeric protective layer known as the solid electrolyte interphase (SEI), which helps prevent further dissolution of the LiMn$_2$O$_4$ surface.

In chapter 3 of this dissertation, we synthesized nanoporous LiMn$_2$O$_4$ powders of several different crystallite sizes using the same method as the thin films, to understand the relationship between crystallite size, fast kinetics and capacity. Sizes of 10, 20, 40 and 70 nm were prepared and cycled to test their kinetics and capacity. As expected, the capacity of these materials
increased linearly with increase crystallite size. The 10, 20 and 40 nm samples showed similar very fast kinetics and impressive cyclability; The 70 nm sample, however, showed significantly slower kinetics and cyclability compared to the smaller sizes. It was concluded that a critical crystallite size must exist between 40 and 70 nm, below which, the pseudocapacitive properties arise in LiMn$_2$O$_4$.

In chapter 4, we study the mechanism of pseudocapacitance in nanostructured LiMn$_2$O$_4$ by in-situ X-ray diffraction during electrochemical cycling. Because phase transitions during cycling are known to be the main contributing factor to slow ion diffusion through solid materials, we hypothesized that below a certain LiMn$_2$O$_4$ critical grain size, a suppression of this phase transition would occur. In fact, it is well known that bulk LiMn$_2$O$_4$ specifically shows two-phase coexistence during charge and discharge. To study the phase changes occurring in nanoscale LiMn$_2$O$_4$, two powders were synthesized, a 15 nm sample, which had good kinetics and cyclability, and a 50 nm sample, which had poorer kinetics and cyclability. Our results showed that indeed the 50 nm sample showed the expected two-phase coexistence that occurs in bulk LiMn$_2$O$_4$, however, the 15 nm sample showed only a single phase through the entire cycling process and far less shifting than observed in the 50 nm system. From this we concluded that indeed the pseudocapacitive properties observed in smaller crystallite sized LiMn$_2$O$_4$ are linked to a phase suppression during cycling. Combining the results of chapters 3 and 4, we can identify the critical crystallite size at below which phase suppression and therefore pseudocapacitive properties occurs is in the 40-50 nm range.

In chapter 5, we investigate the possibility of improving capacity for finely nanostructured LiMn$_2$O$_4$ by changing the surface morphology to be less prone to dissolution in lithium ion battery electrolytes. Two structures of similar crystallite size were synthesized; one with round nanomorphology (R-LMO) and one with needle-like nanomorphology (N-LMO). Although both materials showed similar pseudocapacitive kinetics, the N-LMO showed nearly 30% more
capacity compared to the R-LMO. It was identified that although the R-LMO had no specific surface site preferences, N-LMO showed an overexpression of <111> oriented surfaces along the lengths of the needles. As it turns out, these <111> surfaces have been identified as more dissolution resistant than other surface sites of LiMn$_2$O$_4$. Manganese X-ray photoelectron spectroscopy (XPS) on the lithium metal counter electrode cycled against an N-LMO electrode showed far less manganese concentration than that of a lithium electrode cycled versus the R-LMO. The decreased manganese concentration found in the lithium cycled against the N-LMO suggests less manganese in the electrolyte, since Mn$^{2+}$ in the electrolyte would naturally plate the lithium metal. These result support the theory that the increased capacity seen in N-LMO is indeed due to decreased dissolution compared to R-LMO, which could be due to the overexpression of dissolution resistant <111> sites on N-LMO.

Chapter 6 explores another method for improving nanostructured LiMn$_2$O$_4$ capacity through means of metal ion doping. By increasing the dopant level of magnesium in LiMg$_x$Mn$_{2-x}$O$_4$, a point is reached where capacity increases by about 15% from the un-doped at the expensive of slightly slower rate capabilities. As magnesium concentration is raised beyond the increased capacity point, capacity also begins to drop as well as the rate. Magnesium XPS of the highest capacity magnesium doped powder revealed magnesium concentration to be higher on the surface than the synthesized stoichiometry. This suggested that most of the Mg$^{2+}$ in the doped sample was concentrated on the surface and could be housed in the tetrahedral sites usually occupied by Mn$^{2+}$ on the surface and Li$^+$ in the interior of un-doped LiMn$_2$O$_4$. Although having Mg$^{2+}$ in tetrahedral sites would still cause the surface of LiMg$_x$Mn$_{2-x}$O$_4$ to be inactive since it displaces the Li$^+$, it is possible that it could allow for increased stability of the surface towards dissolution. We therefore theorized that the highest capacity Mg-doped sample, LiMg$_{0.1}$Mn$_{1.9}$O$_4$, had the optimal surface coverage for the surface area of the nanostructured
material, but that it came at the cost of kinetics as the strength of the surface Mg-O bonds would also make lithium penetration more restricted.

Overall, nanostructured LiMn$_2$O$_4$ capable of pseudocapacitive charge/discharge kinetics and long cycle lifetimes have been identified. Capacity of these materials is reduced linearly with decreasing crystallite size, whereas a sudden increase in kinetics and cyclability are recognized below a certain critical crystallite size between 40-50 nm. The critical crystallite size below which pseudocapacitive characteristics occurs is linked to a suppression of phase change usually seen in large crystallite sized systems. Success was found in improve capacity for nanoscale systems by crystallizing nanostructured LiMn$_2$O$_4$ with dissolution resistant surfaces and magnesium doping. The realization of a pseudocapacitive cathode material means production of pseudocapacitive full cell batteries is possible. These fast charging, long cycle lifetime batteries will allow for significantly higher energy densities than supercapacitors, while maintaining charge times of only a few minutes. This technology is likely to be of great use to our growing energy demands and ideally, could help promote electric vehicle usage over those using petroleum thus minimizing the worlds carbon dioxide production.
1.1 References


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2.1 Introduction

Pseudocapacitive charge storage has the potential to allow for faster charge-discharge rates than conventional battery materials while retaining energy densities much greater than that found in double layer type supercapacitors.\(^1\) In a lithium ion battery material, the kinetics of charge storage are controlled by diffusion of lithium ions within the structure. Intercalation occurs when lithium ions insert into the structure and diffuse to an accessible redox site; for micron sized powders, long diffusion lengths correlate with slow intercalation kinetics. Pseudocapacitance describes similar redox reactions, but without the slow diffusion kinetics. For many years, the term pseudocapacitance was synonymous with surface redox reactions, but more recently, the concept of intercalation pseudocapacitance has been proposed. Extraction/intercalation pseudocapacitance occurs primarily in nanostructured materials when lithium ion diffusion rates are fast, and when diffusion distances are short.\(^2,3\) The primary advantage of intercalation pseudocapacitance is that it utilizes the bulk of the nanostructured material, not just the surface, thus allowing greater energy density to be realized in combination with increased power density.\(^3,4,5\) To date, intercalation pseudocapacitance has been seen in a number of nanostructured anodes, including $\alpha$-MoO$_3$ and $T$-Nb$_2$O$_5$.\(^2,4$ Most of these are layered materials which can accommodate lithium ion diffusion between the layers.\(^2,3,6-13\) Nb$_2$O$_5$, in particular, has an open lattice that allows for fast lithium ion diffusion without significant structural change.\(^14\) The lack of structural change is good not only because it circumvents diffusion limitations associated with the development of new phases, but also because it apparently prevents degradation of the material, allowing for long cycling lifetimes.\(^3,7,12\) To date, however, most quantified examples of intercalation pseudocapacitance have been with
materials that show redox in potential ranges more suitable for applications as anode materials rather than as cathode materials. To make a functioning pseudocapacitive device that shows both high energy and power density, we need to extend these phenomena to materials that show redox in higher potential ranges, and that goal is the motivation for the work presented here.

Currently LiCoO$_2$ is the most widely used cathode material for lithium ion batteries. Although LiCoO$_2$ along with other materials of the form LiMO$_2$ (where M is a transition metal) are layered and show good cycling stability in bulk, they do not show reliable cycling stability when nanostructured for fast lithium ion intercalation.$^{15-17}$ One reason for this is that the insertion and removal of lithium ion results in a phase transition between trigonal and monoclinic lattice structures.$^{15-17}$ Aside from the lack of rapid diffusion kinetics, LiMO$_2$ materials are known to operate in the 3-4 V range versus lithium metal.$^{17,18}$ To increase this potential range above 4 V, while maintaining structural stability, one option appears to be the mixed-valent transition metal spinel LiMn$_2$O$_4$.\textsuperscript{19-34} LiMn$_2$O$_4$ shows activity in the 4-4.5 V range with reasonable structural robustness upon cycling. The structure contains lithium ions within tetrahedral sites that can be repeatedly inserted and removed while the structure remains in the tetragonal phase.$^{17,19-35}$ Because it does not contain a planar or linear channeled structure, however, fast ion intercalation is not observed in bulk versions of this material, but creating nanoscale versions of this material including nanocrystals and nanowires shows promise for improved kinetics.$^{15,19-32}$ One complication noted for LiMn$_2$O$_4$ (LMO) is that discharge rates can be much higher than charge rates, and for many applications, it is fast charging that is key to expanded use.$^{31-34}$ For the work presented here, all charge and discharge rates are the same, so that materials with fast kinetics should be useful for both high output power and fast charging applications.
The use of nanoparticles or wires alone does not solve the diffusion problem unless each individual nanoparticle or nanowire can be exposed to the liquid electrolyte. Nanocrystal based nanoporous materials are one method that can be used to create this idealized architecture. These structures are generally made by templating methods where a hard (e.g. silica\textsuperscript{35}) or soft (e.g. polymer\textsuperscript{36}) template is intimately mixed with the material of interest, and then the template is selectively removed to produce the desired porous structure. Block copolymer templating of preformed nanocrystals is one method that has had much success in creating these nanostructures.\textsuperscript{5,37-42} Prior to co-assembly with the organic polymer, the ligands are stripped from the nanocrystals,\textsuperscript{43} enabling the nanocrystals to loosely fuse together, forming the pore walls.\textsuperscript{37,38} Because micropores are created at the intersections between nanocrystals, the electrolyte effectively penetrates into the pore wall, providing short diffusion lengths for Li\textsuperscript{+} within single nanocrystalline grains. Electronic conduction then occurs through the interconnected walls of the mesoporous material. The short ion and electron path lengths should promote pseudocapacitive behavior in otherwise diffusion controlled systems.

The primary difficulty in creating controlled nanoscale architectures from LiMn\textsubscript{2}O\textsubscript{4} spinel is the fact that the compound is very difficult to produce in soluble form. Fortunately, a synthetic route to LiMn\textsubscript{2}O\textsubscript{4} exists from the solid state conversion reaction between Mn\textsubscript{3}O\textsubscript{4} spinel and LiOH.\textsuperscript{44-47} This is beneficial since there is a large body of literature aimed at making soluble transition metal oxide nanocrystals including Mn\textsubscript{3}O\textsubscript{4}.\textsuperscript{48-64} Additionally, control over both size and composition is relatively easy for these transition metal oxide spinels.\textsuperscript{48-64} The spinel nanocrystals can be ligand stripped and co-assembled with diblock copolymer templates to produce nanoporous networks with homogenous nanosized porosity.\textsuperscript{38} The resulting nanoporous LiMn\textsubscript{2}O\textsubscript{4} materials are useful as charge-storage systems not only because of improved kinetics but also because size effects help alleviate various structural changes that contribute to a drop-off of cycling stability. Examples of such structural problems eased by
nanostructure include Jahn-Teller distortion\textsuperscript{65}, formation of two cubic phases,\textsuperscript{66} loss of crystallinity\textsuperscript{67} and development of microstrain.\textsuperscript{68}

Many of these problems can also be reduced by fabricating non-stoichiometric LiMn\textsubscript{2}O\textsubscript{4}.\textsuperscript{17,65-67} Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} where x≥2 is not a good choice for charge storage at high rates as lithiation at or beyond x=2 causes a transformation of the spinel from cubic to tetragonal symmetry, which results in poor cycling reversibility.\textsuperscript{16} Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} where x<1 is also not optimal as it suffers from reduced capacity. Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} where 2>x>1, however, seems the most promising direction as it allows for a material that does not change phase during cycling or suffer from capacity loss due to lithium depletion. Moreover, the non-stoichiometric nature actually helps solve some cycling problems.\textsuperscript{67}

In this paper we thus report on the development of a polymer templating route for fabricating nanoporous thin films of Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} with 1<x<2. These materials are designed as cathodes for lithium ion based pseudocapacitors and are ideal systems for studying charge/discharge kinetics. They are prepared by a solid-state conversion reaction between Mn\textsubscript{3}O\textsubscript{4} nanocrystal-templated films and LiOH. The structural and electrochemical properties of mesoporous Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} films are examined using a combination of high angle X-ray diffraction (XRD), scanning electron microscopy (SEM), porosimetry, X-ray photoelectron spectroscopy (XPS), and a broad range of electrochemical studies. The results show that the films display pseudocapacitive behavior as a result of the extremely short diffusion lengths and mesoporous nature of the electrode material.

2.2 Results

The fabrication of thin film Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} (1<x<2) was achieved by nanocrystal templating of a precursor phase, followed by a solid-state conversion reaction. First, 7-8 nm Mn\textsubscript{3}O\textsubscript{4} nanocrystals were synthesized in solution from a manganese (II) acetate precursor. These nanocrystals were then dissolved in solution with a block copolymer and dipcoated onto indium-
doped tin oxide (ITO) substrates for electrochemical measurements or silicon substrates for structural characterization. The resulting films were calcined at 425 °C in air to remove the block copolymer template. A solution of LiOH•H₂O was spin coated onto the porous Mn₃O₄ films. The films were calcined again at 500 °C in air resulting in nanoporous LiₓMn₂O₄ (1<x<2) films. The structure of the Mn₃O₄ and LiMn₂O₄ films were characterized using synchrotron high angle X-ray diffraction (XRD), scanning electron microscopy (SEM), porosimetry and X-ray photoelectron spectroscopy (XPS). For the electrochemical investigation a three-electrode flooded cell was used with the LiMn₂O₄ film as the working electrode and Li foil was used for both the counter and reference electrodes. Cyclic voltammetry and galvanostatic analysis were both employed.

The crystalline phase of the initial Mn₃O₄ was determined using grazing incidence XRD. All peaks could be indexed to a single phase of cubic spinel Mn₃O₄ (Figure 2.1a). The broad peak widths indicate the nanocrystallinity of the structure. Using the Scherrer formula and a spherical shape factor, the crystallite size was calculated to be 8.4 nm. The mesoporous structure of the Mn₃O₄ can be seen from the SEM (Figure 2.1b); the sample has a wall thickness of 14.4 nm ± 2.9 nm based on over 100 measurements. This value is slightly larger than the calculated crystallite size, indicating that some walls are composed of multiple crystalline domains. Pore size was also measured from SEM images and determined to be 17.0 nm ± 6.4 nm. This image analysis was then correlated with porosimetry (Figure 2.2a and 2.2b), which indicated that the structure was about 70% porous with an average cage-size of 24 nm, calculated from the adsorption isotherm, and an average neck-size of 15 nm, calculated from the desorption isotherm. It is expected that a top view SEM should show some combinations of cages and necks in a random surface, so the SEM and porosimetry results are in good agreement.

XRD data of the post conversion samples (Figure 2.1c) were indexed exclusively to an over-lithiated spinel LiₓMn₂O₄ (JCPDS: 00-051-1582) with a Li:Mn ratio of about 0.7:1. The
JCPDS of pure LiMn$_2$O$_4$ (00-35-0782) is included in the figure for comparison. Note that excess lithium (when 1<x<2 in Li$_x$Mn$_2$O$_4$) does not change the spinel structure of the material. Only when x≥2 is a transformation to tetragonal Li$_2$Mn$_2$O$_4$ observed. It should also be noted that the tetragonal phase is generally reached by over lithiating the LiMn$_2$O$_4$ structure by electrochemical insertion at the 3 V plateau. Any excess lithium above x=1 but less than x=2 added before heat treatment results in the same cubic spinel as LiMn$_2$O$_4$ but shifts the peaks towards higher q (and 2θ) due to change in the lattice parameters. The peaks are once again broad due to the finite thickness of the walls in the porous structure, as indicated by a crystallite size of 13 nm calculated using the Scherrer equation. Slight wall-thickness growth can be observed by SEM (Figure 2.1d) and was found to be 14.8 nm ± 3.8 nm based on over 100 measurements. Scherrer size calculated here is far closer to the measured value from SEM indicating the formation of more single domain walls after conversion from Mn$_3$O$_4$ to LiMn$_2$O$_4$. The mesoporosity retained by the Li$_x$Mn$_2$O$_4$ (1<x<2) film can also be seen by SEM and average pore size based on over 100 measurements was found to be 25 nm ± 11 nm. Porosimetry (Figure 2.2c and 2.2d) indicated a retained porosity of about 30% for Li$_x$Mn$_2$O$_4$ films of various thicknesses (between 100-300 nm) with no presence of micropores. The fact that the pore fraction does not change with film thickness indicates that the mesopores are most likely interconnected throughout the entire thickness of the material. A somewhat broadened cage-size distribution, calculated from the adsorption isotherm, ranges from 20 nm to slightly over 100 nm with two size maxima at ~30 nm and ~100 nm. The 30 nm pores like correspond to those observed by SEM, while the larger cages likely arise from regions of fused pores, which are not easy to directly quantify in a top view SEM image. Pore fusion likely occurs during the solid state transformation process from manganese oxide to lithium manganese oxide. The neck-size calculated from the desorption isotherm was found to be 22 nm, which combined with the smaller adsorption cage-sizes at 30 nm, nicely brackets the 25 nm average pore size calculated from SEM. The surface area of the mesoporous film was calculated to be 24 m$^2$/g based on a
geometric model that assumes spherical pores with a size of 25 nm and a total porosity of 30%, as determined by toluene adsorption experiments. We note that 25 nm is at the small end of our pore size estimates, making this an overestimate of the real surface area.

The \( \text{Li}_x\text{Mn}_2\text{O}_4 \) \((1<x<2)\) films deposited on the ITO substrates were used directly as working electrodes for determining electrochemical properties. Cyclic voltammetry measurements were made from 3.4 to 4.5 V (vs Li/Li\(^+\)) at various sweep rates ranging from 1 to 100 mV/s (Figure 2.3a and 2.3b). A linear base-line correction was used to offset an ohmic response of the electrolyte at high potentials. Two peaks are present during both lithium removal (anodic sweep) and insertion (cathodic sweep) for all sweep rates. The presence of two peaks is explained in the literature as arising from two slight lattice shifts within the spinel structure.\(^{70}\) At the slower sweeps from 1 to 10 mV/s, the anodic peaks A1 and A2 are at 4.0 V and 4.2 V respectively whereas the cathodic peaks C1 and C2 are at 3.9 V and 4.1 V (Figure 2.3a). A1, which is coupled with C1, corresponds to the first 0.5 moles of lithium removed in \( \text{LiMn}_2\text{O}_4 \) and A2, which is coupled with C2, corresponds to the second 0.5 moles of lithium removal. The peaks correspond to 25 and 75% of lithium removed from stoichiometric \( \text{LiMn}_2\text{O}_4 \) which is where the lattice parameter shifts in the spinel.\(^{70}\)

In stoichiometric \( \text{LiMn}_2\text{O}_4 \) the two anodic peaks correspond to the following reversible two-step process upon delithiation:\(^{70}\)

\[
\text{A1: } \text{LiMn}_2\text{O}_4 \rightarrow \text{Li}_{0.5}\text{Mn}_2\text{O}_4 + 0.5\text{Li}^+ + 0.5\text{e}^- \quad \text{(Theoretical Capacity 74 mAh/g)} \\
\text{A2: } \text{Li}_{0.5}\text{Mn}_2\text{O}_4 \rightarrow \text{Mn}_2\text{O}_4 + 0.5\text{Li}^+ + 0.5\text{e}^- \quad \text{(Theoretical Capacity 74 mAh/g)} \\
\text{A1 + A2: } \text{LiMn}_2\text{O}_4 \rightarrow \text{Mn}_2\text{O}_4 + \text{Li}^+ + \text{e}^- \quad \text{(Theoretical Capacity 148 mAh/g)}
\]

The cathodic peaks correspond to the reverse processes. Since the peaks in figure 2.3 are present at nearly identical positions to those reported for \( \text{LiMn}_2\text{O}_4 \) in the literature\(^{71-73}\), it is presumed that this same process occurs in the slightly over-lithiated \( \text{Li}_x\text{Mn}_2\text{O}_4 \) \((1<x<2)\).\(^{17,65-67}\) However, the excess lithium above \( x = 1 \) can only be accessed at the 3 V plateau, and therefore does not contribute to the 4 V capacity. Additionally, it has been suggested that super-
stoichiometric lithium helps support the spinel structure at the 4 V plateau, increasing cycle life.\textsuperscript{16,20}

Our thin film mesoporous Li\(_{x}\)Mn\(_{2}\)O\(_{4}\) (1<x<2) showed significantly lower overall capacity, compared to the same material with larger grain size.\textsuperscript{29,72-74} At a sweep rate of 1 mV/s (corresponding to a charging time of 20 minutes), a reversible capacity of 65 mAh/g is achieved while that at 10 mV/s (corresponding to a charging time of 2 minutes) is 55 mAh/g. Although the theoretical capacity of LiMn\(_{2}\)O\(_{4}\) is 148 mAh/g, less than half of that value is observed in our materials even at slow scan rates. This reduced capacity is not due to electrolyte inaccessibility to the pores, as films between 100 to 300 nm thick showed the same kinetics and mass normalized capacity, indicating that the mesopores are interconnected within the LiMn\(_{2}\)O\(_{4}\) structure and solvent can efficiently access all parts of the porous film. Similar capacity decreases have been observed previously in LiMn\(_{2}\)O\(_{4}\), as well as other similar nanocrystalline cathode systems, such as LiCoO\(_{2}\) below a certain grain size, and are discussed below.\textsuperscript{15,20,75} To understand the capacity loss, we first examine the CV curves. Nanostructured LiMn\(_{2}\)O\(_{4}\) retains the distinctive double peak structure and the same peak positions as bulk LiMn\(_{2}\)O\(_{4}\).\textsuperscript{20} This suggests that the same physical processes are occurring in both the nanoscale and bulk materials.\textsuperscript{70} One possible explanation for the capacity reduction in certain nanostructured materials is discussed by Obuku, \textit{et al.}\textsuperscript{15} In this paper, the authors discuss how LiCoO\(_{2}\), which normally has cobalt in the +3 oxidation state, has lower oxidation state Co\(^{2+}\) on the surface. Because the transition at the 3.5 V plateau in LiCoO\(_{2}\) is Co\(^{3+}\) to Co\(^{4+}\), these surface Co\(^{2+}\) sites cannot be oxidized electrochemically at these high voltages. With decreasing crystallite size and increasing surface area in the material, a point is reached where Co\(^{2+}\) constitutes a significant fraction of the total cobalt in the system, thus reducing the capacity. Similar effects have been shown to occur in LiMn\(_{2}\)O\(_{4}\). Recent work using HAADF STEM images of the surface of LiMn\(_{2}\)O\(_{4}\) (which should contain exclusively Mn\(^{34+}\)) revealed a spinel structure with reduced Mn\(^{2+}\) in the tetrahedral sites rather than the expected Li\(^{+}\).\textsuperscript{76} The paper indexes this surface.
phase of LiMn$_2$O$_4$ as Mn$_3$O$_4$ which would be unable to undergo a Mn$^{3+}$→Mn$^{4+}$ transition and thus would be inactive at potentials relevant to this system, similar to the LiCoO$_2$. These results are also supported by simulations in the literature, which have shown that the surface of LiMn$_2$O$_4$ is only stable when reduced compared to bulk.$^{77,78}$ An interesting feature of this mechanism for capacity loss is that it explains why the same redox processes are observed in bulk and nanoscale materials, but a portion of the structure is not accessible for redox reactions at the expected voltage.

To understand if this phenomenon is occurring in our system, XPS was collected on a pristine mesoporous Li$_x$Mn$_2$O$_4$ ($1<x<2$) thin film (Figure 2.4a). The data reveal that about 40% of the manganese present on the material surface is in the +2 oxidation state. As discussed above, because the 4 V plateau is associated with oxidation of Mn$^{3+}$ to Mn$^{4+}$, this reduced Mn$^{2+}$ should reduce surface capacity.$^{70}$ To confirm this idea, XPS was also collected on a sample after plasma etching (Figure 2.4b), which was used to remove the majority of the surface layer. In this case, the data show that only 10% of the manganese present is in the +2 oxidation state. This shows that the Mn$^{2+}$ is concentrated on the surface and these reduced surface atoms are likely the cause of the reduced capacity in this nanostructured material.

Galvanostatic cycling was also used to study capacity and capacity fade during repetitive charge-discharge cycles. Galvanostatic discharge curves (Figure 2.5a) show continuously sloping voltages during lithium intercalation and deintercalation, rather than plateaus at distinct voltages, which occurs with bulk and larger crystallite systems.$^{15,20-36}$ These sloping voltage profiles are considered one of the hallmarks of pseudocapacitive behavior.$^1$ At a rate of 50C, this material stores approximately 0.3 moles of lithium per mole of Li$_x$Mn$_2$O$_4$ ($1<x<2$), corresponding to a capacity of around 44 mAh/g. The decrease in capacity with increasing C-rate is consistent with the cyclic voltammetric results, and even at 1000C, this material can still reversibly store approximately 20 mAh/g, corresponding to 0.1 mole of lithium per mole of Li$_x$Mn$_2$O$_4$ ($1<x<2$). It should be noted that at these very fast rates, ohmic polarization may
contribute to capacity loss because of the flooded half-cell geometry used in this work. As a result, capacity values at very high current densities should be considered as a lower limit on the intrinsic capacity of the material. Long-term galvanostatic cycling (Figure 2.6) further shows that at a C-rate of 32C, this material retains 90% of its initial capacity after 265 cycles. It should be additionally noted that the majority of the capacity is not the result of electric double-layer capacity. Assuming a value of 10 µF/cm$^2$ (a typical double layer capacitance$^{79}$) and specific surface area of 24 m$^2$/g, the electric double-layer capacity of the nanoporous Li$_x$Mn$_2$O$_4$ (1<x<2) is only 0.7 mAh/g. This value is negligible compared to the measured capacity of 50 to 65 mAh/g. Therefore the vast majority of capacity in these materials can be attributed to redox processes.

2.3 Discussion

The 30% porosity of the nanoporous Li$_x$Mn$_2$O$_4$ (1<x<2) and small wall-thickness of ~15 nm means that the porous materials presented here have both good pathways for electrolyte penetration throughout the mesoporous electrode structure and high internal surface area enabling the electrolyte to have complete access to the cathode material. The small wall-thickness ensures that the majority of the lithium in this material is located in “near-surface” sites. Here we define “near-surface” sites to be those interior sites that can be kinetically accessed on very short time scales because of short diffusion lengths. We note that true surface redox is likely not available in these materials in this voltage range because of the reduced, inactive surface, as discussed above. While we would not expect the cubic Li$_x$Mn$_2$O$_4$ spinel to show particularly fast lithium ion diffusion rates, the 15 nm wall-thickness represents a very short diffusion length which enables the rapid transport of significant amounts of lithium into the lithium manganese oxide framework.

The simplest indication that mesoporous Li$_x$Mn$_2$O$_4$ (1<x<2) represents a viable pseudocapacitive cathode material comes from the retention of well-defined redox peaks at fast
sweep rates (Figure 2.3). A second indication, also visible in figure 2.3, is the voltage offset between the cathodic (C) and anodic (A) peaks. For the coupled C1-A1 and C2-A2 peaks, the degree of reversibility can be quantified by the separation between peak anodic and cathodic potentials ($\Delta E_p = E_{pa} - E_{pc}$). This separation is a measure of the rate of electron transfer at the electrode surface. For an electrochemically reversible process, $\Delta E_p = 0.059/n$, where $n$ is the number of electrons transferred in the electrode reaction. Figure 2.7 illustrates that up to 10 mV/s, the electron transfer reaction is highly reversible showing a $\Delta E_p \leq 0.059$. Such electrochemical reversibility suggests there is relatively little structural change upon lithiation and delithiation. This feature is important because structural change can lead to degradation of the electrode over time, and so a more stable structure can lead to a longer cycling life-time. At rates above 10 mV/s, the process shows a greater degree of irreversibility, with a corresponding peak shift of the anodic peak to more positive potentials, and the cathodic peak to more negative potentials occurs. This implies that at higher rates, higher overpotentials are necessary to deliver higher currents.

In order to gain greater insight into the reaction kinetics, the rate-limiting mechanisms for this material at both coupled redox peaks was investigated. We assume that the current, $i$, obeys a power-law relationship to the sweep rate, given by

$$i = a\nu^b$$

where $a$ is a constant and $\nu$ is the sweep rate. A $b$-value of 0.5 indicates current that is limited by semi-infinite linear diffusion and a $b$-value of 1 indicates current that is not diffusion limited. The latter includes the electrical double layer contribution as well as pseudocapacitive processes. As mentioned previously, the electric double-layer capacity of the nanoporous Li$_x$Mn$_2$O$_4$ ($1<x<2$) was calculated to be only 0.7 mAh/g, a negligible amount compared to the overall capacity attained from this material. Based on this analysis, we attribute the majority of
the charge storage which is characterized by $b \approx 1$ to arise from pseudocapacitive mechanisms and not from electrical double-layer processes.

Figure 2.8 shows a plot of log peak current vs. log sweep rate that was used to calculate the $b$-values for the lower potential redox peaks (3.9 V and 4.1 V) which are associated with Li$^+$-ion intercalation.\textsuperscript{70-73} For charge times up to 110 s (10 mV/s), the $b$-values are 1.0 or nearly so. This indicates capacitor-like behavior for lithium insertion/extraction for charge/discharge times of up to two minutes. At charge times shorter than 110 s, the $b$-value drops to 0.86 and 0.69 for the 3.9 V and 4.1 V redox peaks, respectively. These values signal the onset of diffusion controlled kinetics for charge/discharge times of less than two minutes.

In a complementary analysis, the current contribution $i$ from the power-law relationship can be separated into two functions that describe capacitive (weighted by $k_1$) and diffusion-limited (weighted by $k_2$) processes as a function of potential:

$$i = k_1v + k_2v^{1/2}.$$

Figure 2.9 illustrates how the diffusion-limited and capacitive processes are distributed over the potential range investigated. The data were taken at the slow sweep rate of 1 mV/s to allow diffusion controlled process to contribute to the total current. Despite this fact, the material is 75% capacitive, with only 25% of charge storage comes from diffusion-controlled processes. As expected the potentials where more diffusion controlled currents arise are associated with the redox peaks.

High levels of capacitive energy storage generally result when diffusion rates are fast and diffusion distances are short. It is thus worth considering if diffusion distance or rate is predominantly responsible for the favorable kinetics in this material. We have thus calculated diffusion constants for each redox peak from cyclic voltammetry using the Randles-Sevcik equation (Figure 2.10). The specific values are included in the caption, but all diffusion constants determined for all peaks, both anodic and cathodic are $\sim 2 \times 10^{-11} \text{cm}^2/\text{s}$. These values are in good agreement with previous measurements on bulk LiMn$_2$O$_4$.\textsuperscript{83,84} Interestingly, the first
reaction (A1 and C1) shows slightly slower kinetics than reaction 2 (A2 and C2). This is good agreement with the fact that the b-value for reaction 1 is slightly lower (less capacitive) than reaction 2, as shown in figure 2.8. Overall, this indicates that shorter diffusion pathways, rather than a change in the diffusion constant, are most likely the source of increased kinetics and the high fraction of capacitive current observed in this system.

Nanoporous Li$_x$Mn$_2$O$_4$ (1<x<2) films with small wall-thickness thus exhibit a number of pseudocapacitive characteristics. The existence of b=1 for reasonably high charge/discharge times, the small voltage offset between redox peaks, and the absence of any structural change upon lithiation and de-lithiation are all consistent with pseudocapacitor behavior. However, there are other features which are inconsistent with a classic capacitive response; the CV is not a ‘box’ and while the decrease in voltage in the galvanostatic experiments has substantial linearity (Figure 2.5a), there is evidence of a shoulder which is not consistent with classic capacitive behavior.

Because the Li$_x$Mn$_2$O$_4$ system has been well studied, there is the opportunity to compare thin film mesoporous materials with previous studies of both bulk and nanoscale materials. Micron sized particles of LiMn$_2$O$_4$ exhibit significantly reduced capacity at faster charge/discharge times.$^{29,30}$ For example, Kiani, et al.$^{29}$ showed that micron-sized powders charged in 30 minutes (2C) deliver a capacity of 40 mAh/g whereas nano-sized powders gave this capacity with 4 minutes of charge (15C). By comparison, our system achieves 40 mAh/g charging and discharging in 36 seconds (100C) in the same potential range. One complication for LMO is that the material can show very high discharge rates, but requires charge at a significantly lower rate.$^{31-34}$ Consider, for example, work on 4 nm Li$_x$Mn$_2$O$_4$ nanowires. Lee, et al.$^{31}$ reported that after charging for 1 hour (1C) followed by discharge in 2 minutes (30C), their material exhibited 50% capacity retention, but no 30C charge data was included. This same behavior of fast discharage is also observed for nanocrystal systems. Shaju and Bruce show that ~50 nm sized LiMn$_2$O$_4$ powders show nearly 90% capacity retention after 1000 cycles using
C/2 charge times and 10C discharge times, further supporting the idea that discharge kinetics are linked to size in LiMn$_2$O$_4$ systems.$^{32}$ To achieve fast charge times as well, however, smaller structures are needed. For the system presented here, 50% capacity retention is achieved with both charge and discharge at 100C (Figure 2.5a).

Although the overall charge storage capacities are not terribly high, the rate behavior and cycle life for Li$_x$Mn$_2$O$_4$ (1<x<2) is very good. Moreover, the ability to charge ~50 mAh/g in one minute (figure 2.11) makes this material interesting for high rate charge storage devices. Additionally, Li$_x$Mn$_2$O$_4$ has the distinction of being the first cathode material to exhibit pseudocapacitive charge storage above 4 V. Finally, because Li$_x$Mn$_2$O$_4$ (1<x<2) is just one member of a large family of related spinel structured lithium transition metal oxide materials, there is opportunity to optimize and improve kinetics, the stability, and even the potential range of similar nanostructured materials.$^{85,86}$

### 2.4 Conclusion

Nanoporous thin films of the cathode material, Li$_x$Mn$_2$O$_4$ (1<x<2) were prepared by solid state conversion in which a nanoporous Mn$_3$O$_4$ thin film was reacted with LiOH. The resulting thin films with 30% porosity and wall-thickness of ~15 nm were characterized using both potentiostatic and galvanostatic cycling to determine their charge storage properties. The reversible lithium-ion capacities were significantly less than theoretical values likely due to over-expression of low oxidation-state Mn defects on the surface which are electrochemically inactive at high voltage, an effect seen in other nanostructured cathode systems.$^{15,20}$ Despite the inactive surface, the small voltage offset in peak potentials at sweep rates up to 10 mV/s, combined with $b$-values close to 1 further indicates that these materials show capacitor-like kinetics. Indeed, kinetic analysis indicates that some 75% of the charge storage is associated with capacitive behavior. The predominance of fast, reversible redox reactions in nanoporous Li$_x$Mn$_2$O$_4$ (1<x<2) is attributed to the direct access of the electrolyte through the mesopores in
combination with the short diffusion path lengths, which stem from the small wall-thickness in these porous materials. Moreover, the small wall-thickness allows for both fast charge and fast discharge; while fast discharge is common in nanostructured cathode materials, fast charging is not usually observed. These results thus demonstrate that nanoporous Li₅Mn₂O₄ (1<x<2) can behave as a pseudocapacitive cathode material with exciting potential for application in high rate, asymmetric, energy storage devices.

2.5 Experimental

**Materials**: The following chemicals were purchased and used as received: oleylamine (90% Aldrich), stearic acid (95%, Aldrich), xylene (98%, Aldrich), manganese(II) acetate (98%, Aldrich). Poly(butylene oxide)-b-poly(ethylene oxide), with a mass ratio of PBO(5000)-b-PEO(6500), a block ratio PBO90-b-PEO114, and with a PDI = 1.09, was purchased from Advanced Polymer Materials. Lithium hydroxide, 1-hydrate, reagent crystals (Acros Organics).

**Synthesis and Ligand Exchange of Mn₃O₄ Nanocrystals**: A previously reported procedure was followed to synthesize 4-5 nm Mn₃O₄ nanocrystals stabilized by oleylamine ligands.²³,⁴⁹ Briefly, 0.17 g manganese (II) acetate, 0.57 g of stearic acid and 3.2 mL of oleylamine were dissolved in 15 mL xylene at 90 °C for 3 hours in air to produce Mn₃O₄ nanocrystals. Mn₃O₄ nanocrystals were washed several times with ethanol before being dispersed in hexane (10-15 mg/mL). To remove the surface passivating ligands, Mn₃O₄ nanocrystals were treated with NOBF₄ according to a previously reported procedure.²³,⁴³ In a typical ligand-exchange reaction, 5 mL of nanocrystal dispersion in hexane was combined with 5 mL of NOBF₄ solution in N,N-dimethylformamide (DMF) (10 mg/mL) with stirring (5 min), or until the nanocrystals were transferred to the DMF phase. The nanocrystals were precipitated with toluene then centrifuged, followed by multiple washings with DMF/toluene and ethanol. The ligand-stripped nanocrystals were dispersed in DMF/ethanol (1:5 v/v) to give a final concentration of 15-20 mg/mL.
Synthesis of Mesoporous Mn$_3$O$_4$ Films: Films were prepared in a manner similar to previous reports$^{23}$. In a typical synthesis, 40 mg of poly(butylene oxide)-b-poly(ethylene oxide) was dissolved in 0.5 mL of ethanol with gentle heating. To this solution, we added 3 mL of the ligand free Mn$_3$O$_4$ in DMF/ethanol (15-20 mg/mL). From this mixture, thin films were produced by dipcoating onto clean, polar substrates (silicon or ITO) at a constant withdrawal rate of 1-10 mm/s with a constant 30% relative humidity. Thermal decomposition of the template was done by a 12 hour ramp to 425 °C in air.

Conversion of Mn$_3$O$_4$ to Li$_x$Mn$_2$O$_4$ Mesoporous Films: Conversion reactions were performed by spin-drying 9.0 µL/cm$^2$ of a 0.25 – 0.75 mg/mL LiOH•H$_2$O solution in ethanol (concentration depends on the film thickness) onto mesoporous Mn$_3$O$_4$ thin films ranging in thickness from 100 – 300 nm. The term “spin-drying” is used to denote a process where an aliquot of solution is spread over a porous sample by slow spin coating and then allowed to dry. All films were thermally converted to Li$_x$Mn$_2$O$_4$ using a 2 hour ramp to 500 °C in air, followed by a 2 hour soak at 500 °C. To optimize the amount of LiOH•H$_2$O used during synthesis, Mn$_3$O$_4$ films were dosed with different amounts of LiOH and heated at 500 °C to yield various stoichiometries of Li$_x$Mn$_2$O$_4$. Samples were then electrochemically cycled to determine which materials showed the characteristic electrochemistry of LiMn$_2$O$_4$. Promising samples were then fully digested and atomic composition was investigated using inductive coupled plasma atomic emission spectroscopy (ICP-AES) to determine Li and Mn content. Samples with the highest capacities and with electrochemical characteristics indicative of LiMn$_2$O$_4$ were all found to be in the range of 1<x<2 for Li$_x$Mn$_2$O$_4$ thin films.

Characterization of Mn$_3$O$_4$ and Li$_x$Mn$_2$O$_4$ Mesoporous Films: X-Ray Diffraction (XRD) was taken using both Synchrotron High Angle X-ray Diffraction (XRD) carried out on beamline 11-3 at the Stanford Synchrotron Radiation Laboratory as well as in-house on a Panalytical X’Pert Pro X-ray Powder Diffractometer using a Bragg-Brentano setup. Scherrer widths were calculated and corrected using peak broadening parameters specific to the instrument setup.
used: Debye-Scherrer and Bragg-Brentano for synchrotron and panalytical instruments respectively. Scanning Electron Microscopy (SEM) images were obtained using a model JEOL JSM-6700F field emission electron microscope with 5 kV accelerating voltage and secondary electron detector configuration. Over 100 measurements were taken using ImageJ to obtain the average wall-thickness and pore size of the Mn$_3$O$_4$ and LiMn$_2$O$_4$ thin films. Thin film Porosimetry on both Mn$_3$O$_4$ and LiMn$_2$O$_4$ films made use of a Sopra model GES5E elipsometric porosimeter using toluene as the adsorbant. Data was analyzed by Spectroscopic Elipsometry Analyzer version 1.4.56. X-ray Photoelectron Spectroscopy (XPS) was taken using a Kratos XPS Axis Ultra DLD spectrometer with a monochromatic Al (Kα) radiation source. Fitting was done using CasaXPS software with Gaussian/Lorentzian 75/25 for Mn $p_{3/2}$ and 30/70 for Mn $p_{1/2}$ peaks. The samples were etched with an Ar beam (raster size 5 mm × 5 mm) for 1 minute. To determine the sample mass, samples were fully dissolved in 1 mL each of concentrated ICP-grade HCl and HNO$_3$ at room temperature and the dissolved solutions were then analyzed for total Mn and Li content using Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). A Varian 720-ES ICP-OES was used to assess the manganese and lithium content, which was used to calculate both the stoichiometry and the active mass of Li$_x$Mn$_2$O$_4$.

**Electrochemical Analysis:** All electrochemical experiments were made in an argon filled glovebox with oxygen and moisture levels below 1 ppm. Electrochemical measurements were carried out in a three-electrode cell using a BIOLOGIC VMP-3 potentiostat. The working electrode consisted of LiMn$_2$O$_4$ films coated onto ITO glass. The electrolyte solution used was 1.0 M LiClO$_4$ in propylene carbonate (PC), and lithium metal was used as both the counter and reference electrodes. Cutoff voltages at 4.5 and 3.4 V vs Li/Li$^+$ were used for cyclic voltammetry and galvanostatic cycling. The active mass was calculated using ICP-OES, as described above.
Figure 2.1. a) XRD and b) SEM of Mn$_3$O$_4$ film on silicon wafer. c) XRD and d) SEM of Li$_x$Mn$_2$O$_4$ (1<x<2) film on silicon wafer.
Figure 2.2. Adsorption and desorption isotherms a) and c) and BJH pore size and wall-thickness distributions b) and d) for nanoporous Mn$_3$O$_4$ a) and b), and Li$_x$Mn$_2$O$_4$ c) and d).
Figure 2.3. Cyclic voltammetry of Li$_x$Mn$_2$O$_4$ (1<x<2) using a lithium counter and reference electrode, cycled between 3.4 and 4.5 V using sweep rates of a) 1, 5 and 10 mV/s and b) 10, 50 and 100 mV/s.
Figure 2.4. X-ray photoelectron spectra of Mn 2p for Li$_x$Mn$_2$O$_4$ (1<x<2) mesoporous thin film a) before plasma etching and b) after plasma etching. Fitting done using CasaXPS software with Gaussian/Lorentzian 75/25 for Mn p$_{3/2}$ and 30/70 for Mn p$_{1/2}$ peaks.
Figure 2.5. a) Galvanostatic charge and discharge curves of Li$_x$Mn$_2$O$_4$ at various C-rates (50C, 100C, 500C, and 1000C) which correspond to current rates of 3.3 A/g, 6.5 A/g, 32 A/g, and 65 A/g, respectively. b) Capacity versus cycle number for discharge at the same four C-rates.
Figure 2.6. Normalized capacity as a function of cycle number for \( \text{Li}_x\text{Mn}_2\text{O}_4 \) \( (1<x<2) \) over 500 cycles at 32C discharge rate. Here 90% capacity retention is maintained at 265 cycles and 80% capacity retention at 445 cycles.
Figure 2.7. $\Delta E_p$ versus log of the sweep rate for $\text{Li}_x\text{Mn}_2\text{O}_4$ (1<x<2) showing the degree of reversibility at various sweep rates.
Figure 2.8. $b$-value plots showing the log(peak current) vs. log(sweep rate) for the 3.9 and 4.1 V intercalation redox peaks.
Figure 2.9. Capacitive contributions to the total current for Li$_x$Mn$_2$O$_4$ ($1 < x < 2$). At 1 mV/s. The current is 72% pseudocapacitive (shaded region).
Figure 2.10. Diffusion coefficients at each peak calculated using the Randles-Sevcik equation with cyclic voltammetry data showing relevant peaks and associated values. It is assumed that the process is reversible in the calculations. The peak current and square root of the sweep rate were plotted and the slope was used to extrapolate the diffusion coefficient. Sample data is included here with the peaks used to calculate the diffusion constants labeled.
Figure 2.11. Rate dependence of the discharge capacity for Li$_x$Mn$_2$O$_4$ (1<x<2) as a function of sweep rate a) and charge time b).
2.6 References


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CHAPTER 3

Using Nanoscale Domain Size to Control Charge Storage Kinetics in Pseudocapacitive
Nanoporous LiMn$_2$O$_4$ Powders

3.1 Introduction

The standard Li-ion battery found in mobile devices today has reasonable energy density, but requires charging on the hour time-scale. Capacitors are capable of charging on the seconds time-scale, but have low energy density. To bridge this gap, one can either make capacitors store more energy by significantly increasing their surface area, such as graphene supercapacitors,$^{1-6}$ or as we will discuss here, make batteries charge faster by reducing the solid state diffusion distance for lithium ions within the electrodes.$^{7-14}$ Indeed, much the kinetic limitation in lithium ion batteries that causes slow charging comes from the slow solid-state diffusion of Li-ions through the micron-length scale powders making up the electrodes. However, if the electrodes were made out of nano- rather than micron-scale powders, diffusion path lengths would be shorter and charging times could be faster. Care must be taken not to increase electrical resistance when using nanoscale materials, however, Li intercalation and extraction are an essential part to the charging and discharging of Li-ion batteries, since redox sites are located within the bulk of the electrode materials. When these diffusion processes are fast due to sufficiently small diffusion lengths with respect to the diffusion coefficient of the material (usually between 10-20 nm), the term intercalation pseudocapacitance is used to describe the fast intercalation/extraction redox processes.$^{7-14}$ To date, many intercalation pseudocapacitive anode systems have been investigated including α-MoO$_3$, MoS$_2$, T-Nb$_2$O$_5$ and others.$^{3-13}$ Pseudocapacitive cathode materials, on the other hand, which typically display higher oxidation/reduction potentials (>3 V vs Li/Li$^+$), are far more scarce.
Although there are several promising fast charging cathode systems which could potentially be pseudocapacitive, such as 17 nm LiCoO$_2$ and 100 nm LiVPO$_4$F, only VOPO$_4$ nanosheets and 15 nm nanoporous LiMn$_2$O$_4$ have effectively characterized the mechanism.\textsuperscript{14-17} One reason for the lack of pseudocapacitive cathode materials is the high crystallization temperature required to synthesize most cathode materials. This high crystallization temperature makes it difficult to form fine nano-structured materials, making them hard to use in sol-gel chemistry. This in turn makes them hard to use with solution phase processing such as polymer templating, which is one of our primary methods for making electrically interconnected yet still nanosized electrode materials.\textsuperscript{18} Despite these problems, fabrication of nanostructured cathode materials capable of intercalation pseudocapacitance is necessary for full cell fast charging Li-ion batteries.

In general, improving nano-scale architectures for intercalation pseudocapacitance is complex and requires optimization of many parameters. Simply reducing the grain size of a powder from the micron-scale to the nano-scale is not enough to improve kinetics. A typical slurry electrode consists of active material powder, conductive additives such as carbon black, and a binder such as PVDF. Active material consisting of individual nano-sized grains incorporated into the slurry can produce electrodes that are kinetically slow due to poor electrical conductivity between nanosized grains and reduced electrolyte penetration into regions of agglomerated nanoparticles, even though Li-ion diffusion lengths are short. One way to reduce the grain size and still maintain good conductivity and electrolyte penetration, is to use micron sized powders of porous materials with nano-scale pores and walls. These arrangements are commonly fabricated via soft or hard templating of nanocrystals or sol-gel precursors, which produces a porous structure when the template is removed.

Unfortunately, with many nanostructured systems, new issues can arise due to the increased surface area. Specifically, either reduced or oxidized electrochemically inactive surfaces can form which can reduce overall capacity in systems with high surface areas. Anode materials can have oxidized surfaces, such as MoO$_2$ with an
inactive MoO₃ surface or Si with an inactive SiO₂ surface. By contrast, cathode materials can have reduced surfaces, such as LiCoO₂ and LiMn₂O₄, which show surface Co²⁺ and Mn²⁺, respectively, while the bulk is composed entirely of 3+ and 4+ transition metal ions. LiNi₀.₈Co₀.₁₅Al₀.₅O₂ also suffers from an inactive surface layer of improperly mixed cations. Moreover, it’s high temperature of crystallization (~800°C) makes it particularly difficult to nanostructure. Some pseudocapacitive anode materials, such as MoS₂ and Nb₂O₅, don’t seem to suffer from inactive surfaces and can thus be fabricated as small as needed for intercalation pseudocapacitive applications.

To achieve full cells, optimized nanostructured cathode materials requires the most attention, and spinel LiMn₂O₄ is one of the most promising candidates. Although the capacity of LiMn₂O₄ is lower than the layered cathode materials, it is the easiest to fabricate into nanostructures due to its low crystallization temperature of ~550°C. This is in stark contrast to the layered cathode materials like LiCoO₂ and LiNi₀.₈Co₀.₁₅Al₀.₅O₂, which require temperatures several hundreds of degrees higher to form. Because of the low crystallization temperature of LiMn₂O₄, nanostructures can easily be synthesized through solid state conversions of nanostructured manganese oxides such as MnO₂ or Mn₃O₄ mixed with a lithium salt. When heated to temperatures around 550°C, the nanostructure remains intact and the correct crystal structure is achieved. Additionally, LiMn₂O₄ contains no particularly expensive or toxic elements, making it both affordable and environmentally benign. The electrochemical window of LiMn₂O₄ occur between 3.3V and 4.5V, which is nearly ideal as it is high enough to give a good cell voltage, but not so high that it causes electrolyte decomposition.

In our previous report, we show that LiMn₂O₄ is capable very fast charge and discharge when finely nanostructured on conductive thin films. The capacity was reduced, however, due to the electrochemically inactive surface discussed above. We
expect capacity and charge/discharge rate to be inversely proportional, and so in this letter, we study nanoporous LiMn$_2$O$_4$ materials with various crystallite sizes. It is important to note that we will be focusing on the kinetics of both charge and discharge in nanostructured LiMn$_2$O$_4$, since much of the literature in nanostructured LiMn$_2$O$_4$ is primarily focused on improved discharging rates. To maximize discharging capacity, slow charging can be employed.$^{29-31}$ The data presented here thus helps shed light on the different capacity and kinetic behavior seen throughout nanostructured LiMn$_2$O$_4$ in the literature. We note that earlier studies have shown crystallite size dependent trends for LiMn$_2$O$_4$ cycled below the cubic-to-tetragonal transition.$^{20}$ Cycling through this transition destabilizes the structure, however, so is not relevant for typical cathode operation.

Many nanostructured, porous LiMn$_2$O$_4$ systems have been explored in the literature with various crystallite sizes and electrochemical performances.$^{30,32-34}$ As mentioned above, we focus here on the LiMn$_2$O$_4$ literature that show fast kinetics for both extraction and intercalation of Li-ions. One such example is hollow LiMn$_2$O$_4$ nanofibers with crystallite sizes of ~60 nm which shows 120 mAh/g charge capacity at 1C rate and retains 75% capacity retention at 10C.$^{32}$ Another example is nanoporous LiMn$_2$O$_4$ spheres with crystallite size around 20 nm which has 100 mAh/g charge capacity at 1C and retains 90% of this capacity at 10C.$^{33}$ It should be noted that some systems are less crystalline due to lower heating and often show slower kinetics as a result.$^{35,36}$ For example, polymer templated nanostructured LiMn$_2$O$_4$ heated to 500°C with 15 nm crystallite size shows 92 mAh/g charging capacity at 1C with 85% capacity retention at 10C.$^{34}$ In this letter, we show kinetic analysis of a series of samples made in the same way and then flash crystallized at high temperatures to increase the domain size. We find increasing capacity with increased crystallite size and decreasing
charge/discharge kinetics, but the non-linear nature opens the potential for material optimization.

3.2 Results and Discussion

Nanoporous LiMn$_2$O$_4$ powders were fabricated by polymer templating of Mn$_3$O$_4$ nanocrystals, followed by a solid-state conversation reaction with LiOH to form the LiMn$_2$O$_4$ spinel phase at 550°C for 2 hours. Full synthetic details are provided in the SI. The thickness and crystallinity of the LiMn$_2$O$_4$ walls was then modified by a high temperature coarsening step at 700, 800 or 900°C for 1 minute. This processed four nanoporous LiMn$_2$O$_4$ powder samples with increasing crystallite sizes and wall thicknesses that were used for electrochemical kinetic analysis. Figure 3.1a shows the X-ray diffraction patterns of all four nanoporous powders along with their average crystallite size calculated from the Scherrer equation. All patterns match LiMn$_2$O$_4$ (JCPDS card 00-35-0782). As expected, samples heated to lower temperatures show broader peaks corresponding to smaller crystallite sizes. The sample heated at 550°C for 2 hours gave a crystallite size of 10 nm; when heated for an additionally 1 minute at 700°C, 800°C and 900°C, the crystal size grew to 20 nm, 40 nm and 70 nm, respectively. Figure 3.1b shows SEM images of the four LiMn$_2$O$_4$ samples with different crystallite sizes. The SEM images show that the samples sintered at the lowest temperatures show the smallest grain size, which corresponds well the Scherrer analysis. Nitrogen sorption of the samples is shown in Figure 3.2. Wall-thicknesses for 10, 20 and 40 nm calculated from the desorption isotherm are in good agreement with the calculated Scherrer-size. The 70 nm sample was not included as its surface area was too small for effective isotherms to be generated without significant scale-up.

Slurry electrodes of the nanoporous LiMn$_2$O$_4$ powders were prepared using 75% active mass, 10% carbon black, 5% carbon fibers and 10% PVDF with a final LiMn$_2$O$_4$
mass loading of 1-2 mg/cm². Swagelok cells using the various porous LiMn₂O₄ electrodes were prepared in a glovebox with Li metal as the counter electrode and 1 M LiPF₆ in EC:DMC 1:1 as the electrolyte. Charging and discharging was always done at the same rate. The samples were cycled galvanostatically at rates of 5, 10 and 20C (Figure 3.3a) with 1C defined using the theoretical current density of 148mA/g. The first galvanostatic charge/discharge curves for each sample at 5, 10 and 20C can be seen in Figure 3.4. The capacity increases with increasing crystallite size as the amount of electrochemically inactive surface is reduced.¹⁴,¹⁵,²⁰ To better separate the effects of the inactive surfaces from capacity loss at high rate, capacities were also normalized to their 5C rate and the capacity drop with increasing rate was examined (Figure 3.3b). Surprisingly, the kinetics are rather similar for the 10 nm, 20 nm and 40 nm samples, but drop significantly for the 70 nm sample. Figure 3.3c shows that in addition to dramatically better rate behavior, the 40 nm sample also retains ~75% capacity after 2000 cycles at 10C, whereas the 70 nm sample shows significant capacity fade of ~50% after just 500 cycles at 10C.

To better understand the differences in these samples, we examined the charge storage kinetics using sweep rate dependent cyclic voltammetry (CV). CV curves for the four LiMn₂O₄ samples with sweep rates (v) of 1, 0.5 and 0.2 mV/s are shown in figure 3.5. The redox peaks in the CV curves are associated with bulk redox processes in LiMn₂O₄ during Li⁺ intercalation and detrination.³⁷ Greater polarization shifts can be seen with increasing sweep rate, particularly for larger crystallite sizes. Fitting of this data can be used to differentiate the diffusion controlled current (normal battery intercalation, which varies as v¹/²) from the capacitive current (which should vary linearly with the scan rate, v) for each given voltage (V) using the equation ¹⁻¹⁴

\[ i/V = k_1 \cdot v + k_2 \cdot v^{1/2} \]  
(1)
The current at any given sweep rate can then be divided into a capacitive and a diffusion controlled or standard battery-intercalation based component. The 0.2 mV/s sweep rates for each crystallite size shown in figure 3.5 contain shaded regions which correspond to the capacitive contribution to the current responses at every voltage. The percentage of the current that is shaded is therefore the percent capacitive character for a given material at slow rate, when both capacitive and diffusion controlled processes can occur. Note that there is less capacitive character around the redox peaks for all samples which indicates that these bulk (i.e, non-surface) redox process are the slowest. The 10, 20 and 40 nm samples show significantly improved capacitive character around the peaks compared to the 70 nm sample, which supports the idea of phase change suppression in the smaller systems. As such, the smaller crystallite sized samples, which showed better kinetics in galvanostatic cycling, also show increased capacitive character in this kinetic analyses. Capacitive character increases with decreasing crystallite size, with the exception of the 10 nm sample, which is slightly less capacitive than the 20 nm sample, likely due to reduced crystallinity in this lower temperature sample. Close inspection of the capacitive contributions again shows that the 10, 20 and 40 nm samples are very similar, and that the 70 nm sample shows a significantly reduced capacitive fraction.

An alternative analysis maps a single exponent (b) onto the sweep rate dependent data that can vary between 0.5 and 1, with a b-value of 0.5 again representing diffusion controlled processes, and a b-value of 1 representing capacitive processes. Here we focus only on the peak current, so that $i_{peak}$ varies as $\nu^b$, given by equation 2. $^{35,36}$

$$\log(i_{peak}) = b\log(\nu) + C$$  (2)
Figure 3.6 shows the b-value analysis plots for all samples for the anodic (charge) peaks with both charge and discharge data summarized in Table 1 with visual guidance from Figure 3.7. For 10 nm and 20 nm samples, b-values around 0.9 were calculated, clearly suggesting highly capacitive redox processes. The 40 nm sample displayed b-values averaging around 0.76, implying more mixed behavior. The 70 nm sample’s average b-value of 0.67 indicates that Li⁺ intercalation and deintercalation in this sample is dominantly diffusion controlled.

It is interesting to speculate about the origin of the significant difference in kinetic behavior that occur with increasing crystallite size. These changes may result from suppression of the phase transitions that normally occur in bulk LiMn₂O₄ upon lithiation and delithiation.³⁷ Such suppression of phase transition is seen in other nanoscale systems and is correlated with faster kinetics.⁶,⁷,³⁹,⁴⁰ One would expect suppression of phase transition to also affect long term cyclability since phase changes are a large contributor to capacity fade over many cycles. The data presented here suggest that such phase change suppression would likely occur between 40 nm and 70 nm crystallite size in LiMn₂O₄ with some blurring of the range occurring due to polydispersity on the crystallite sizes of each sample. Samples just below this critical size (apparently ~40 nm) should show the best combination of good capacity due to a limited amount of inactive surface area, and good rate capabilities. This is further supported by previous reports on LiMn₂O₄ which have suggested that a critical size exists around ~40 nm, below which a solid solution mechanism takes place when cycled at the cubic to tetragonal transition (occurring below 3 V vs Li/Li⁺).¹⁵ Our work confirms this value and additionally shows that this phenomenon occurs not only below the 3 V range, but additionally in the more practical 4 V range.

### 3.3 Conclusion
Nanoporous powders of the cathode material, LiMn$_2$O$_4$ were prepared by solid state conversion of a nanoporous Mn$_3$O$_4$ powder with LiOH. The resulting powders were flash crystallized at different temperatures leading to four distinct average crystallite sizes: 10, 20, 40 and 70 nm. The powders were characterized using both potentiostatic and galvanostatic cycling to determine their charge storage properties. Reduced capacity was observed in smaller crystallite sized LiMn$_2$O$_4$ powders due to over expression of inactive surface sites but charge storage kinetics were fast due to shorter Li-ion diffusion lengths. Kinetic analysis of the nanoporous powders showed that in general, smaller crystallite size gave increased capacitive character. The capacitive character was similar for 10, 20 and 40 nm samples (70-85 % capacitive) and differed from the 70 nm sample (~50 % capacitive). The large drop in capacitive character at 70 nm could result from suppression of Li-intercalation induced phase changes below 70 nm domain sizes. This idea is supported by long term cycling data for the 70 nm sample, which drops to 50% capacity retention before 500 cycles, while the 40 nm sample retains ~75 % capacity after 2000 cycles. Because the 40 nm sample has similar kinetics to the smaller crystallite sizes but has higher capacity, it is perhaps the most ideal of the crystallite sizes studied here for practical applications as a fast charging pseudocapacitive cathode material.

The prevalence of fast charging and discharging as well as stable long term cycleability of the smaller nanoporous LiMn$_2$O$_4$ powders is ascribed to the direct access of the electrolyte through the porous structure, in combination with the short diffusion path lengths and possibly phase change suppression. These results suggest that nanoporous LiMn$_2$O$_4$ around 40 nm crystallite size may be a suitable cathode material for fast charging lithium ion batteries.

3.4 Experimental
**Materials.** The following chemicals were purchased and used as received: oleylamine (90% Aldrich), stearic acid (95%, Aldrich), xylene (98%, Aldrich), manganese(II) acetate (98%, Aldrich), lithium hydroxide, 1-hydrate, reagent crystals (Acros Organics). Poly(butylene oxide)-b-poly(ethylene oxide), with a mass ratio of PBO(5000)-b-PEO(6500), a block ratio PBO90-b-PEO114, and with a PDI = 1.09, was purchased from Advanced Polymer Materials.

**Synthesis and Ligand Exchange of Mn3O4 Nanocrystals.** A previously reported procedure was followed to synthesize 4-5 nm Mn3O4 nanocrystals stabilized by oleylamine ligands. Briefly, 0.17 g manganese (II) acetate, 0.57 g of stearic acid and 3.2 mL of oleylamine were dissolved in 15 mL xylene at 90 °C for 3 hours in air to produce Mn3O4 nanocrystals. Mn3O4 nanocrystals were washed several times with ethanol before being dispersed in hexane (10-15 mg/mL). To remove the surface passivating ligands, Mn3O4 nanocrystals were treated with NOBF4 according to a previously reported procedure. In a typical ligand-exchange reaction, 5 mL of nanocrystal dispersion in hexane was combined with 5 mL of NOBF4 solution in N,N-dimethylformamide (DMF) (10 mg/mL) with stirring (5 min), or until the nanocrystals were transferred to the DMF phase. The nanocrystals were precipitated with toluene then centrifuged, followed by multiple washings with DMF/toluene and ethanol. The ligand-stripped nanocrystals were dispersed in DMF/ethanol (1:5 v/v) to give a final concentration of 15-20 mg/mL.

**Synthesis of Nanoporous Mn3O4 Powders.** Powders were prepared in a manner similar to previous reports. In a typical synthesis, 280 mg of poly(butylene oxide)-b-poly(ethylene oxide) was dissolved in 2.8 mL of ethanol with gentle heating. To this solution, we added 11.6 mL of the ligand free Mn3O4 in DMF/ethanol (15-20 mg/mL). This mixture was gently mixed for a few minutes and then poured into a glass petri dish to evaporate overnight. Thermal decomposition of the template was done by heating using a 12-hour ramp to 425 °C in air followed by cooling naturally to room temperature.
Conversion of Mn3O4 to LiMn2O4 Nanoporous Powders. Conversion reactions were performed by vacuum infiltration of a 10 mg/mL LiOH•H2O solution in ethanol into an evacuated vial of the Mn3O4 powder. Briefly, 80 mg of Mn3O4 nanoporous powder was crushed in a mortar and pestle and transferred to a septa vial. The septa vial with powder inside was subjected to a 100-300 mTorr vacuum via a needle inlet for 2-3 hours. Before infiltration, the vacuum line was closed but vacuum not turned off nor vial exposed to ambient pressure. A needle with 2.4 mL of the sonicated 10 mg/mL LiOH•H2O solution (1.1x stoichiometry of Li addition to make LiMn2O4) was injected by simply poking through the septacap and allowing the contents of the syringe to be pulled into the vial. The powder filled solution bubbled for several seconds before transferring via pipette to a mortar and pestle to dry. After drying for several hours, the white/brown powder was crushed, scraped and mixed well before transferring to an aluminia crucible and heating in a muffle furnace at 550 °C in air for 2 hours with a 1-hour ramp up to 550 °C. For larger crystal sizes of 20, 40 and 70 nm, a second heating step was implemented involving sandwiching 15-20 mg of the 10 nm LiMn2O4 powder between two 2 x 3 cm silicon wafers and holding them together with long stainless steam tongs clamped at one end. This sandwich was then inserted into a tube oven at 700, 800 and 900 °C for 1 minute to produce 20, 40 and 70 nm LiMn2O4 samples, respectively.

Characterization of LiMn2O4 Nanoporous Powders. X-Ray Diffraction (XRD) was taken using an in-house Panalytical X’Pert Pro X-ray Powder Diffractometer using a Bragg-Brentano geometry. Scherrer widths were calculated and corrected using Bragg-Brentano peak broadening parameters. Scanning Electron Microscopy (SEM) images were obtained using a model JEOL JSM-6700F field emission electron microscope with 3 kV accelerating voltage and secondary electron detector configuration.
**Electrochemical Analysis.** All powders were turned into slurry electrodes using 75% active material, 10% carbon black, 5% carbon fiber, and 10% PVDF using NMP as the solvent. Mass loading of all electrodes was approximately 2 mg/cm². Lithium metal was used as the counter electrode within a Swagelok cell for all LiMn₂O₄ electrodes with a Safeguard glass fiber separator and a 1.0 M LiPF₆ in ethylene carbonate : diethylene carbonate 1:1 as the electrolyte solution. Cutoff voltages of 4.5 and 3.0 V vs Li/Li⁺ were used for both cyclic voltammetry and galvanostatic cycling. All charging and discharging was done at the same rates.
Figure 3.1: a) XRD of nanoporous LiMn$_2$O$_4$ powders with different crystallite sizes obtained by thermal coarsening of the smallest samples. Scherrer domain sizes and heating conditions are shown on the figure. b) Low (top) and high (bottom) resolution SEM images of nanoporous LiMn$_2$O$_4$ powders with different average crystallite sizes (shown on the image). The images show both the primary and secondary particle sizes. All larger domain size samples were made by thermal coarsening of the 10 nm material.
Figure 3.2: Nitrogen porosimetry adsorption/desorption isotherms a), b) and c) and d) desorption wall-thickness distribution for 10, 20 and 40 nm LMO samples.
Figure 3.3: a) Galvanostatic capacity testing at 5, 10 and 20C for four sizes of nanoporous LiMn$_2$O$_4$ powders as slurry electrodes. Smaller samples have lower capacity due to an increased fraction of inactive surface atoms. b) Charge time versus normalized capacity for nanoporous LiMn$_2$O$_4$ powders with different crystallite sizes. Samples with domain sizes up to 40 nm show similar capacity loss at higher rate, but the kinetics slow down appreciably for the 70 nm sample. c) Comparison of long term galvanostatic rate testing at 10C for 40 nm and 70 nm LiMn$_2$O$_4$ samples. The 70 nm sample shows rapid capacity fade, while the 40 nm sample shows much more stable cycling.
Figure 3.4: First cycle charge and discharge curves 5 (black), 10 (blue) and 20C (red) rate galvanostatic discharge curves for all nanoporous LiMn$_2$O$_4$ powders with average crystallite sizes shown in the figure.
Figure 3.5: CV curves sweep rates of 1 (green), 0.5 (red) and 0.2 (black) mV/s for all nanoporous LiMn$_2$O$_4$ powders with average crystallite sizes shown on the figure. Shaded fits to equation 1 are shown within the 0.2 mV/s curve. Total percent capacitive contribution for each sample is noted in the bottom left corner of each plot. All samples with average crystallites sizes less than 70 nm show dominantly capacitive behavior.
Figure 3.6: $b$-values for the two anodic (charge) peaks (A1 and A2) calculated from the slope of the logged peak current versus the logged sweep rate for all crystallite sized samples.
Table 3.1: b-values for anodic (charge) and cathodic (discharge) peaks for all crystallite sized samples.

<table>
<thead>
<tr>
<th>Peak</th>
<th>10 nm</th>
<th>20 nm</th>
<th>40 nm</th>
<th>70 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.89</td>
<td>0.90</td>
<td>0.77</td>
<td>0.68</td>
</tr>
<tr>
<td>A2</td>
<td>0.89</td>
<td>0.91</td>
<td>0.73</td>
<td>0.66</td>
</tr>
<tr>
<td>C1</td>
<td>0.94</td>
<td>0.95</td>
<td>0.86</td>
<td>0.70</td>
</tr>
<tr>
<td>C2</td>
<td>0.89</td>
<td>0.85</td>
<td>0.66</td>
<td>0.63</td>
</tr>
<tr>
<td>Average</td>
<td>0.90</td>
<td>0.90</td>
<td>0.76</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Figure 3.7: CV of 40 nm sample displaying anodic (A1 and A2) and cathodic (C1 and C2) peaks. Note that the coupled pairs, A1/C1 and A2/C2 are reverse reactions of each other, respectively.
3.5 References


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Chapter 4

Suppression of Phase Transitions in Nanoporous LiMn$_2$O$_4$ during Electrochemical Cycling

4.1 Introduction

Improvements in battery technology are essential to meet the demand for today's wide range of mobile electronics and electric vehicles. Improvements, particularly in charging speed and cyclability of Li-ion batteries, are paramount for broadened and sustained use. Many of the kinetic limitations in today's commercial batteries are due to long solid state Li-ion diffusion distances in micron sized electrode powders. Reducing these solid state Li-ion diffusion distances by fabricating smaller sized electrode powders can lead to improved kinetics.$^{1-5}$ When fast kinetics are observed in electrode materials, the term pseudocapacitance is used to describe the fast near surface redox reaction. When these near surface redox reaction extend into the bulk of a nanoscale material and can occur without a structural phase transition, the fast insertion (intercalation) and removal (detercalation) of Li-ions within the material has been termed intercalation pseudocapacitance.$^{1-5}$ These fast kinetics arise when solid state diffusion lengths within the materials are sufficiently small, usually due to nanostructuring, compared to the Li$^+$ diffusion coefficient in the material. In addition to short solid state diffusion distances, the fast kinetics of intercalation pseudocapacitance are characterized by electrical interconnections between the active material grains and effective electrolyte penetration between the particles to reach an effective surface area.$^{4-21}$ For materials that normally undergo phase transitions upon Li$^+$ cycling, suppression of those phase transitions in finite size is also needed.$^{6-19}$ Optimization of the first two parameters leads to porous nanostructures which have been studied and optimized for many materials. When the crystallite size is sufficiently small, suppression of
phase transition can also occur and has been demonstrated using *in-situ* X-ray diffraction for a number pseudocapacitive anode materials such as MoO$_2$, MoS$_2$ and TiS$_2$.\textsuperscript{6-8} This phase suppression is important since phase transitions play a major role in the sluggish kinetics of bulk Li-ion intercalation and deintercalation. These sluggish kinetics arise when new phases undergo nucleation and growth, a process that can becomes the rate limiting step in solid state lithium ion diffusion. Additionally, phase transitions cause slight structural deterioration with each cycle, which can contribute to capacity fade over many cycles.\textsuperscript{22-24} The mechanism of capacity reduction from phase transitions has been largely contributed to the fracturing of particles, which lose contact to the electrode matrix.\textsuperscript{22-24}

To date, many pseudocapacitive materials have been identified through electrochemical kinetic techniques, which reveals their redox processes to be largely capacitive (non-diffusion controlled) by separating the current response at any given voltage into a diffusion controlled and non-diffusion controlled component.\textsuperscript{5-13,18,19} Among these identified pseudocapacitive materials, nanostructured LiMn$_2$O$_4$ stands out as a material with a high enough voltage (> 3.2 V vs Li/Li$^+$) to be ideal for the positive electrode in Li-ion batteries.\textsuperscript{13-18} Because pseudocapacitive cathode materials are needed to complete a pseudocapacitive full cell, understanding the nature of charge storage in nanostructured LiMn$_2$O$_4$ and other pseudocapacitive cathodes is of significant importance. Many other cathode materials, however, are not as easy to nanostructure as LiMn$_2$O$_4$, since LiMn$_2$O$_4$ has a relatively low crystallization temperature (550 °C vs 700-900 °C for many other materials), which allows for fabrication of fine nanostructures without fear of coarsening. Additionally, LiMn$_2$O$_4$ is less toxic and cheaper than many other commercial cathode materials and exhibits relatively fast kinetics even in the bulk.\textsuperscript{25}

Our previous work on pseudocapacitive LiMn$_2$O$_4$ includes a kinetic study where nanoporous materials with various crystalline domain sizes from 10 to 70 nm were compared.\textsuperscript{18} From this work we recognized that the electrochemical properties of nanostructured LiMn$_2$O$_4$ below a
crystallite size of 40 nm exhibited a relatively sharp change compared to bigger sizes. Nanoporous materials with crystallite sizes below 40 nm seemed to show significantly more capacitive current than the larger 70 nm domain sample. The smaller domain sizes nanoporous materials also showed greatly improved cyclability when compared to materials with the larger crystallite size of 70 nm. From these data, it was hypothesized that a critical grain size exists, below which the material behaved as a pseudocapacitor, possibly due to suppression of Li\(^+\) induce phase transitions. It is well known that structural changes occur in bulk LiMn\(_2\)O\(_4\) during cycling, including a two-phase coexistence and modest lattice expansions/contractions upon lithium deintercalation/intercalation, respectively.\(^{26}\) Indeed it has been hypothesized that the disturbance in the structure due to this phase change and two-phase co-existence is responsible for the poor cyclability observed in bulk LiMn\(_2\)O\(_4\) systems.\(^{26}\) Additionally, previous reports have used indirect methods to show that phase changes in nanoparticles of LiMn\(_2\)O\(_4\) below 40 nm in size are suppressed upon Li\(^+\) addition to the structure (< 3 V vs Li/Li\(^+\)).\(^{27}\) This suppression, however, has never been demonstrated for the primary voltage region in LiMn\(_2\)O\(_4\) above 3 V vs Li/Li\(^+\) where Li\(^+\) is removed during cycling.

In this paper, we aimed to study the changes in the crystal structure of nanostructured LiMn\(_2\)O\(_4\) while cycling above 3 V versus Li/Li\(^+\) for small and large crystallite sizes of 15 nm and 50 nm, respectively. Synchrotron in-situ XRD was employed during charging and discharging in order to structurally understand the improved kinetics and cyclability observed in the 15 nm nanostructured LiMn\(_2\)O\(_4\) system compared to the 50 nm system. The structures of both the 15 and 50 nm LiMn\(_2\)O\(_4\) are made in similar ways with porous structures and as close to single domain wall thicknesses as possible.
4.2 Results and Discussion

Two nanoporous powders of LiMn$_2$O$_4$ with interconnected grains were synthesized via a templated sol-gel method with crystallite sizes of 15 and 50 nm. The sol-gel method used involved combining lithium and manganese salts in a ratio of 1.1:2 to reach the stoichiometric ratios needed for slightly over lithiated Li$_{1.1}$Mn$_2$O$_4$. The salts were dissolved in a 50 mg/mL aqueous colloidal suspension of 60-80 nm diameter poly(methylmethacrylate) (PMMA) nanospheres. Solution were mixed and heated in air at 95 °C until the volume of the mixture was reduced to 2/3 of the initial solution volume by evaporation and the solution became viscous. The resulting gels were poured into borosilicate petri dishes and heated at 550 °C for 10 hours and 750 °C for 10 hours, for the 15 and 50 nm samples, respectively. Crystallite sizes were calculated from diffraction peak widths using the Scherrer equation, as shown in Figure 4.1(a)(b). From the Scanning Electron Microscopy (SEM) in Figure 4.1(c)(d) the nanoscale structure of the powders can be observed, which appear to be made of interconnected particles in a porous structure with wall thicknesses similar to the XRD domain size. This architecture allows for optimal electrical connectivity between the particles as well as ample pathways for electrolyte to permeate during cycling.

Slurry electrodes were prepared from both 15 and 50 nm LiMn$_2$O$_4$ nanostructured powders. Slurries were made using a mixture of 75% active powder, 10% carbon black, 5% carbon nanofibers and 10% polyvinylidene fluoride (PVDF) in an N-methyl-2-pyrrolidone (NMP) solvent. Polished stainless steel foil was used as the current collector for the slurries; this material was chosen to minimize peak interference with LiMn$_2$O$_4$ in XRD, compared with aluminum foil (see Figure 4.2). Resulting slurries with mass loadings around 2 mg/cm$^2$ were punched into electrodes with surface area 0.71 cm$^2$ and loaded into Swagelok cells in a glovebox (under argon atmosphere) with lithium metal as the counter electrode, LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte, and a glass fiber separator. Four such cells
were prepared, two with 15 nm nanostructured LiMn$_2$O$_4$ and two with 50 nm nanostructured LiMn$_2$O$_4$. One cell of each sample was used for galvanostatic long term cycling and cyclic voltammetry (CV) while the other was precycled for use in the *in-situ* experiment. Figure 4.3 shows the results of long term cyclability for the 15 and 50 nm samples as well as the results of kinetic studies based on CV curves measured at different scan rates (see Figure 4.4 for CVs).$^5$-$^{13,18,19}$ The 15 nm nanostructured LiMn$_2$O$_4$ shows superior capacity retention over 3,000 cycles, compared to the 50 nm sample. This disparity suggests that the 15 and 50 nm samples have divergent structural evolutions during cycling, which could potentially be explained by the lack and presence of a phase transition, respectively. Additionally, a clear disparity in the percent capacitive contribution between the two nano samples can be observed by using the $k_1/k_2$ kinetic analysis discussed earlier,$^5$-$^{13,18,19}$ where the 15 nm sample is upwards of 90% capacitive, while the 50 nm sample is only 74% capacitive. The high capacitive fraction in the 15 nm domain size material suggests that this sample displays intercalation pseudocapacitance, a process where non-diffusion controlled kinetics are accompanied by Li$^+$ intercalation without a phase transition.$^1$-$^5$ All diffusion controlled processes observed in the CVs for both samples are concentrated near the redox peaks, which further reinforce the possibility of structural evolution playing a key role in the performance differences between the two samples.

Galvanostatically precycled cells were cycled at a rate of C/5 in a Swagelok cell to assess stability of the electrodes before transfer to coin cells for the *in-situ* study (see Figure 4.5 for precycle charge/discharge curves). The Swagelok cells with the precycled samples were then opened in a glovebox and the LiMn$_2$O$_4$ electrodes were transferred into coin cells with a lithium metal anode, LiPF$_6$ in EC:DMC as the electrolyte, and a glass fiber separator. The coin cells each had ~3 mm diameter round holes cut into the top and bottom caps and were sealed with kapton tape to allow the X-rays to pass through the cell during the *in-situ* experiments.
In-situ synchrotron X-ray diffraction was performed on coin cells containing 15 and 50 nm domain size nanoporous LiMn\textsubscript{2}O\textsubscript{4} powders during galvanostatic cycling at C/5. Resulting diffraction for the 50 nm sample over one charge and discharge cycle at C/5 can be seen in Figure 4.6. Fully discharged patterns (blue) with peak positions of \(~2.6\ \text{Å}^{-1}\) and \(~4.0\ \text{Å}^{-1}\) correspond to the \(\langle311\rangle\) and \(\langle511\rangle\) Bragg reflections of LiMn\textsubscript{2}O\textsubscript{4}, respectively. Both peaks shift towards higher Q-value and therefore lower d-spacing upon lithium delocalation (charge) and return to their initial values upon intercalation (discharge). Upon close inspection, however, one can see that the shift in both the \(\langle311\rangle\) and \(\langle511\rangle\) peaks is monotonic only up to \(~4.1\ \text{V vs Li/Li}^{+}\) upon charging, at which point a second peak, shifted to higher Q, appears, giving the impression of significant peak broadening. As the original peak loses intensity, this new peak again shifts linearly to highest voltages reached in this study. Upon discharge, this same broadening/two peak effect appears to take place between 4.0 V and 3.95 V. Guiding lines have been added to the stacked diffraction patterns in figure 4.6, showing the trajectory of the peak shifts from the fully discharged state to the full charged state and back to the discharged state for both the \(\langle311\rangle\) and \(\langle511\rangle\) reflections. The lines help emphasize the fact that the broadening is actually a transition region involving two-phase coexistence between the fully charged and fully discharged states. To reinforce this observation, \(\langle311\rangle\) and \(\langle511\rangle\) Bragg reflections were fit to Gaussians using peak fitting software (PeakFit) and the resulting peak positions and peak widths are shown in Figure 4.7. The total peak shifts for the 50 nm \(\langle311\rangle\) and \(\langle511\rangle\) patterns were calculated to be \(\Delta Q = 0.0456\ \text{Å}^{-1}\) and 0.0738 \text{Å}^{-1}, respectively. Peaks which appeared broaden compared to the pristine peak widths were fit with two Gaussians to represent regions of two-phase coexistence. The peak widths accompanying each fit are also included in Figure 4.7 and are given as the full width at half max height (FWHM). A relatively low spread is observed for the FWHM, particularly given the inclusion of multiple Gaussians in the two-phase coexistence region, which indicates that our model is correct. If instead, the reflections for the 50 nm sample are fit to only one Gaussian across the entire voltage range, we find that the
FWHM shows marked broadening only in the region around the phase transition, as expected (Figure 4.8).

The existence of two-phase coexistence in the 50 nm domain size nanoporous LiMn$_2$O$_4$ sample during both charge and discharge indicates that for this crystalline domain size of 50 nm, a first order phase transition occurs upon cycling with Li$^+$, similar to that seen in bulk systems. A first order phase transitions here is classified as having a discontinuity in the first derivative of free energy and a discontinuous change in unit cell volume, both with respect to Li-ion displacement. That discontinuous change in unit cell volume appears as the two phase coexistence seen in both figures 4.6 and 4.7. This suggests that much like in the bulk, de-intercalation/intercalation of Li-ions in 50 nm domain size nanoporous LiMn$_2$O$_4$ requires kinetically limited nucleation of a new phase, likely followed by propagation of the phase front across each grain. This high energy process should directly affect the kinetics of these systems, leading to a relatively smaller fraction of capacitive charge storage and more diffusion controlled processes. Since the phase transitions occur at the galvanostatic plateau or the peak in the CVs, we expect to see most diffusion controlled current around the peaks in CV, which we do in fact observe in the 50 nm system (Figure 4.3). Additionally, because the nucleation and growth requires the formation of a 2-phase boundary, we would expect wear and tear on the system to be significant during charge and discharge. That wear and tear experienced during cycling should lead to reduced capacity retention over many cycles as the active material cracks and loses electrical connectivity, which indeed we do observe for the 50 nm sample (Figure 4.3). From this we can deduce that the relatively slow charge/discharge kinetics and poor cyclability seen in the LiMn$_2$O$_4$ with a crystallite size greater than 50 nm is due to a rate-limiting and structurally disruptive first order phase transition that occurs upon Li$^+$ extraction and reintercation. In contrast to the nanoporous LiMn$_2$O$_4$ powders with domains sizes on the order of 50 nm that show two-phase coexistence, diffraction from the 15 nm domain size sample shows very
different structural evolution upon charge and discharge. Figure 4.9 shows the resulting synchrotron X-ray diffraction patterns for the 15 nm LiMn$_2$O$_4$ sample as it is charged and discharged at C/5. A smooth transition in peak position can be observed for both the <311> and <511> Bragg reflections of LiMn$_2$O$_4$ during cycling. The patterns for the fully discharged 15 nm sample (blue) show peak positions similar to that of the 50 nm sample but with far less shifting and no apparent two-phase coexistence. Figure 4.10 shows peak positions and widths obtained by fitting all data with a single Gaussian. Resulting FWHM values show little deviation throughout the charge and discharge cycle, indicating that the data is well fit with a single Gaussian. Moreover, the total shifting of the <311> and <511> peaks is calculated to be $\Delta Q = 0.020 \text{ Å}^{-1}$ and $0.028 \text{ Å}^{-1}$, respectively, which is only about 40% of the total shifting observed in the 50 nm sample.

The absence of two separate peaks in 15 nm LiMn$_2$O$_4$, the smooth shift in peak position, and the relatively small magnitude of the peak shift all indicates a continuous free energy function and no discontinuous volume change upon lithium detercalation/intercalation. This, in turn, indicates that any phase transitions occurring in the 15 nm domain size material are second order, unlike that of the 50 nm sample which we concluded was first order. Mechanistically, a second order phase transition for solid state de-intercalation/intercalation of Li-ions can be represented by a solid-solution mechanism. Within a solid-solution reaction, the entirety of the material de-intercalates/intercalates lithium simultaneously, without the need for nucleation and growth of a new phase. This effect allows for lithium to pass in and out the structure without formation of grain boundaries and thus eliminates much of the wear and tear on the material. This, in turn, reduces the probability of parts of the material losing electrical connections with the slurry matrix, thus increasing capacity retention over many cycles, which we indeed see with the 15 nm sample in Figure 4.3. Additionally, the lack of a two-phase intermediate means less of a kinetic barrier for detercalation/intercalation on charge/discharge, leading to faster and more
capacitive cycling kinetics in the 15 nm sample. Finally, the reduced shifting in Q-spacing up Li$^+$ deintercalation/intercalation means less flexing of the overall crystal structure during charge and discharge, which in turn means a more reversible process.

We thus conclude that the improved kinetics and cyclability observed in the 15 nm domain size sample compared to the 50 nm domain sample is a result of phase suppression in the 15 nm crystallite size nanoporous LiMn$_2$O$_4$. The observation of a bulk-like phase transition in 50 nm domain size materials, but its suppression in materials with 15 nm domains, supports the existence of a critical crystallite size for the onset of pseudocapacitive behavior in LiMn$_2$O$_4$, above which phase transitions occurs and below which, phase transitions are suppressed. In general, the improved kinetics observed when phase transitions are suppressed in redox active materials are associated with intercalation pseudocapacitance.$^6$-$^8$ We thus conclude that the 15 nm sample exhibits intercalation pseudocapacitance, whereas the 50 nm sample shows only standard surface or redox pseudocapacitance, combined with battery-like intercalation at the interior of each domain. The largest domain size where these nanoporous powders can be fully cycled without a phase transition would thus correspond to the critical size for the onset of intercalation pseudocapacitance. Taking into consideration our previous work on kinetics of LiMn$_2$O$_4$ nanoporous powders, large kinetic and cyclability differences were observed between 40 and 70 nm crystallite sized LiMn$_2$O$_4$ samples.$^{18}$ We can combine the results of that work with this work, to narrow our determination of the critical crystallite size for nanoporous LiMn$_2$O$_4$ to be between 40 and 50 nm. These results agree with the previously referenced work on the cubic to tetragonal transition that occurs below 3 V vs Li/Li$^+$ in LiMn$_2$O$_4$ and corresponds to the addition of Li$^+$ to the LiMn$_2$O$_4$ structure. That work placed the critical size for the onset of solid solution behavior to be around 43 nm.$^{27}$ We note that it is not obvious that the critical size for both phase transitions should be the same, given that different combinations of interfacial energies are involved. Knowing the critical crystallite size for pseudocapacitance in LiMn$_2$O$_4$ is
very useful for optimizing capacity, cyclability, and kinetics with a goal of producing fast charging cathode material for Li-ion pseudocapacitors.

4.3 Conclusion

Two nanoporous LiMn$_2$O$_4$ powders were synthesized via a solgel templating method yielding average crystallite sizes of 15 and 50 nm. Electrochemical testing of these powders revealed that the 15 nm domain size sample had significantly improved kinetics and cyclability compared to the 50 nm sample. To understand if the disparity in electrochemical performance was due to a difference in structural evolution during charge and discharge, in-situ synchrotron X-ray diffraction was utilized during cycling to study the phase transitions taking place within the materials. Resulting XRD patterns from the 50 nm domain size material showed two-phase coexistence using both the $<311>$ and $<511>$ Bragg reflections upon Li$^+$ extraction and reintercalation. By contrast, XRD patterns from the 15 nm cycling showed no evidence of two-phase coexistence, suggesting that Li$^+$ induced phase changes were suppressed in the smaller domain size sample. We hypothesize that this phase transition suppression leads to both improved cyclability and improved charge storage kinetics in the small domain size material. Combining this data with other electrochemical studies allows us to identify the critical point at which phase change suppression and thus intercalation pseudocapacitance emerges for LiMn$_2$O$_4$; this size was estimated to be between 40 and 50 nm.

4.4 Experimental Section

Synthesis of 50 nm poly(methylmethacrylate) (PMMA) template: The PMMA spheres were prepared by emulsion polymerization of methyl methacrylate (Aldrich) monomer (MMA) using ammonium persulfate (APS, Alfa Aesar) as the initiator in deionized water; the method is a
modified version of an established method from the literature. First, 165 mL DI water were bubbled with nitrogen for 20 min under stirring to remove any oxygen. Then, 0.3 mL ammonium lauryl sulfate (Aldrich), which serves as a surfactant, and 12.55mL of MMA were added. The APS initiator solution was prepared separately by dissolving 0.075 g APS in 10 mL non-degassed water. The initiator solution was then added to the surfactant and monomer solution at 65 °C under stirring. The solution was heated to 73 °C and reacted for 3 h. As-prepared colloidal PMMA solution has a concentration of about 50 mg/mL, and were used without further purification. The average size of the PMMA colloids was determined to be 70 nm based on SEM.

**Synthesis of 15 nm LiMn$_2$O$_4$:** In this method, 2.2 mmol of lithium acetate dihydrate (Sigma) and 4.0 mmol of manganese (II) acetate (Sigma) were mixed with 7.5 mL of the 50 mg/mL aqueous solution of 50 nm PMMA colloids. The solution was then heated and stirred in a round bottom flask for 20 minutes at 90 °C in an oil bath to evaporate part of the water. The resulting viscous solution was poured into a glass petri dish and left to dry for several hours in a fume hood. The resulting solid was heated in a muffle furnace with a ramp of 50 °C/hour from room temperature to 550 °C and soaked for 1 hour. The nano-sized LMO powder was obtained by scraping the solid from the petri dish surface.

**Synthesis of 50 nm LiMn$_2$O$_4$:** This synthetic method was almost the same as the 15 nm LiMn2O4 synthesis described above, except as noted here. The inorganic salts used were 2.2 mmol of lithium acetate (Sigma) and 4.0 mmol of manganese (II) nitrate tetrahydrate (Sigma). Also, the final solid formed in the petri dish was heated at 50 °C/hour from room temperature to 750 °C and soaked for 10 hours.

**Slurry electrode and cell fabrication:** Typically, 36.5 mg of nanostructured LiMn$_2$O$_4$ powder was ground in a mortar and pestle with 5.0 mg of carbon black (Super P) and 2.5 mg carbon fiber (Sigma) for 5 minutes. Approximately 100 mg of a 5% polyvinylidene fluoride (PVDF)
solution in N-Methyl-2-pyrrolidone (NMP) was added to the homogenized powder along with 10 additional drops of NMP. The resulting slurry was doctor bladed onto a stainless steel substrate with a height of ~0.3 mm. The slurry was then placed under a heat lamp for 1 hour to dry, and then transferred to a vacuum oven heated to ~130 °C while pulling vacuum overnight. The dried slurry electrode sheet was then punched out using a 0.71 cm$^2$ puncher and the electrodes transferred to Swagelock cells which were assembled with Li metal in a glove box with 1M LiPF$_6$ in 1:1 EC:DMC as the electrolyte, and a glass fiber separator.

**Electrochemical Analysis:** Swagelock cells were cycled using a 4-channel Bio-Logic VSP potentiostat controlled using EC-Lab version 10.4 software with LiMn$_2$O$_4$ as the positive electrode, Li as the negative and Li as the reference. Samples were cycled using both galvanostatic and potentiostatic methods to produce charge/discharge curves and cyclic voltammetry used in the kinetic analysis (from 0.2, 0.5 and 1 mV/s).

**In-situ Preparation and Measurements:** After precycling, the electrodes were taken out of the Swagelock cells in an Ar-filled glovebox and reassembled into coin cells with 3 mm Kapton tape windows for the *operando* studies. Kapton was chosen for its combination of X-ray transparency and low gas permeability. The coin cells were stored in an Ar atmosphere until cycling was performed to further prevent oxygen and water exposure. All *operando* cycling was performed at 0.22 °C.

**Operando studies on 15 and 50 nm domain size nanoporous LiMn$_2$O$_4$:** Operando powder X-ray diffraction (XRD) was performed in a transmission geometry at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 using an X-ray energy of 12300 eV. *Operando* data was collected using a MAR 345 Image Plate with 130 mm work distance, which corresponded to a Q range from Q = 0 to 5.0 Å$^{-1}$. All diffraction data was plotted as a function of the scattering vector, $Q = \frac{4\pi}{\lambda} \sin(\theta) = \frac{2\pi}{d}$ prior to fitting; here $\theta$ is half of the scattering angle and
\( \lambda \) is the wavelength of the incident radiation. All diffraction peaks were normalized to the intensity of the Li peak at \( Q = 1.34 \text{ Å}^{-1} \) using Wxdiff and Area Diffraction Machine. Backgrounds subtraction of all spectra were later performed in Origin; diffraction from a blank cell (a regular coin cell with Li metal, a separator and Kapton window but no active material) and a linear subtraction was used as the background. Peaks were then fit using PeakFit version 4.11 using Gaussian functions with an additional linear background subtraction.
Figure 4.1. XRD patterns indicate both a) 15 nm and b) 50 nm domain size samples are phase pure LiMn$_2$O$_4$; average domain sizes were calculated from these patterns using the Scherrer equation. SEM shows images show that both the c) 15 nm and d) 50 nm domain size materials are made of interconnected particles in a nanoporous network.
Figure 4.2. XRD of aluminum (orange), stainless steel (blue) and JCPDS 35-0782 for LiMn$_2$O$_4$ (black). Peaks for aluminum overlap with LiMn$_2$O$_4$ peaks more than the stainless steel. <311> and <511> peaks are clearly unhindered by stainless steel peaks and thus were used for comparison.
Figure 4.3. a) Long term galvanostatic cycleability and b) and c) cyclic voltammetry at 0.2 mV/s with inlayed capacitive contribution for 15 nm and 50 nm domain size nanoporous LiMn$_2$O$_4$ samples cycled in Swagelok cells versus Li metal in LiPF$_6$ EC:DMC 1:1 electrolyte.
Figure 4.4. Cyclic voltammetry used in the $k_1/k_2$ kinetic analysis for a) 50 nm and b) 15 nm nanoporous LiMn$_2$O$_4$. Sweep rates used were 1 mV/s (red), 0.5 mV/s (blue) and 0.2 mV/s (black).
Figure 4.5. Charge and discharge curves for Swagelok cells precycled at C/5 for a) 50 nm and b) 15 nm nanoporous LiMn$_2$O$_4$. 
Figure 4.6. *In-situ* XRD patterns of the 50 nm domain size LiMn$_2$O$_4$ sample during charge and discharge. The $<311>$ and $<511>$ peaks show substantial shifting as well as the existence of a two-phase coexistence region. Dotted lines have been added to help guide the eye for the two-phase coexistence. The total discharge capacity of this cycle was 66 mAh/g.
Figure 4.7. Peak positions and full width at half max values for all *in-situ* XRD patterns of the 50 nm domain size LiMn$_2$O$_4$ sample during charge and discharge. The <311> and <511> peak positions are fit with one peak until two peaks were needed to maintain the peak width. Full width half max values are relatively constant for all patterns, including the two peak coexistence regions, suggesting proper fits. The total change in $Q$-spacing was found to be 0.0456 Å and 0.0738 Å for the <311> and <511> peaks, respectively.
Figure 4.8. Peak positions and full width at half max values for all *in-situ* XRD patterns of the 50 nm LiMn$_2$O$_4$ sample during charge and discharge fitting to a single peak. Higher full width at half max values are observed at the area where two-peak coexistence was observed.
Figure 4.9. *In-situ* XRD patterns for the 15 nm domain size LiMn$_2$O$_4$ sample during charge and discharge. The <311> and <511> peaks show modest shifting with no visible two-phase coexistence region, suggesting solid solution behavior. Dotted lines have been added to help guide the eye. The total discharge capacity of this cycle was 50 mAh/g.
Figure 4.10. Peak positions and full width at half max values for all *in-situ* XRD patterns of the 15 nm domain size LiMn$_2$O$_4$ sample during charge and discharge. The <311> and <511> peak positions are fit with one peak for all patterns. Full width half max values are relatively constant for all patterns, suggesting proper fits. The total change in Q-spacing was found to be 0.0201 Å and 0.0277 Å for the <311> and <511> peaks, respectively. The total change in Q-spacing for the 15 nm domain size sample is around 40% of that for the 50 nm domain size sample.
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CHAPTER 5

Increasing the Capacity of Nano-Structured LiMn$_2$O$_4$ Pseudocapacitors by Selective Crystallization of Dissolution Resistant Surface Facets

5.1 Introduction

In a typical lithium ion battery, charge and discharge times are kinetically limited by long Li-ion solid state diffusion through micron-length-scale powders in the cathode material. Because of the boom in battery operated mobile electronics such as phones and electric vehicles, however, we are experiencing an ever increasing demand for faster recharge times without greatly diminishing energy density. To answer this call, pseudocapacitive electrode materials capable of overcoming the slow solid state limitations of their predecessors have been studied in recent years.$^{1-5}$ These materials undergo the same kind of redox processes experienced in typical batteries, but can operate at power densities at least an order of magnitude greater than those currently used in most commercial electrodes thanks to shorter Li-ion diffusion distances.$^{1-5}$ Currently, carbon-based double layer supercapacitors are used in most high power applications, but these materials have significantly lower energy densities than lithium ion batteries.$^6$-$^9$ Pseudocapacitors, by contrast, maintain the same order of magnitude energy density as lithium ion batteries, while still having the capability to deliver high power densities. The fast kinetic abilities observed in pseudocapacitive materials is due to fast solid state diffusion processes, which arise when the diffusion length in the solid state is short compared to the diffusion coefficient of the material.$^{1-5}$ Although some materials have innately high diffusion coefficients, pseudocapacitance can be achieved in a broader range of systems by nanostructuring conventional materials such that solid state diffusion lengths are short.$^{3,5,10-25}$ We find that ideal pseudocapacitive nanomaterials are created by making materials with interconnected particles arranged in a porous network, so as to facilitate both electrolyte...
diffusion through the material and electrical connectivity between the grains. To date, many pseudocapacitive nanomaterials have been identified such as MoO$_3$, MoS$_2$, T-Nb$_2$O$_5$, LiMn$_2$O$_4$ among others. Of the many materials studied for pseudocapacitive kinetics, LiMn$_2$O$_4$ has a high enough voltage to be particularly interesting as a cathode in lithium ion pseudocapacitors. LiMn$_2$O$_4$ is indeed an exciting candidate for fast charging cathodes, as nanostructuring it is relatively easy due to its low crystallization temperature. LiMn$_2$O$_4$ is also attractive as a cathode since it is cheaper and less toxic than other common cathode materials such as LiCoO$_2$, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, LiNi$_x$Co$_{2-x}$Mn$_y$O$_2$ and the like. It should be noted that although LiMn$_2$O$_4$ was originally rejected as a viable commercial cathode material due to poor cyclability in bulk, much more promising behavior is observed in nanostructured material with crystalline sizes below 40 nm. Although fast charge/discharge kinetic and good cycling stability are observed in nanostructured LiMn$_2$O$_4$, materials with crystallite sizes below 40 nm also show capacity reduction which worsens with decreasing crystallite size and increasing surface area. This reduction in capacity compared to bulk is partially due to an inactive surface which contains Mn$^{2+}$ in 8a tetrahedral sites, which is the site where active Li$^+$ sits in the bulk. While these inactive surface sites are the most discussed reason for low capacity in nanostructured LiMn$_2$O$_4$, additional capacity loss arises from surface dissolution of Mn during the first charge, before the solid electrolyte interphase forms to protect the surface. In our previous work, we attempted to find the crystallite size that gave the best balance of fast kinetics and reasonable capacities. A better option, however, is to address the fundamental capacity loss mechanism, so that capacity can be improved without increasing crystallite size, thus retaining the ideal kinetics found in smaller domain size materials. Although coating LiMn$_2$O$_4$ with ALD and other external modifications can be effective in stabilizing the surface and preventing dissolution, these coatings add weight to high surface area nanomaterials, which can reduce the
overall capacity of the system. As it turns out, however, although all surfaces of LiMn$_2$O$_4$ are susceptible to Mn$^{2+}$ rearrangement, the (111) surface has been shown to be resistant to dissolution in common Li-ion electrolytes. Therefore, synthesizing nanostructured LiMn$_2$O$_4$ with selectively more (111) surface sites should result in higher capacity for the resulting material.

Previous reports have in fact managed to fabricate high capacity nanostructured LiMn$_2$O$_4$ by having dominantly (111) surfaces along the length of nanowires or rods. To form these structures, however, first a manganese oxide was formed with the desired nanostructure and then converted into LiMn$_2$O$_4$ by a solid state conversion using lithium salts. This two-step route is used to fabricate nearly all highly nanostructured LiMn$_2$O$_4$ structures since the manganese oxide precursors are far easier to solution process into impressive nanostructures via inorganic (hard) or polymer (soft) templating than their lithiated counterpart. Hard or soft templating is particularly common in nanostructuring materials for pseudocapacitance as they tend to form good electrolyte pathways and keep interconnectivity between grains for electrical connectivity as mentioned previously. Although templating is relatively easy to scale, the two-step route is less than ideal compared to a single step method for industrial applications.

One alternative to this two-step process is to use a polymer template directly with lithium and manganese salts in a sol-gel type synthesis to form nanostructured LiMn$_2$O$_4$ in a single crystallization step without the manganese oxide intermediate. Although sol-gel polymer templating of LiMn$_2$O$_4$ has been done, it typically requires the use of environmentally harmful additives such as resorcinol and has no selectivity with regard to surface structure. In other sol-gel systems, however, the anion in salt precursors has been extensively used to obtain preferential surface faceting. By combining the concept of selective surface faceting with a one pot sol-gel polymer templating method, a cheap method of producing (111) surface site
dominant nanostructured LiMn$_2$O$_4$ should be possible. This (111) surface dominated structure should show all the benefits of nanostructuring LiMn$_2$O$_4$ including fast rate kinetics and improved cycle life-time while being more resistant to dissolution and therefore retain more capacity than a structure without the (111) surface selectivity.

Herein we thus report an environmentally benign polymer templated, aqueous sol-gel synthesis where we form nanoporous LiMn$_2$O$_4$ materials with and without dominant (111) surface faceting for use as cathode materials for lithium ion batteries. The nanostructured LiMn$_2$O$_4$ powders produced using acetate salt precursors showed no faceting and had a rounded morphology (R-LMO) with no dominant facets. The nanostructured LiMn$_2$O$_4$ powder produced using nitrate salt precursors formed needle-like morphology (N-LMO) with (111) dominant faceting along the length of the needles. The structural and electrochemical properties of both R-LMO and N-LMO are examined using a combination of high angle X-ray diffraction (XRD), scanning electron microscopy (SEM), N$_2$ porosimetry, high resolution transmission electronic microscopy (HR-TEM), and a range of electrochemical studies including the use of X-ray photoelectron spectroscopy (XPS) to look at dissolved lithium plated on the counter electrode. The results show that both nanostructured LiMn$_2$O$_4$ materials have comparable kinetics but that the N-LMO displays higher capacity than the R-LMO.

5.2 Results and Discussion

Fabrication of R- and N-LMO made use of a sol-gel reaction where either acetate or nitrate Li and Mn(II) salts, respectively in a molar ratio 1.1 to 2 were mixed with colloidal poly(methyl methacrylate) spheres of 70 nm average diameter in water and heated at 95 °C for 30 minutes to evaporate water until the solution became viscous. The resulting solution was poured into a glass petri dish and allowed to sit for several hours to evaporate the remaining water before heating to 550 °C with a ramp of 50 °C/hour and soaking for 1 or 10 hours for R- or
Figure 5.1 shows the resulting XRD patterns, adsorption/desorption isotherms from N\textsubscript{2} porosimetry and resulting BJH pore size distributions for the two nanostructured powders. All peaks in both XRD patterns index to pure Li\textsubscript{1.1}Mn\textsubscript{2}O\textsubscript{4} (JCPDS: 00-035-0782) with Fd3m space group. Scherrer widths calculated for both patterns gave similar average crystallite sizes of 15 nm and 13 nm for R- and N-LMO, respectively. N\textsubscript{2} porosimetry shows BET surface areas on the same order of magnitude for both R- and N-LMO of 17 m\textsuperscript{2}/g and 67 m\textsuperscript{2}/g, respectively. The disparity in surface area can be understood from the BJH adsorption and desorption pore size distributions. Note that although the vocabulary of porosimetry analysis terms measured values as ‘pores’ and ‘porosity’ that it in fact measures all free space within a material, pore or not. Although the space between the nano-needles of N-LMO may not be considered ‘pores’ they are none the less included in total porosity. Unlike R-LMO which demonstrates a range of pore sizes from 1-100 nm, N-LMO demonstrates a fairly uniform adsorption distribution from 10-50 nm representing the spaces between the needles and a unimodal distribution for pores between the interconnected needle clusters from 50-70 nm. The disparity in surface area and pores size distribution between the two samples originates from the differing nanostructures of the two LiMn\textsubscript{2}O\textsubscript{4} systems which can be seen from SEM in Figure 5.2(a) and (b). R-LMO seems to show fused, rounded particles with pores formed only between the fused inorganic walls. By contrast, N-LMO exhibits more of a pom-pom like structures made of many needle-like projections which appear to have considerable space between them. This structure results in both the higher surface area and the higher pore volume of the N-LMO. Based on this data alone, we would expect the N-LMO to show lower capacity than the R-LMO because similar domain sizes are accompanied by increased surface area that could lead to both more inactive surface sites and more Mn dissolution.

A closer look at the morphology of the nanostructures, seen through HR-TEM (Figure 5.2c and 2d), shows other differences between the two materials. The R-LMO shows a somewhat curved
surface with a range of surface facets. The <111> lattice plane, identified by a lattice spacing of ~4.7 Å is observed for both structures. Surfaces parallel to the <111> lattice spacing direction correspond to (111) surfaces, whereas surfaces intersecting the <111> lattice planes (red arrows) are terminated with other faces such as (110) or (001). The TEM images show that the needle-like structures of the N-LMO have the <111> lattice traveling parallel to the long direction, thus the surfaces all along the length of the structures correspond to (111) surfaces, with only the ends displaying non-(111) surfaces. The N-LMO thus display dominant (111) surface character, since the length is significantly longer than the radius (See SI for calculation details). In contrast, the R-LMO does not show any one dominant surface termination due to its relatively round morphology. Note that a true sphere would have less than half of its surfaces parallel to the <111> planes, but because the structure is partly faceted, this value could be a bit higher. We can still safely assume that no more than 50% of the surface is (111) terminated. Overall, we conclude that N-LMO has a higher percentage of (111) surface termini than that of R-LMO.

Slurry electrodes were fabricated from the N-LMO and R-LMO powders for electrochemical testing in Swagelok cells. Slurries composed of 75 % active mass, 10 % carbon black, 5 % carbon fibers and 10 % PVDF were prepared with mass loadings between 1 and 2 mg/cm². Electrodes were cycled versus lithium metal with LiPF₆ in EC:DMC 1:1 electrolyte. The resulting galvanostatic cycling can be seen in Figure 5.3, which includes charge/discharge curves, rate tests and normalized rate data of N- and R-LMO electrodes. From the charge/discharge curves cycled at a relatively slow rate of 1C in Figure 5.3(a), we can see that despite its higher surface area which should lead to reduced capacity, N-LMO achieves about 28 % higher discharge capacity (88 mAh/g) than R-LMO (69 mAh/g). Of course, differing capacity alone does not eliminate the possibility that some kinetic limitation within the R-LMO could be preventing it from achieving the same capacity as N-LMO. If indeed kinetic limitations
were a large contributing factor to the capacity disparity between the R- and N-LMO, we would expect to observe poorer overall kinetics in the R-LMO at faster rates. The normalized capacity for both samples at varying C-rates (Figure 5.3c), however, is nearly identical for both R- and N-LMO, which indicates that the capacity difference of R-LMO compared to N-LMO is not related to kinetic differences between the two materials. Additional evidence of similar kinetic behavior was obtained through a kinetic analysis that uses cyclic voltammetry (CV) curves collected at different scan rates to decouple diffusion controlled or battery-like current from capacitive/pseudocapacitive current (Figure 5.4). We find that the resulting capacitive current contributions for both samples were ~85%, further supporting the claim that kinetics aren’t playing a significant role in capacity differences between the R- and N-LMO samples.

As mentioned earlier, there are two primary mechanisms contributing to capacity reduction in nanostructured LiMn$_2$O$_4$. The first is due to the inactive surface of LiMn$_2$O$_4$ which originate from the inclusion of reduced Mn$^{2+}$ in the surface 8a tetrahedral sites which normally hold Li$^+$ in the bulk. The absence of Li$^+$ in these surface tetrahedral sites reduces the number of active lithium positions, thereby decreasing the overall capacity substantially in high surface area nano-systems. Because relative surface area is inversely proportional to crystallite size, nanoscale materials with smaller domains should have higher surface area and thus more of these inactive sites. The second mechanism for capacity reduction in nanostructured LiMn$_2$O$_4$ is dissolution of the surface Mn$^{2+}$ upon direct contact with the electrolyte, followed by reduction of bulk Mn$^{3+/4+}$ to form more Mn$^{2+}$ on the freshly revealed surface. This effect is most evident upon charge but because a solid electrolyte interphase (SEI) is formed after the first cycle, direct contact with the electrolyte ceases unless the SEI layer is somehow disturbed. Because finely nanostructured systems of LiMn$_2$O$_4$ have high surface areas, they are particularly vulnerable to dissolution during the first cycle. Subsequent cycles, however, show impressive reversibility, suggesting that the SEI in these systems are relatively stable.
From these results, we can gather that much of the capacity loss in nanostructured LiMn$_2$O$_4$ occurs during the first cycle, and therefore having resistance to this initial dissolution could potentially allow for much higher capacity for subsequent cycles.

As discussed previously, (111) terminated surfaces in LiMn$_2$O$_4$ have been shown to resist dissolution in non-aqueous electrolytes in contrast to non-(111) terminated surface.$^{29,35,36}$ Because the round morphology of R-LMO displays far less (111) surfaces than N-LMO, which has (111) terminated surfaces along the length of the needles, we would expect N-LMO to suffer less from surface dissolution and thus display higher capacity than R-LMO. Indeed, the increased dissolution resistance of the N-LMO could explain why we see improved capacity in N-LMO compared to R-LMO with no substantial difference in kinetics.

To support the idea of reduced dissolution in N-LMO compared to R-LMO, we examined cells after cycling for signs of dissolution. One of the most straightforward ways to do this is to look for Mn that dissolved into the electrolyte, and then was plated out on the counter electrode. The lithium metal anode from each cell was thus analyzed using X-ray photoelectron spectroscopy (XPS) for evidence of plated manganese metal. Li metal surface analysis is ideal for identifying relative amount of solvated Mn$^{2+}$ in the electrolyte as the ions are prone to plating onto the Li metal by the spontaneous redox reaction: $2\text{Li}^0 + \text{Mn}^{2+} \rightarrow 2\text{Li}^+ + \text{Mn}^0$, $E_{\text{cell}} = -1.86$. To perform this experiment, R- and N-LMO electrodes were cycled in Swagelok cells using Li as counter electrode at C/10 for one charge-discharge cycle. Cells were then disassembled and the Li foil was used for XPS measurements to identify the relative ratio of Mn to Li (Mn/Li+Mn)). Figure 5.5 shows the resulting Mn 2P and Li 1s XPS peaks from the Li foils from the R- and N-LMO cells. As can be observed from the XPS data, R-LMO displays much higher Mn concentration (and signal) of 1.5% compared to that of N-LMO which shows only 0.3%. The lower Mn/(Li+Mn) % seen at the surface of the Li foil counter electrode of the N-LMO suggest that despite having higher surface area, less Mn was dissolved from N-LMO than from the R-LMO after the first
cycle. The lower concentration of Mn in the electrolyte of the N-LMO cell compared to the R-LMO cell after the first cycle supports the theory that N-LMO is more resistant to dissolution than R-LMO. This resistance to Mn dissolution of the N-LMO electrode corroborates the hypothesis that the higher capacity of N-LMO is due to the preservation of active material in the N-LMO sample. Perhaps more importantly, it shows that simple solution processing routes can lead to nanostructured LiMn$_2$O$_4$ with both a favorable nanoscale structure and favorable surfaces faceting for application in high power density Li-ion energy storage devices.

5.3 Conclusion

In summary, two nanostructured LiMn$_2$O$_4$ powders were produced through a polymer templated sol-gel synthesis using nitrate or acetate salts in order to study their electrochemical attributes. Nanostructured powders synthesized using acetate salts produced materials with a round grain morphology (R-LMO) which displayed the expected fast cycling kinetic and low capacity typical of small nanostructured LiMn$_2$O$_4$. Powders synthesized with nitrate salts produced nanostructured networks with a needle-like morphology (N-LMO) with similar cycling kinetics to the R-LMO system, but displayed higher overall capacity. The disparity in capacity between the two samples was understood by identifying that the majority of surfaces in the N-LMO were dissolution resistant (111) surfaces that run along the length of the needles. The dissolution resistance of N-LMO allows for a more intact structure after the first cycle, when Mn$^{2+}$ dissolution often dominates, therefore allowing for higher capacity than in the R-LMO material. The ability to improve capacity without harming cycling kinetics in a well characterized, well understood system marks an exciting advance in our understanding of how to control the electrochemical properties of nanostructured LiMn$_2$O$_4$ systems using both nanoscale architecture and surface structure. These findings show great promise for producing scalable, cheap nanostructured LiMn$_2$O$_4$ with few processing
steps for use as a fast charging cathode material for lithium ion batteries and pseudocapacitors.

5.4 Experimental Section

Synthesis of 50 nm poly(methylmethacrylate) (PMMA) template: The PMMA spheres were prepared by emulsion polymerization of methyl methacrylate (Aldrich) monomer (MMA) using ammonium persulfate (APS, Alfa Aesar) as the initiator in deionized water; the method is a modified version of an established method from the literature. First, 165 mL DI water were bubbled with nitrogen for 20 min under stirring to remove any oxygen. Then, 0.3 mL ammonium lauryl sulfate (Aldrich), which serves as a surfactant, and 12.55mL of MMA were added. The APS initiator solution was prepared separately by dissolving 0.075 g APS in 10 mL non-degassed water. The initiator solution was then added to the surfactant and monomer solution at 65 °C under stirring. The solution was heated to 73 °C and reacted for 3 h. As-prepared colloidal PMMA solution has a concentration of about 50 mg/mL, and were used without further purification. The average size of the PMMA colloids was determined to be 70 nm based on SEM.

Synthesis of round morphology nanostructured LiMn$_2$O$_4$ (R-LMO): In this method, 2.2 mmol of lithium acetate dihydrate (Sigma) and 4.0 mmol of manganese (II) acetate (Sigma) were mixed with 7.5 mL of the 50 mg/mL aqueous solution of 50 nm PMMA colloids. The solution was then heated and stirred in a round bottom flask for 20 minutes at 90 °C in an oil bath to evaporate part of the water. The resulting viscous solution was poured into a glass petri dish and left to dry for several hours in a fume hood. The resulting solid was heated in a muffle furnace with a ramp of 50 °C/hour from room temperature to 550 °C and soaked for 1 hour. The nano-sized LMO powder was obtained by scrapping the solid from the petri dish surface.
**Synthesis of needle-like nanostructured LiMn$_2$O$_4$ (N-LMO):** This synthetic method was almost the same as the acetate salt synthesis described above, except as noted here. In this method, 2.2 mmol of lithium nitrate (Sigma) and 4.0 mmol of manganese (II) nitrate tetrahydrate (Sigma) were used and the resulting solid formed in the petri dish was heated 50 °C/hour from room temperature to 550 °C and soaked for 10 hours.

**Slurry electrode and cell fabrication:** Typically, 36.5 mg of nanostructured LiMn$_2$O$_4$ powder was ground in a mortar and pestle with 5.0 mg of carbon black (Super P) and 2.5 mg carbon fiber (Sigma) for 5 minutes. Approximately 100 mg of a 5% polyvinylidene fluoride (PVDF) solution in N-Methyl-2-pyrrolidone (NMP) was added to the homogenized powder along with 10 additional drops of NMP. The resulting slurry was doctor bladed onto a stainless steel substrate with a height of ~0.3 mm. The slurry was then placed under a heat lamp for 1 hour to dry, and then transferred to a vacuum oven heated to ~130 °C while pulling vacuum overnight. The dried slurry electrode sheet was then punched out using a 0.71 cm$^2$ puncher and the electrodes transferred to Swagelock cells which were assembled with Li metal in a glove box with 1M LiPF$_6$ in 1:1 EC:DMC as the electrolyte, and a glass fiber separator.

**Electrochemical Analysis:** Swagelok cells were cycled using a 4-channel Bio-Logic VSP potentiostat controlled using EC-Lab version 10.4 software with LiMn$_2$O$_4$ as the positive electrode, Li as the negative and Li as the reference. Samples were cycled using both galvanostatic and potentiostatic methods to produce charge/discharge curves and cyclic voltammetry used in the kinetic analysis (from 0.2, 0.5 and 1 mV/s).

**Characterization:** X-Ray Diffraction (XRD) was taken using both Synchrotron High Angle X-ray Diffraction (XRD) carried out on beamline 11-3 at the Stanford Synchrotron Radiation Laboratory as well as in-house on a Panalytical X’Pert Pro X-ray Powder Diffractometer using a Bragg-Brentano setup. Scherrer widths were calculated and corrected using peak broadening parameters specific to the instrument setup used: Debye-Scherrer and Bragg-Brentano for
synchrotron and panalytical instruments respectively. Scanning Electron Microscopy (SEM) images were obtained using a model JEOL JSM-6700F field emission electron microscope with 3 kV accelerating voltage and secondary electron detector configuration. X-ray Photoelectron Spectroscopy (XPS) was taken using a Kratos XPS Axis Ultra DLD spectrometer with a monochromatic Al (Kα) radiation source. Fitting was done using CasaXPS software with Gaussian/Lorentzian 90/10 fit used for all peaks. HRTEM micrographs were collected using an FEI Titan S/TEM operating at 300 kV in transmission mode.
Figure 5.1: XRD of a) R-LMO and b) N-LMO with average Scherrer widths calculated to be 15 nm and 13 nm, respectively; N$_2$ porosimetry of c) R-LMO and d) N-LMO with surface areas of 17 m$^2$/g and 67 m$^2$/g, respectively; Adsorption pore size distribution for e) R-LMO and f) N-LMO, respectively. Note that red lines represent adsorption and black represent desorption.
Figure 5.2: SEM of a) R-LMO and b) N-LMO showing different nanostructure; TEM of c) R-LMO and d) N-LMO showing lattice spacing of $<111>$ LiMn$_2$O$_4$ and identifying the parallel (111) surface facets. Red arrows indicate dissolution susceptible surfaces of which R-LMO has more of.
Figure 5.3: Electrochemistry of N- and R-LMO electrodes in Swagelok cells; a) Galvanostatic discharge at 1C showing disparity in capacity between N- and R-LMO; b) Galvanostatic cycling at 5, 10 and 20C rates; and c) Kinetic comparison with normalized capacity.
Figure 5.4: The current at any given voltage, $i[V]$, can then be divided into a capacitive component (goes by sweep rate, $v$) and a diffusion controlled component (goes by square root of sweep rate, $v^{1/2}$) by the equation $i[V] = k_1v + k_2v^{1/2}$. By taking multiple sweep rates the $k_1/k_2$ values can be determined for each voltage and capacitive current separated from the diffusion controlled to give a percent capacitive contribution representing the overall kinetic viability of the material. The percentage of the current that is shaded is therefore the percent capacitive character for a) N-LMO and b) R-LMO based on 1, 0.5 and 0.2 mV/s scan rate cyclic voltammograms and fixed onto 0.2 mV/s plots. Both systems show similar capacitive contributions, further confirming the kinetic similarity between the two materials. Capacitive character is dominant over diffusion-limited kinetics for both systems, thus confirming pseudocapacitive mechanisms.
Figure 5.5: Mn 2p and Li 1s XPS of the surface of the lithium metal used as anodes during the cycling of a) N-LMO and b) R-LMO at C/5 for one cycle. Total Mn deposited onto Li anode used for R-LMO was 1.5% (Mn/(Mn+Li)) and total Mn deposited onto Li anode used for N-LMO was 0.3% (Mn/(Mn+Li)). The fivefold higher concentration of Mn deposited onto the Li from the R-LMO cell compared to the N-LMO suggests dissolution was higher for R-LMO, supporting the theory that N-LMO is comparatively less susceptible to dissolution.
5.5 References


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CHAPTER 6

The Effects of Mg and Ru Doping on Nanostructured LiMn$_2$O$_4$

6.1 Introduction

Fast charging in lithium ion batteries have been dreamed about since their conception nearly 30 years ago. Today, we find our lithium ion batteries still require charging times on the hours' time scale, which is a great inconvenience as clean energy storage attempts to compete with fossil fuels. The kinetic limitations in standard lithium ion batteries comes from long lithium ion solid state diffusion lengths through the micron sized grains making up the electrode materials. By shortening the distance through nanostructuring, however, common electrode materials can be utilized in fast charging without detrimental loss to energy density. When an electrochemically active material exhibits fast charging characteristics, the term pseudocapacitance is often used to describe the electrochemical process since its kinetics are similar to that of a capacitor only with a redox mechanism rather than double layer capacitance.\(^1\) In general, many materials have been studied which exhibit pseudocapacitance such as MoO$_3$, MoS$_2$, T-Nb$_2$O$_5$ and LiMn$_2$O$_4$ among others.\(^2,9\) Of these materials studied for pseudocapacitance, nearly all are more suitable for use as low voltage anode materials with the exception of LiMn$_2$O$_4$ which is sufficient for use as a cathode material.\(^8,9\) Because both anode and cathode are required to make a full cell fast charging battery, LiMn$_2$O$_4$ is of particular interest.

In general, the lack of fast charging cathode materials comes from the issue of the crystallization temperature required to form the proper phase.\(^10-14\) All common layered cathode materials such as LiCoO$_2$, LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ require temperatures above 700 °C to form which is problematic as coarsening of fine nanostructure is accelerated at high temperatures, and without nano-structuring, these materials cannot achieve fast
charging.\textsuperscript{10-14} LiMn$_2$O$_4$ on the other hand, has a relatively low crystallization temperature around 550 °C, which is low enough to retain nanostructure and still crystallize to the proper phase.\textsuperscript{8,9} Within the process of nano-structuring these materials, one must consider a variety of factors for optimization.

Simply reducing the grain size of a material is generally not enough to ensure pseudocapacitive kinetics. Perhaps the most optimal nanostructures for fast charging are 3D porous networks of interconnected nano-sized grains. The pores provide channels through which the electrolyte can easily penetrate into the particles, the interconnecting grains provide a robust electrically connected structure and the nano-sized grains allow for short lithium ion diffusion distances. To form these nanostructures, typically a template such as an organic polymer is mixed with the active material precursors or nanoparticles in solution, dried out and then heated to remove the template.\textsuperscript{15} Although the resulting nanomaterials typically charge far faster than their bulk counter-parts, they often suffer from reduced capacity.

Capacity reduction in nano-scale materials is a far reaching phenomenon and is linked to surface effects that are overexpressed in high surface area nano-systems.\textsuperscript{2,8-10,16} In anode materials, these effects are generally from oxidized surfaces, such as SiO$_2$ on Si, MoO$_3$ on MoO$_2$ and others.\textsuperscript{2,16} In cathode materials, reduced surfaces are far more common, such as Co$^{2+}$ on LiCoO$_2$ and Mn$^{2+}$ on LiMn$_2$O$_4$.\textsuperscript{8-10} These reduced surfaces are electrochemically inactive and therefore the more nano the material, the more capacity reduction is typically experienced. In LiMn$_2$O$_4$, the Mn$^{2+}$ on the surface has been shown to sit in tetrahedral sites where electrochemically active lithium usually resides in the interior, therefore preventing surface sites from undergoing redox at the desired potentials.\textsuperscript{8-10,17-20} The capacity reduction caused by this effect is compounded by the fact that the Mn$^{2+}$ rich inactive surface readily dissolves in common lithium ion electrolytes and then reforms on the freshly revealed under layer.\textsuperscript{21-23} This process would repeat until the material dissolved completely if not for the protection of a solid electrolyte interphase (SEI) formed from electrolyte degradation on the
electrodes surface during cycling. Preventing this degradation in the first place, however, can prevent surface dissolution on the first cycle and retain much of the capacity otherwise lost in nanostructured LiMn$_2$O$_4$. Preceding this degradation in the first place, however, can prevent surface dissolution on the first cycle and retain much of the capacity otherwise lost in nanostructured LiMn$_2$O$_4$.

Previously we have shown that surface dissolution can be somewhat mitigated in LiMn$_2$O$_4$ nanostructures with dominant <111> surface sites. In this work, we discuss a new method for mitigating surface dissolution in nanostructured LiMn$_2$O$_4$ by utilizing doping with the cations, Mg and Ru. Doping LiMn$_2$O$_4$ with cations is not uncommon and has been done to a significant degree, however, the effects of doping in nanoscale materials smaller than 50 nm, to our knowledge, has yet to be reported. Throughout this literature, doping larger crystallite sized LiMn$_2$O$_4$ leads to improved cycle life but reduced capacity. The improved cyclability has been hypothesized to be due to structural stabilization of the LiMn$_2$O$_4$ surface, whereas the reduced capacity is a result of the doped cation replacing active Mn$^{3/4+}$ in the interior. Because the cycling improvement is likely caused from a surface effect and the surface fraction is far larger in fine nanomaterials than that of bulk systems, we would expect doping to be more effective the more nano-sized the LiMn$_2$O$_4$. Here we find that, indeed, capacity is improved for nanostructured LiMn$_2$O$_4$ for both Mg and Ru-doped samples at lower doping concentrations but is reduced at higher concentrations. Furthermore, the Mg-doped samples, seem to trade improved capacity at the cost of kinetics, whereas kinetics appears to be unhindered in the Ru-doped samples, even when capacity is significantly improved. These results suggest that there is variation in the crystal site placement of the doping cations which plays a major role in kinetics but that both appear to reduce dissolution effects at the surface. These findings allow for fast charging without significant capacity trade-offs in nanostructured LiMn$_2$O$_4$ and is perhaps useful in other nanoscale electrode materials that suffer from capacity loss due to surface effects.
6.2 Results and Discussion

Nanoporous LiMn$_2$O$_4$ powders with two different kinds of cation doping in various concentrations were synthesized, characterized and tested electrochemically. Three Mg-doped nanoporous LiMg$_x$Mn$_{2-x}$O$_4$ powders and three Ru-doped nanoporous LiRu$_x$Mn$_{2-x}$O$_4$ were prepared with $x = 0.05$, 0.1 and 0.15. An undoped sample was also prepared using the same method as a control. The synthesis included the use of a colloidal template mixed with metal salt precursors in a sol-gel reaction, dried and heated at 550 °C to produce an interconnected nanoporous material. Figure 1A shows X-ray diffraction (XRD) of all synthesized nanoporous powders. The black pattern represents the undoped pure LiMn$_2$O$_4$ which indeed indexes to standard LiMn$_2$O$_4$ (JCPDS card 00-35-0782). All other samples show the same Bragg reflections with slight shifting depending on the degree of doped ion incorporation. The Ru 0.15 sample shows a few additional peaks corresponding to RuO$_2$, possibly due to supersaturation of sites capable of holding the Ru ion. Figure 1B shows the lattice parameters derived from the d-spacing from XRD for all samples. The Mg 0.05 sample has a decreased lattice parameter compared to the undoped LiMn$_2$O$_4$, however, further Mg incorporation appears to increase the lattice parameter. The Ru 0.05 sample experiences the opposite trend as Mg, showing an initial increase in lattice parameter with further Ru incorporation leading to a decrease in lattice parameter. These trends suggest that both Mg and Ru occupy a single interstitial site at the 0.05 concentration within the LiMn$_2$O$_4$ spinel crystal structure but upon increased dopant concentrations, the additional cations occupy different sites. The idea of multiple dopant interstitial sites is supported by the fact that surface sites in LiMn$_2$O$_4$ have different cation ordering than the bulk.$^{17-20}$ Because LiMn$_2$O$_4$ has different cation ordering in the bulk than on its surface, we could imagine lower concentrations could selectively fill surface sites until saturation, at which point further doping could lead to cation incorporation in new sites within the interior. By taking X-ray photoelectron spectroscopy (XPS) of the Mg 0.1 sample’s surface
(Figure S1), the ratio of Mg to Mn was specified to reflect a concentration three times higher than the stoichiometry. This increased surface Mg to Mn ratio indicates the majority of Mg is located on the surface, thus supporting the idea of preferential surface interstitial sites in Mg-doped LiMn$_2$O$_4$. Because the majority of Mg ions are present on the surface, we might expect increased dissolution resistance during cycling, since Mg$^{2+}$ should be less soluble than Mn$^{2+}$. In order to properly compare the electrochemistry of these materials, their sizes and structures must be relatively constant between samples. Figure 2 shows scanning electron microscopy (SEM) for all doped and the undoped LiMn$_2$O$_4$ samples. All nanostructures are porous and of similar size with interconnected rounded grain morphology. Crystallite sizes attained from the average XRD Scherrer widths for all samples were in the range of 24 $\pm$ 2 nm (Table S1), in agreement with the SEM images.

Slurry electrodes were fabricated identically for all active LiMn$_2$O$_4$ powders with 75% active material and cycled against lithium metal in a Swagelok configuration with LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 ratio. Figure 3 includes plots of various electrochemical quantifications and trends for Mg-doped LiMn$_2$O$_4$. Figure 3A demonstrates the capacity of the Mg-doped samples compared to the undoped at 1, 5 and 10C rates for multiple cycles, with a return to 1C to demonstrate rate-resistant cycling stability. Figure 3B shows the average capacity for all Mg-doped samples at various C-rates, including the slowest rate at C/5, indicating the superior capacity retention at faster rates. Figure 3C plots the maximum capacity of the materials (at C/5 rate) as a function of Mg dopant concentration. Note that absolute capacity improves for Li$_{1+x}$Mg$_x$Mn$_{2-x}$O$_4$ till $x = 0.1$ compared to the undoped sample, but drops at $x = 0.15$. This indicates competitive effects in Mg-doping related to increasing and decreasing capacity. As Mg incorporates into the surface of LiMn$_2$O$_4$, dissolution resistance could increase allowing less capacity reduction, however, as Mg incorporation increases in the bulk of the material, electrochemically active sites are replaced with inactive Mg, thus reducing capacity. Figure 3D summarizes the kinetics for all dopant concentrations of
Mg through the use of their relative rates calculated by averaging the % difference in capacity between all rates: Capacity at 1C/0.2C, 5C/1C and 10C/5C averaged and normalized to the kinetics of the undoped nanostructured LiMn$_2$O$_4$. As can be seen from the plot, the kinetics typically reduce with higher Mg incorporation, an effect suggesting that the Mg sites interfere with Li-ion pathways.

Figure 4 documents the electrochemical trends of Ru-doped LiMn$_2$O$_4$. Figure 4A exhibits the capacity of the Ru-doped samples compared to the undoped at 1, 5 and 10C rates with a return to 1C similarly to that shown for Mg in Figure 3A. Figure 4B displays the average capacity for all Ru-doped samples at various C-rates. Figure 4C plots the maximum capacity of the materials as a function of Ru dopant concentration. Note that absolute capacity improves for Li$_{1.1}$Ru$_x$Mn$_{2-x}$O$_4$ at both x = 0.05 and 0.1 as it did for Mg, however, the maximum is at 0.05 dopant incorporation rather than 0.1, and continues to drops below the undoped at x = 0.15. Analogous to the Mg-doped system, this trend indicates competitive capacity influencing effects in Ru-doping possibly related to occupation in sites that increase dissolution resistance and those that block active sites. Figure 4D summarizes the kinetics for all dopant concentrations of Ru as explained earlier for Mg through the rate relative to the undoped nanostructured LiMn$_2$O$_4$. Interestingly, the kinetics of the Ru-doped LiMn$_2$O$_4$ does not appear to be hindered much by increased Ru concentration. This effect could be related to the fact that RuO$_2$ is conductive, and that small amounts Ru in the structure could increase the LiMn$_2$O$_4$ conductivity. An increase in conductivity of the structure would positively influencing the rate and thus compete against any Li-ion pathway hindrance caused by foreign Ru ions. The net result of these competing rate factors could consequently lead to only minor changes if any, in kinetics.

Although the many nanostructured LiMn$_2$O$_4$ dopant systems explored here have varying capacity and kinetic effects, long term cycling stability is apparently uninfluenced by doping. Figure S3 demonstrates the first 500 cycles at 5C for all systems versus normalized capacity. As can be observed from the plot, all samples have nearly identical stability, retaining over 90%
capacity after 500 cycles. This trend is unusual for doped LiMn$_2$O$_4$ as generally in larger crystallite sized systems, a great improvement in cyclability is observed. Because nanostructured LiMn$_2$O$_4$ already has superior cycle stability past the first few cycles, the doping does not improve this aspect. Overall, cation doping in nanostructured LiMn$_2$O$_4$ with Mg and Ru improve capacity, but kinetics is effected negatively by Mg, and negligibly by Ru, with cation doping playing no role in cycling stability. These results suggest that Ru-doped nanostructured LiMn$_2$O$_4$ could be a promising candidate for fast charging lithium ion batteries without significant capacity reduction due to nanoscale surface effects. Mg-doping in nanostructured LiMn$_2$O$_4$ could be a cheaper, higher capacity alternative to the undoped nanostructured material for applications that do not require such fast rates but do require long cycling lifetimes.

6.3 Conclusion

In summary, nanostructured LiMn$_2$O$_4$ with various amounts of Mg and Ru doping were prepared via a sol-gel templating method. Resulting Mg-doped LiMg$_x$Mn$_{2-x}$O$_4$ with stoichiometries of $x = 0.05$ and $0.1$ showed improved capacity at slow rates compared to the undoped sample, but reduced overall kinetics. When LiMg$_{0.15}$Mn$_{1.85}$O$_4$ reached $x = 0.15$, capacity and kinetics were both worse than the undoped sample. Ru-doped LiRu$_x$Mn$_{2-x}$O$_4$ also showed improved capacity for $x = 0.05$ and $0.1$, but showed no significant change in kinetics, leading to an overall better material. The LiRu$_{0.15}$Mn$_{1.85}$O$_4$ where $x = 0.15$ experienced reduced capacity, but retained its kinetics as well. All materials retained the same superior cyclability expected for nanostructure LiMn$_2$O$_4$. The LiRu$_{0.05}$Mn$_{1.95}$O$_4$ where $x = 0.05$ was by far the most superior material in capacity, retaining upwards of 100 mAh/g compared to the undoped at 85 mAh/g at C/5, and because it retained both the kinetics and cyclability of the undoped, it should be investigated more closely to understand the mechanism of its superior attributes.
6.4 Experimental Section

Synthesis of 50 nm poly(methylmethacrylate) (PMMA) template. The PMMA spheres were prepared by emulsion polymerization of methyl methacrylate (Aldrich) monomer (MMA) using ammonium persulfate (APS, Alfa Aesar) as initiator in deionized water at 73 °C for 3 h according to a modified recipe from literature. First, 165 mL DI water was bubbled by nitrogen for 20 min under stirring to remove any oxygen. Then 0.3 mL ammonium lauryl sulfate (Aldrich) as surfactant and 12.55mL MMA was added. The APS initiator solution was prepared on the side by dissolving 0.075 g APS in 10 mL water. The initiator solution was added to surfactant and monomer solution at 65 °C under stirring. The solution was heated to 73 °C and reacted for 3 h. As-prepared PMMA solution has a concentration of about 50 mg/mL, and is used without any further purification.

Synthesis of doped and undoped nanostructured LiMn$_2$O$_4$. For undoped, 2.2 mmol of lithium acetate dihydrate (Sigma) and 4.0 mmol of manganese (II) acetate (Sigma) were mixed with 7.5 mL of a 50 mg/mL aqueous solution of 50 nm PMMA heated and stirred in a round bottom flask for 20 minutes at 90 °C in an oil bath. The resulting solution was poured into a glass petri dish and left to dry for several hours in a fume hood till it no longer flowed. The resulting solid was heated in a muffle furnace with a ramp of 50 °C/hour from room temperature to 550 °C and soaked for 1 hour. The nano-sized LMO powder was obtained by carefully scrapping the solid from the petri glass surface. For doped, the synthesis was exactly the same except 0.1 mmol of manganese (II) acetate was replaced with 0.1 mmol of either magnesium acetate (Sigma) or ruthenium (III) chloride hydrate (Sigma) for each $x = 0.05$ dopant level in LiM$_x$Mn$_{2-x}$O$_4$ ($M = Mg$ or Ru).

Slurry electrode and cell fabrication. Typically 36.5 mg of nano LiM$_x$Mn$_{2-x}$O$_4$ powder was grinded in a mortar and pestle with 5.0 mg of carbon black (Super P, MTI) and 2.5 mg carbon
fiber (MTI) for 5 minutes. Approximately 100 mg of a 5% polyvinylidene fluoride (PVDF, MTI) solution in N-Methyl-2-pyrrolidone (NMP, Acros) was added to the homogenized powder along with 10 additional drops of NMP. The resulting slurry was mixed for 2 minutes and then applied in a line to one side of a carbon coated Al substrate flattened on glass before being spread by a doctor blade with a height of ~0.3 mm. The slurry was then placed under a heat lamp for 1 hour and then transferred to a vacuum oven heated to ~130 °C while pulling vacuum overnight. The dried slurry electrode sheet was then punched out using a 0.71 cm² puncher and the electrodes transferred to Swagelok cells which were assembled in a glove box against a Li metal anode with a glass fiber separator soaked with LiPF₆ in EC:DMC 1:1 as the electrolyte.

**Electrochemical Analysis:** Swagelok cells were cycled using a 4-channel Bio-Logic VSP potentiostat controlled using EC-Lab version 10.4 software with LiMn₂O₄ as the positive electrode, Li as the negative and Li as the reference. Samples were cycled galvanostatically to assess functionality.

**Characterization.** X-Ray Diffraction (XRD) was taken on a Panalytical X’Pert Pro X-ray Powder Diffractometer using a Bragg-Brentano setup. Scherrer widths were calculated and corrected using peak broadening parameters using Bragg-Brentano. Scanning Electron Microscopy (SEM) images were obtained using a model JEOL JSM-6700F field emission electron microscope with 3 kV accelerating voltage and secondary electron detector configuration. X-ray Photoelectron Spectroscopy (XPS) was taken using a Kratos XPS Axis Ultra DLD spectrometer with a monochromatic Al (Kα) radiation source. Fitting was done using CasaXPS software with Gaussian/Lorentzian 90/10 fit used for all peaks.
Figure 6.1: a) XRD of doped and undoped nanostructured LiMn$_2$O$_4$. Middle black pattern is undoped LiMn$_2$O$_4$. Top patterns are representative of Ru-doped samples of LiRu$_x$Mn$_{2-x}$O$_4$ with $x = 0.05$, 0.1 and 0.15. Bottom patterns are representative of Mg-doped samples of LiMg$_x$Mn$_{2-x}$O$_4$ with $x = 0.05$, 0.1 and 0.15. b) Lattice parameter spacing of LiMn$_2$O$_4$ unit cell for all samples. Mg-doping initially experiences a drop in lattice parameter with further doping leading to an increased lattice parameter. Ru-doping displays an initial increase in lattice parameter with further doping leading to decreasing lattice parameter.
Figure 6.2: X-ray photoelectron spectroscopy (XPS) of LiMg$_{0.1}$Mn$_{1.9}$O$_4$ showing Mn 2p and Mg 1s photoemission peaks. Ratio of surface Mg to Mn was determined from these spectra to be 1 to 6, corresponding to a stoichiometry three times larger than expected for LiMg$_{0.1}$Mn$_{1.9}$O$_4$. This data suggests that most of the Mg in the sample is retained on the surface of the material.
Figure 6.3: SEM of all doped and undoped nanostructured LiMn$_2$O$_4$ powders. Left side SEM is
undoped. Top are Mg-doped samples with stoichiometry LiMg$_{x}$Mn$_{2-x}$O$_4$ where $x$ is noted as either
0.05, 0.1 or 0.15 doping concentrations. Bottom are Ru-doped samples with stoichiometry
LiRu$_{x}$Mn$_{2-x}$O$_4$ where $x$ is noted as either 0.05, 0.1 or 0.15 doping concentrations. All morphologies
are similar grain sized porous interconnected nanostructures.
Table 6.1: Summary of trends for all doped and the undoped nanostructured LiMn$_2$O$_4$ powder: crystallite size, calculated unit cell lattice parameter, maximum capacity and relative rate. Crystallite size is relatively constant for all samples with average being 24 ± 2 nm. Lattice parameter experience slight changes depending on cation incorporation sites of each dopant. Maximum capacity obtained at C/5 rate for each doped sample with percent change from the undoped. Relative rate compared to the undoped sample.
Figure 6.4: Cycling data and electrochemical trends for Mg-doped LiMn$_2$O$_4$ and undoped for comparison. All materials were charge and discharged at the same rate. a) Capacity vs. cycle number for charge (open circles) and discharge (closed circles) with electrodes cycled at 1, 5 and 10C rates and returned to 1C to demonstrate kinetics and stability, respectively. b) Average capacity at different C-rates. c) C/5 discharge capacity as a function of Mg incorporation in LiMn$_2$O$_4$. d) Relative rate as a function of Mg incorporation.
Figure 6.5: Cycling data and electrochemical trends for Ru-doped LiMn$_2$O$_4$ and undoped for comparison. All materials were charge and discharged at the same rate. a) Capacity vs. cycle number with electrodes cycled at 1, 5 and 10C rates and returned to 1C to demonstrate kinetics and stability, respectively. b) Average capacity at different C-rates. c) C/5 discharge capacity as a function of Mg incorporation in LiMn$_2$O$_4$. d) Relative rate as a function of Ru incorporation.
Figure 6.6: Long term cyclability with normalized capacity of all Mg and Ru doped and the undoped nanostructured LiMn$_2$O$_4$ powders cycled for 500 times at 5C rate. All samples appear to have similar cyclability with retention >90% after 500 cycles.
6.5 References


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