Synthesis of Nanocrystal Heterostructures for Li-ion Battery Cathode with Increased Interfacial Stability

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THESIS

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LIST OF ABBREVIATIONS

ABF	Annular bright field
ADF	Annular dark field
ALD	Atomic layer deposition
CS	Core-shell
CVD	Chemical vapor deposition
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EDX	Energy dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EMC	Ethyl methyl carbonate
EY	Electron yield
FY	Fluorescence yield
НОМО	Highest occupied molecular orbital
LAADF	Low angle annular dark field
LIBs	Lithium-ion batteries
LUMO	Lowest unoccupied molecular orbital
MAS NMR	Magic angle spinning nuclear magnetic
NMP	N-methylpyrrolidone
NMR	Nuclear magnetic resonance
OAm	Oleylamine

PEY	Partial electron yield
PVDF	Polyvinylidene difluoride
RT	Room temperature
SEI	Solid electrolyte interface
SEM	Scanning electron microscope
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TM	Transition metal
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

SUMMARY

Throughout this thesis, interfacial stabilization has been demonstrated in various compositions and structures of cathodes by designing heterostructure nanocrystals. A colloidal synthetic route is employed as a platform to enable coverage of all surfaces of particles while the nanocrystals are highly dispersed in a solution, to build core-shell architectures. Conformal and epitaxial shells are tailored to satisfy the chemical and morphological requirements to stabilize electrode-electrolyte interfaces in Li-ion batteries. Chapter 1 provides an introduction to the context of the research. In Chapter 2, we expand our original report of core-shell nanocrystals based on spinel-type LiMn₂O₄ by redesigning our synthetic method to grow passivating layers at varying thicknesses on nanocrystal cores with increased size. Control of the shell to core ratio was achieved to make comparisons of electrode stability while maintaining the nanocrystal core constant, thus evaluating the durability of batteries predominantly versus the characteristics of the shell. In all cases, the modified crystals show enhanced capacity retention with respect to the contents of Al-passivating shells. In chapter 3, we demonstrate the versatility of the core-shell architecture with a different crystal structure, layered LiCoO₂, as a cathode for Li-ion batteries. The composition of the layer was tailored by thermal annealing, which induces inter-diffusion of Co/Al. Despite of the decreased electronic conductivity, the presence of the conformal shell enhanced the electrochemical performance as Li-ion battery cathodes. In chapter 4, finally, we expand the strategy to more complex layered oxides, $LiN_{0.25}Mn_{0.25}Co_{0.5}O_2$, resulting from replacing Co^{3+} by Ni^{2+} and Mn^{4+} in $LiCoO_2$. Using this compound as a core, shells with a concentration gradient of Al³⁺ were synthesized through post-thermal treatments to induce interdiffusion. The effect of both the initial content of Al and the temperature of treatment was evaluated. The modified crystals enhanced the capacity retention without significant loss of original capacity compared to the bare materials, particularly in harsh cycling conditions. The demonstration of these compositionally diverse heterostructure cathodes strongly suggests a beneficial role of the concept of passivating layers deposited onto single nanocrystals through a colloidal synthetic route. The versatility of this synthetic procedure has the potential to create new avenues for the design of functional electrode materials for Li-ion batteries.

CHAPTER 1

1. GENERAL INTRODUCTION

1.1 Principles of Li-ion batteries

Currently, the world is confronted with the challenge of shifting the generation of electricity from fossil fuels to renewable energy sources, motivated by environmental and sustainability issues. Yet the use of renewable sources requires the availability of suitable technology for the storage of this energy because of its intermittency and incompatibility with mobile and distributed technology. Therefore, energy storage is essential to integrate renewable energy sources into power grids, enabling technologies such as electric vehicles or backup systems.^{1,2} Batteries are established as the most promising storage system because of their light weight, compactness and long-term stability. Among various possible battery technologies, Li-ion devices offer the highest density of energy.³

Figure 1-1 represents a basic Li-ion battery, which is composed of a positive (cathode) and a negative electrode (anode) separated by a liquid electrolyte, enabling ion transfer between the two electrodes. To maximize energy density, the electrodes are in close proximity, but electronically isolated by a porous plastic film (separator) to avoid a short circuit. During charge and discharge of the battery, Li⁺ ions transfer between the anode and cathode across the electrolyte, while electrones simultaneously move through external wires, generated by redox reactions at the electrodes.⁴ More specifically, when the battery circuit is closed without externally applying a current or potential, charge can only flow from the anode to the cathode in a spontaneous manner because the former has a higher chemical potential than the latter. This process is, therefore, spontaneous, and it delivers energy to the circuit. If the battery can be charged by an external power source,

Li ions in the cathode move to the anode while electrons flow to the anode through an external wire to maintain neutrality.⁵



Figure 1-1. A schematic presentation of the commonly used Li-ion battery based on a graphite anode and a $LiCoO_2$ cathode.⁴

Energy and power density in batteries are defined directly by the thermodynamic relationships for electrochemical reactions in a cell.⁶ The energy stored by a battery is ultimately determined by the Gibbs free energy, ΔG , of a given net reaction, as defined by

$$\Delta G = -nFE \tag{1.1}$$

where *n* is the moles of transferred electrons (and, correspondingly, Li^+ ions) per mol of reactants, F is the Faraday constant, and E is the potential of the net chemical reaction in the cell. In turn, the potential of the cell is determined by the difference in the chemical potentials in each electrode. This potential varies according to the atomic and electronic structure (e.g., covalency) of the compound undergoing the redox reaction. In general, the higher the ionic character of the compound, the higher the potential of the

reaction (Figure 1-2). In equation 1.1, nF is the amount of electrical charge (Q) per mole of compound. In the battery field, Q is identified as the capacity of the cell, in mA \cdot h (Q = $I \times t$, where I is current and t is time), expressed in specific terms, divided by the mass of the redox-active species.⁷ Further, the amount of stored electrical energy is expressed per unit of weight (Wh/kg, specific energy) or per unit of volume (Wh/l, energy density). In addition, the calendar life of the battery is generally determined by the number of times that the redox reactions can be reversibly cycled with minimal loss of electrical charge (i.e., capacity). Two general types of phase transitions are observed during intercalation/de-intercalation of Li⁺ into/from the host structure. One corresponds to a first-order, or two-phase transition, transition showing a clear potential plateau, as shown in Li_xCoPO_4 of figure 1-2 (a) during the formation of a distinct new structural phase. The other corresponds to a second-order phase transition, involving a continuous change in redox potential due to the correspondingly gradual change of chemical potential during a homogeneous change in concentration of Li⁺ in phases along a continuous solid solution path.



Figure 1-2. (a) Voltage profiles versus Li^+/Li^0 of the discharge curves of Li_xC_6 , Li_xTiS_2 , and $Li_xTi_2S_4$, Li_xCoO_2 and $LiCoPO_4$. (b) Schematic of their energy versus density of states showing the relative positions of the Fermi energy.⁷

Intercalation reactions are the most common mechanism to store charge inside a Li-ion battery. In this mechanism, lithium ions enter a crystalline solid framework at thermodynamically favored, unoccupied sites, compensated by changes in redox state in the compound. This reaction only requires small atomic rearrangements without breaking or forming new bonds, which favors high chemical reversibility of the process. A natural design rule thus becomes finding structures with a high concentration of unoccupied sites available for Li intercalation.⁸ Furthermore, the solid framework should also present low diffusion barrier for Li⁺, high electronic conductivity, and structural stability at wide ranges of concentration of Li ions.

Transition metal oxides are an obvious choice as intercalation hosts and, thus, battery electrodes. Many react at redox potentials that are high enough to make them suitable cathodes. Indeed, many such phases have been investigated extensively due to their high energy densities and power, which is critical for mobile storage.⁹ Their structures are adaptable to Li ions being intercalated into available interstitials.¹⁰ Among the different candidates explored, layered oxides with the general formula LiMO₂ (M=Co, Ni, or Mn) have seen widespread application. Their main structural feature is a series of layers of edge-sharing LiO₆ octahedra stacked alternatively with layers of edge-sharing MO₆ octahedra (or combinations of LiO₆ and MO₆), in a cubic closed-packed arrangement of oxide ions. This layered arrangement enables fast 2D diffusion of Li⁺ ions, which are also present at very high concentrations to enable high theoretical capacity.¹¹ LiCoO₂ is the classical layered cathode material.¹² (Figure 1-3) The high redox potential of the Co⁴⁺/Co³⁺ couple, ~4 V vs. Li⁺/Li⁰, combines with a very high theoretical capacity of ~274 mAh/g when all Li ions are extracted from the structure,

according to:

$$LiCoO_2 \leftrightarrow Li^+ + e^- + CoO_2$$
 (1.2)

However, in practice, the level of Li that can be cycled in and out of the compound reversibly is limited to ~0.5 mole. This procedure produces ~150 mAh/g, due to the onset of secondary irreversible reactions, both internally and at interfaces with the electrolyte. Its low practical capacity and the high cost of Co have led to search for alternative layered materials through replacement of Co^{3+} by Ni^{2+} and $Mn^{3+, 4+}$, leading to complex oxides with the general composition $LiNi_xMn_yCo_{1-x-y}O_2$, also known as NMC. These oxides crystallize in the same hexagonal, layered structure as $LiCoO_2$. While Ni is introduced as a redox active center to maintain a high capacity, the addition of Mn ions even if in the redox-inactive +4 state enhances thermal stability.



Figure 1-3. Crystal structures of (a) layered LiCoO₂ and (b) spinel LiMn₂O₄. [12]

As an alternative, oxides with a spinel structure, such as $LiMn_2O_4$, have attracted interest thanks to the combination of a 3D lattice, which enables fast reaction rates and, thus, provides high power capability, and the Mn^{+3}/Mn^{+4} ($LiMn_2O_4-Mn_2O_4$) couple, which is located at a high redox potential, ~4 V. It undergoes the following reaction:¹³

$$LiMn_2O_4 \leftrightarrow Li^+ + e^- + Mn_2O_4 \tag{1.3}$$

LiMn₂O₄ has a cubic spinel structure with Li ions in tetrahedral sites and Mn ions in octahedral sites in a cubic closed-packed arrangement of oxide ions (Figure 1-3b). Li ions diffuse within the structure through a tetrahedral site to the neighboring octahedral site then to the next tetrahedral site. The distribution of sites in the structure is such that diffusion occurs quickly in the three dimensions. However, one major issue of the spinel is the severe capacity loss during electrochemical cycling, especially elevated temperatures. Possible mechanisms of degradation have been proposed, such as instability of the structure due to Jahn-Teller distortions induced by Mn^{3+} with $t_{2g}^{3-}e_{g}^{1}$ of electron configuration¹⁴ and irreversible interfacial reactions, discussed below. The fact that no single electrode material has led to devices with the storage metrics desired for applications such as electric vehicles has motivated the continued exploration of redoxactive compounds for this purpose (Figure 1-4 (a)).

1.2 Mechanisms of degradation of cathode-electrolyte interfaces

Undesired chemical interactions can occur at the interface between a battery electrode and electrolyte.¹⁵ These interfacial reactions lead to layers that are often both electronically and ionically insulating, thus shutting down charge transfer,¹⁶ and can induce cathode corrosion, anode contamination, and electrolyte depletion.⁴ Understanding them is essential to produce solutions that enable the construction of batteries with high performance. Since the electrolyte is in contact with both electrodes, it

is subject to their respective redox potentials. Therefore, the energy separation of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) in the electrolyte determines an applicable potential window of battery operation as shown in figure 1-4b. If injection of electrons (and lithium) at the anode occurs at energy level higher than the LUMO, it will be reduced. In a similar way, oxidation of the electrolyte will occur if the extraction of electrons (and lithium) from the cathode involves energy levels lower than the HOMO of the electrolyte.¹⁵ These electronic incompatibilities can be exacerbated in the presence of highly oxidized metal ions at the surface of the cathode. These oxidized ions can unlock novel pathways through their direct reaction with electrolyte molecules.¹⁷



Figure 1-4. (a) Potentials and expected capacities of various lithium storage materials for Li-ion batteries. (b) Differences between electron energy levels associated with electrode redox and the HOMO/LUMO levels of the electrolyte govern the thermodynamic stability of electrode/electrolyte interfaces.¹⁵

Another mechanism of degradation occurs when the salt based on polyfluoroanions salts used in modern electrolytes can react with the few ppm of H₂O present in all commercial formulations to form HF. In the case of LiPF₆, the reaction is proposed to follow the mechanism discussed below. LiPF₆ can decompose to form LiF, which is deposited onto electrode surface.¹⁸ (Figure 1-5) This equilibrium is displaced by water through its reacting with PF₅, finally producing HF.¹⁹ (Equation 1.5) The mechanism is summarized below:

$$\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5 \tag{1.4}$$

$$PF_5 + H_2O \rightarrow PF_3O + 2HF \tag{1.5}$$

The resulting acidic environment can dissolve the transition metal ions of the cathode surface, and lead to the deposition of insulating transition metal fluorides at the electrode-electrolyte interface. In the case of LiMn₂O₄, dissolution occurs even in the pristine state, through a disproportionation reaction ($Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$), as shown in Figure 1-5.²⁰ Dissolved ions can migrate to the negative electrode across the cell, affecting charge transfer on the anode.



Figure 1-5. Schematic mechanisms at a cathode-electrolyte interface in a Li-ion battery, represented by LiMn₂O₄. (a) Possible degradation mechanisms at a cathode-electrolyte interface in a Li-ion battery, represented by LiMn₂O₄. (b) Presentation of irreversible loss of Li storage by Mn reduction at the anode surface. Mn²⁺ ions come from corrosion of the LiMn₂O₄ cathode.²⁰

1.3 Strategies for stabilization of the electrode-electrolyte interface

Intense efforts to enhance the interfacial stability of Li-ion battery cathodes have focused on modifying their surface. Creating solid passivation films on the active oxides is one way to reduce the undesired reactions, for instance, by screening the redox potential of the surface through blocking the conduction of electrons.²¹ Compounds containing elements in the *s* or *p*-blocks of the Periodic Table, especially Al₂O₃, AlF₃, and MgO, are classical choices to suppress unwanted redox activities.¹⁸ Aside from electronically insulating the surface, some of these oxides or fluorides can scavenge acidic impurities and react with hydrofluoric acid to create metal fluoride or oxyfluoride bonds, which further stabilize the surface against reaction with the electrolyte, and as a result, improve battery performance.

Unfortunately, these compounds also interrupt ionic diffusion through the interface due to the fact that the solid layers essentially contain no such charge carriers in their structure. Thus, it is preferable to introduce compounds with the ability to act as solid electrolytes, thereby conducting ions while blocking electrons. Another issue with conventional coatings comes from their compositional and structural mismatch with the underlying oxide structure.²² This dissimilarity leads to atomic misfits at the interface, resulting in lattice strain, or even voids, which create additional kinetic barriers to charge transfer. This phenomenon is significantly exacerbated when the host oxide undergoes structural expansion or contraction during electrochemical cycling because the coating is inactive and, therefore, it retains its original framework. As a consequence of this accumulated stress, delamination of the coating would be possible. From this perspective, a potential solution to these issues is to create epitaxy between coating and cathode, where the atoms occupy a similar structural framework that shares an underlying stacking.²³

In terms of spatial location, a primary requirement is to grow the coating layers conformally on all possible surfaces of the electrode. Because most protective compounds are not redox-active, the layers need to be thin to maintain the storage capacity of the overall cell. These requirements are typically met by exposing the cathode powders to precursors of the desired coatings, in either liquid or gas form, under moderate to high temperature. However, these procedures are usually applied on presynthesized powders of the cathode, where secondary particles or large aggregates exist. Depositing onto these structures limits the coverage of the surfaces, especially if they are buried. These buried unprotected surfaces can subsequently become exposed to the electrolyte during operation, especially given that fracture and particle shuffling are common upon cycling.²⁴ Despite the improvements brought about by this strategy, novel approaches continue to be sought to cover all reactive sites with inactive oxides. The atomic control over deposition that is required to achieve this goal is beyond the intrinsic capabilities of traditional methods, which creates a need for creative sophistication of the synthetic procedures.

Demands on controlling the thickness and comformality of passivating layers have led researchers to design sophisticated physical and chemical deposition recipes.²⁵ These approaches are based on deposition of gas state species with a target composition, which enhances the ability to reach the surface of inner space. Atomic layer deposition (ALD) is currently the most common method in this family.²⁶ It has been used to fabricate conformal coatings with controllable thickness at relatively low temperatures. This versatility enables deposition of Li conductors, although the complexity of several cathode materials remains to be fully demonstrated.²⁷ Microscopic studies of the layers have revealed a highly conformal character in many cases, but evidence of deficiencies in the coverage and uniformity in certain particles also exists,²⁸ probably due to lack of exposure of the material to the organometallic precursor. Furthermore, the treatment at low temperature often generates amorphous phases, removing the ability to introduce epitaxy with the coated material.

1.4 A colloidal synthetic approach to heterostructure nanocrystals for cathode

The challenge faced by post-synthetic routes to grow conformal protective layers that preserve atomic epitaxy with the active material, while lowering the concentration of transition metals at the surface, has led to the development of synthetic methods for the direct synthesis of heterostructure architectures, particularly core-shell.²⁹ To satisfy these requirements, colloidal methods of nanocrystal growth provide a platform to manipulate assembly at the level of individual primary particles, thus protecting every single possible surface.

Colloidal oxide nanocrystals (NCs) have attracted considerable attention in the development of tunable electronic, optical, and magnetic materials.³¹ Their high surface to volume ratio leads to properties dominated by surface effects over the bulk properties, which provides tunability depending on the applications.^{31,32} Colloidal synthetic approaches provide an efficient way to synthesize nanoscale particles with highly precise sizes and high dispersibility. The possibility of surface functionalization while maintaining their dispersibility leads to tremendous potential toward the modification of their chemical properties.³¹ A classic example is the core-shell architecture. It is composed of an inner material (core) and outer layer (shell) with varying chemical compositions and shell to core ratio. The selection of the shells strongly depends on their role in a specific application. In a core-shell architecture, the ultimate goal is to achieve a uniform and conformal coating on the entire nanocrystal with precise thickness. Coreshell morphologies have been extensively emphasized due to their unique electronic and catalytic properties.³³⁻³⁵ The architectures offer new opportunities of synergy between distinct functionalities that the core and shell provide, to tune reactivity and stability.

Since colloidal chemistry provides a platform to effectively passivate all possible active sites on the surface of a particle, our group developed the concept of core-shell architecture to stabilize the cathode-electrolyte interface in Li-ion batteries.²³ In these new heterostructures, the conformal shells shared the crystalline framework with the redox-active oxide in the cores, showing a sharp increase in concentration of inactive ions from the interior to the exterior, consequently passivating all possible surfaces. To control the architectures, shell compounds were grown at nanometer thickness in the same reaction environment as the cores to maintain their colloidal state (Figure 1-6). In the original report, the heterostructure was composed of spinel-type LiMn₂O₄ in the core with an Al³⁺-rich spinel-type shell. The desired epitaxy of the shell was tailored by post-annealing. The novel heterostructures enhanced durability of the electrodes in batteries while reducing the side reactions at the interfaces with the electrolyte.



Figure 1-6. Schematic diagram of a synthetic procedure to synthesize core-shell nanocrystal heterostructures of cathode materials.

This first demonstration of core-shell architectures constitutes the beginning of this thesis. We started by exploring the effects of core-shell ratio in the original $LiMn_2O_4$ heterostructures. To demonstrate the versatility of the approach, we extended it to new

oxide chemical species with layered structures. In all cases, the introduction of passivating layers was found to introduce rich chemical and structural effects, combined with enhanced electrochemical properties.

CHAPTER 2

2. EFFECT OF PASSIVATING SHELLS ON THE PROPERTIES OF SPINEL-TYPE LiMn2O4 AS BATTERY CATHODE

2.1 Introduction

Lithium-ion batteries are considered to be the most efficient energy storage system to power electrical drive vehicles, due to their relatively high power and energy density.^{1,2} Among energy storage materials, spinel-type $Li_{1+x}Mn_{2-x}O_4$ is a mature choice for the cathode due to its high operating potential (> 4.0 V vs Li^+/Li^0), robust durability and rate performance.^{3,4} However, the material suffers from interfacial instabilities, mainly derived from dissolution of Mn from the surface, through a disproportionation reaction triggered by the presence of acidic impurities present in the electrolyte, and is generated during cycling.^{5,6} These undesired interfacial processes induce fading of the storage capacity at temperatures, especially at above standard operating conditions, which occur in real life applications. Therefore, the development of the material for more widespread applications in electric vehicles requires identifying methods to suppress interfacial reactions to further enhance durability, while preserving high energy storage and power capability.

Replacing transition metal ions with redox-inactive ions can create stable interfaces by reducing the unwanted side reactions associated with corrosion/dissolution and the redox activity of the surfaces.⁷ However, this substitution must take place in the form of very thin layers so as to avoid unacceptable loss of capacity for charge storage and electronic conductivity. Furthermore, these layers must completely cover each single particle to avoid exposure of buried, unprotected surfaces during inevitable particle shuffling upon battery cycling.⁸ Lastly, the specific structure of these layers needs to be controlled to avoid barriers to ionic conduction, which would create kinetic impediments to the transfer of Li ions to/from the electrolyte. All in all, careful tailoring the chemical composition, conformality, and thickness of the layers of surface modification on particles of a battery cathode is pivotal to improving its electrochemical properties. This goal challenges our current ability to synthesize and assemble complex multifunctional structures at the level of single particles.

In the literature, various methods and materials have been applied to attempt to achieve ideal surface modifications. Plasma-assisted chemical vapor deposition (CVD), atomic laser deposition (ALD), and methods based on wet chemistry, such as sol gel, are arguably the most common.⁹⁻¹¹ However, these post-synthetic methods are typically employed to modify aggregated powders, which poses limitations on the ability to passivate buried interfaces and the homogeneity of any applied layers, especially given the possible inter-diffusion of elements during subsequent annealing to remove residual precursors.¹² The lack of physical and chemical features of shells creates inefficient formation of protective layers, and reduces the energy density with excessive use of inactive chemical species.

Recently, our group designed a strategy to prepare nanocrystal heterostructures containing a ~18 nm core of spinel $Li_{1+x}Mn_{2-x}O_4$ covered by a ~2 nm shell where Al replaced Mn while preserving structural epitaxy.¹³ To create the optimum core-shell architecture, here we employed a colloidal synthetic route that was designed to grow the thin shell enriched with Al^{3+} on the individual nanocrystals while they were present in fully dispersible form in a solution containing a surfactant to ensure conformal coverage

of all the nanocrystals. The core-shell nanocrystals showed improved cycling stability even at high temperature and resistance to corrosion by acidic environments, while maintaining similar levels of storage capacity as the bare counterparts. In order to further reduce the total amount of inactive Al in the oxide, it would be desirable to increase the volume of the core while maintaining shell thickness. In parallel, it would be valuable to study the effect on electrochemical properties of the variation of shell thickness. Broadly, the careful control and morphological homogeneity of colloidal chemistry turns the resulting heterostructures into useful model systems to study the fundamental effect of surface modifications on stability and electrode kinetics.

Here, we expand our original study by redesigning our synthetic method to grow passivating layers containing Al³⁺ at varying thicknesses, on nanocrystal cores that were ~60 nm. Control of the bulk structure and composition was achieved to make comparisons of electrode stability where only the characteristics of the shell were a variable.^{14,15} Each individual spinel nanocrystal then presents an ultra-thin shell, consisting of a gradient of concentration of Al on the surface, as characterized by electron microscopy. The local structure and chemical state of the shell was further investigated by a combination of spectroscopies. In all cases, the modified crystals show enhanced capacity retention with respect to the contents of passivating shells. The effect of shell thickness and composition on storage capacity and rate capability was established, providing valuable insight, broadly, into design rules for protective layers on battery cathodes.

2.2 Methods

2.2.1 Preparation of spinel $Li_{1+x}Mn_{2-x}O_4$ with epitaxial shells

Precursor MnO nanocrystals were prepared by a colloidal synthetic method. First, 4 mM manganese (II) acetate (Product No. 330825, Sigma-Aldrich) was dissolved in 30 mL of oleylamine (OAm) solution (Product No. O7805, Sigma-Aldrich) at room temperature under a nitrogen blanket in a Schlenk line. The mixture was subsequently degassed at 100 °C for 20 minutes under vacuum, followed by heating at 250 °C for 3 hours in nitrogen, under strong magnetic stirring. In order to introduce the Al-based shells, the vessel was first cooled to 220 °C and kept for 2 hours, when 20 mL of OAm solution containing aluminum acetylacetonate (Product No. 208248, Sigma-Aldrich) was added dropwise into the colloidal solution. The concentration of aluminum acetylacetonate was selected as 0.2, 0.4 and 0.8 mM (0.0648, 0.1297, and 0.2594 g) to evaluate the effect of Al content in the protective layers. The corresponding core-shell manganese oxide precursors are labeled as CS-MnO 1, 2, and 3, respectively. The solution was further annealed for 2 hours at 220 °C to form an aluminum oxide layer over coating all the nanocrystals. Finally, the resulting nanocrystals were cooled to room temperature, collected by centrifugation for 5 minutes at 10000 rpm, re-dispersed in 15 mL of hexane and washed with 20 mL of ethanol, followed by centrifugation. This process was repeated four times. After washing the nanocrystals, the powder was dried overnight at 60 °C. To prepare Li-containing oxides, the nanocrystals were thoroughly mixed with lithium acetate (Product No. 517992, Sigma-Aldrich) at different ratios of Li and Mn, and calcined in air at 600 °C for 4 hours at a ramping rate of 5 °C/min. Throughout this chapter, bare LMO and CS-LMO are used as labels for the products without and with Al shells, respectively. CS-LMO 1, 2 and 3 represent the modified spinel samples prepared from the CS-MnO 1, 2 and 3 precursors, respectively. Detailed synthetic conditions can be found in Table 2-1.

2.2.2 Characterization

Powder X-ray diffraction was performed on a Bruker D8 Advance using Cu Ka $(\lambda_{avg}=1.5418 \text{ Å})$ radiation. Scan rates were 0.04 ° s⁻¹ from 10° to 80 ° (2 θ). Fitting of the patterns to calculate lattice parameters of the different samples was carried out using GSAS-II.

Scanning electron microscopy was conducted on a Hitachi S-3000N, fitted with energy dispersive X-ray (EDX) detector. Transmission electron microscopy at low magnification was carried out on a JEOL JEM 3010, operated at 300 kV. The images were analyzed to extract the distribution of particle size by measuring approximately 200 nanocrystals using ImageJ from the Research Services Branch of NIMH & NINDS. Scanning transmission electron microscopy was performed on an aberration-corrected JEOL JEM-ARM200CF, operated at 200 kV, which can achieve a spatial resolution of ~73 pm. Images were acquired in angle annular dark field (ADF), low angle annular dark field (LAADF) and annular bright field (ABF) mode, wherein the resulting imaging contrast is approximately Z^2 . The ARM200CF is equipped with an Oxford X-Max 100TLE windowless silicon drift EDX detector. Electron energy-loss spectroscopy (EELS) was performed at an acceleration voltage of 200 kV. The EELS spectra of Mn Land O K-edges were collected from the surface to bulk in core-shell Li_{1+x}Mn_{2-x}O₄ nanocrystals. The background was removed and normalized using Digital MicrographTM software by Gatan Inc.

Mn L_{II, III}- and O K-edge X-ray absorption spectroscopy (XAS) measurements were carried out at beamline 6.3.1.2 ISAAC endstation at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Spectra were collected in total electron yield (TEY) and fluorescence yield (FY) modes at room temperature and under ultra-high vacuum conditions (below 10^{-8} Torr). Contributions from visible light were carefully minimized before the acquisition, and all spectra were normalized by the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber. Mn L-edge and O K-edge spectra were aligned to a beamline reference material, and normalized using a linear background.

²⁷Al MAS NMR experiments were performed at 11.7 T (500 MHz) on Bruker Advance III spectrometer at a Larmor frequency of 130.318 MHz. A rotor synchronized echo pulse sequence ($\pi/2 - \tau - \pi - acq.$), where $\tau = 1/v_r$ (spinning frequency), was used to acquire the spectra with a 2.5 mm probe at spinning speed of 30 kHz. A pulse width of 1.0 µs and a pulse delay of 2 seconds were used. The spectra were referenced to 1M Al(NO₃)₃ at 0 ppm. ⁷Li MAS NMR spectra were acquired at a magnetic field of 7.02 Tesla (300 MHz) on a Bruker Advance III HD spectrometer operating at a Larmor frequency of 116.700 MHz. A rotor synchronized echo pulse was used to acquire the spectra with a 1.3 mm probe at a spinning speed of 60 kHz. A pulse width of 1.6 µs and a pulse delay of 0.2 seconds were used. The spectra were referenced to 1M LiCl at 0 ppm and all experiments were performed at constant temperature of 283K.

2.2.3 Electrochemical measurements

The electrochemical properties were measured on composites containing the spinel nanocrystals as working electrodes. Electrode slurries were prepared by mixing active materials and carbon black (Denka) in 6 wt% of a solution of polyvinylidene difluoride (PVDF, Kynar) in N-methylpyrrolidone (NMP, Sigma-Aldrich), to result in 80:10:10 wt % of the three components (oxide, carbon, and polymeric binder). Then, the slurry was casted on electrochemical-grade aluminum foil using a doctor blade, and dried under vacuum at 80 °C overnight to evaporate solvent moieties. The loading level in the dry electrodes was ~ 3.5 mg/cm^2 . Circular pieces with a diameter of $\frac{1}{2}$ inch were punched and assembled in two-electrode coin cells in a glovebox filled with Ar gas (the level of contents of water and oxygen were ≤ 0.1 ppm). Three coin cells were prepared for each sample to generate statistical significance. High purity lithium foil (Product No. 10769, Alfa Aesar) and 25 µm-thick polypropylene membrane (Celgard 2400) were the counter/reference electrode and separator, respectively. The electrolyte (BASF) consisted of 1 M LiPF₆ in a 3:7 (wt%/wt%) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). Electrochemical measurements were performed on a Biologic BCS-805 at room temperature, or a VMP3 if cycled at 50 °C. The charge and discharge cutoff potentials were 4.3 and 3.5 V, respectively. All potentials in this chapter are referenced to the Li⁺/Li⁰ couple. The rate, C/n, was defined as the current density required to achieve a theoretical capacity of C = 148 mAh/g in n hours. The rate capability measurement was performed by fixing the charge current to C/10 while discharge currents were varied from C/10 to 10 C.

2.3 Analysis and evaluation of core-shell architectured spinel nanocrystals

2.3.1 Materials characterization

2.3.1.1 X-ray diffraction analysis

Colloidal MnO nanocrystals were prepared by thermal decomposition in oleylamine, which plays a role as surface-stabilizing ligand and high boiling point solvent.¹⁶ Al oxide layers were grown by thermal decomposition of a molecular precursor while the nanocrystals were in dispersed form to ensure even surface coverage. Bare and CS-MnO and core-shell (CS) MnO presented powder X-ray diffraction patterns (Figure 2-1a) consistent with a cubic rock-salt structure (JCPDS card number: 24-0735) without visible impurities. Reaction with lithium acetate at 600 °C for 4 hours in air was used to produce $Li_{1+x}Mn_{2-x}O_4$ cores. The annealing temperature was tailored to produce the phase of interest while minimizing crystal coarsening. The resulting XRD patterns matched well with the expected cubic spinel structure (Figure 2-1b), with a minor impurity of Mn₂O₃ (JCPDS card number: 35-0782) in some cases. This impurity is common during the synthesis of this active oxide.¹⁴ The Li/Mn ratio in the precursor mixture was adjusted to account for the presence of Al to maximize the content of redox-active Mn³⁺ in the $Li_{1+x}Mn_{2-x}O_4$ cores, by correlating the resulting cell parameters of the spinel structure to variations with x established in the literature (Figure 2-2 and Table 2-1).¹⁴ The lattice parameters varied between 8.208 and 8.222 Å when changing the Li/Mn ratio, corresponding to x values between 0.07 and 0.05, respectively, implying all samples contained similar bulk structures. At each Al content, the Li/Mn was set to get the highest cell parameter value while avoiding other impurities.


Figure 2-1. (a) XRD patterns of precursor rock-salt oxides. (The inset numbers indicate bare MnO, CS-MnO 1, CS-MnO 2, and CS-MnO 3, respectively) (b) XRD patterns of representative bare and three types of core-shell Li_{1+x}Mn_{2-x}O₄ spinel nanocrystals prepared by calcination at 600 °C with lithium acetate. (The inset numbers represent bare MnO, CS-LMO 1, CS-LMO 2, and CS-LMO 3, respectively)



Figure 2-2. (a) XRD patterns of bare and core-shell Li_{1+x}Mn_{2-x}O₄ nanocrystals prepared by varying the ratio of Li to Mn in calcination at 600 °C, as listed in Table 2-1. The numbers in Figure 2-2a indicate the products corresponding to synthetic conditions in table 2-1. (b) Diffraction patterns of bare and core-shell spinel nanocrystals between 35° and 39°.

Precursor	a (Å)	Li : Mn	Phase composition	No.	Sample	a (Å)	Atomic ratio of Al ³⁺ (Al / (Mn + Al))
MnO	4.44	1:02	Spinel + Mn_2O_3	(1)	LMO	8.222	
CS-MnO 1	4.44	1:02	Spinel + Mn_2O_3	(2)	CS-LMO 1	8.215	0.016
CS-MnO 2	4.43	1:02	Spinel	(3)		8.191	
CS-MnO 2	4.43	0.95:2	Spinel	(4)		8.194	
CS-MnO 2	4.43	0.9:2	Spinel	(5)	CS-LMO 2	8.201	0.032
CS-MnO 3	4.43	0.9:2	Spinel	(6)		8.189	
CS-MnO 3	4.43	0.85:2	Spinel	(7)	CS-LMO 3	8.21	0.088

Table 2-1. Lattice parameters and composition of precursor rock-salt and Li-containing spinel nanocrystals prepared by calcining at 600 °C for 4 hours with controlled Li to Mn ratio. The atomic ratio of Al is defined with respect to the total content of ions (Mn+Al), and it was extracted from SEM-EDX results.

2.3.1.2 Electron microscopy and elemental analysis

Figure 2-3 shows representative electron micrographs and histograms of crystal sizes for MnO, bare $Li_{1+x}Mn_{2-x}O_4$ and a representative set of core-shell $Li_{1+x}Mn_{2-x}O_4$ nanocrystals (CS-LMO 3). In all cases, the nanocrystal size was ~ 60 nm, without significant growth upon calcination. Elemental microanalysis by SEM-EDX showed a gradual increase in Al concentration in the sample by varying the contents of injected aluminum acetylacetonate solution (Table 2-1). The atomic ratios, defined as Al/(Al+Mn), were 0.016, 0.032 and 0.088 in CS-LMO 1, 2 and 3, respectively. These values correspond to approximately 32, 33, and 48 % of Al precursors having reacted to form a coating on the colloidal manganese oxide nanocrystals.



Figure 2-3. Representative TEM image and histogram of (a) precursor MnO, (b) bare LMO and CS-LMO 3 nanoparticles. The numbers in the histograms indicate their averages and errors of particle size.

The core-shell architecture of the spinel nanocrystals was directly confirmed by scanning transmission electron microscopy (STEM). Atomic resolution STEM images in Figure 2-4a, taken along a [110]-type direction, confirmed the epitaxy of the atomic stacking between core and shell in the nanocrystals with only slight differences in lattice spacings between the surfaces and bulk. The change in intensity of the B-site in AB₂O₄ spinel structure, and appearance of apparent hexagonal 'rings' ~ 2 nm from the surface could suggest a different local arrangement, but may also be due to overlap with a neighboring crystal. In any case, a similar structure was seen in the bare spinel as well, suggesting that it is not a consequence of the formation of a shell (Figure 2-4 and 2-5). EDX mapping of the crystallites in Figure 2-4 (b) shows a relatively uniform contrast of Al over the particle, indicating the shell layer is quite uniform. EDX line scans of the Mn-

L and Al K emission lines were conducted across the surface of a single particle (Figure 2-4 (c)). The elemental profile revealed a sharp upward slope in the Al signal near the surface of the nanocrystal, which spanned ~5 nm into the bulk. There was a corresponding decrease in the intensity of the Mn signal, indicating that an Al-rich oxide layer was present. Together with the homogeneous distribution of Al in the EDX map, this information leads to the conclusion that a contiguous shell existed over the entire spinel nanocrystal, even after a heat treatment at 600 °C. Another method of examining subtle chemical changes from doping is possible from electron energy loss spectroscopy (EELS, Figure 2-4 (e)). Variations in the valence state of Mn can be measured by examining the offset, shape, and relative peak volume of the L_{II} and L_{III} Mn edges.¹⁷ The Mn L-edge EELS measures dipole allowed transitions from Mn 2p orbital to unoccupied 3d orbitals, separated by the spin-orbital interaction of the Mn 2p core hole.^{18,19} The onset of the Mn L_{III} edge varied by ~1eV between the surface and the bulk, which also matched the change in the white line ratio. These changes are ascribed to variations in valence from $Mn^{3+/4+}$ in the bulk, to $Mn^{2+/3+}$ at the surface. A plot of Mn L_{III}-edge position through the single particle indicates that the reduced surface layer was as thick as 3~5 nm for this particle. Considering that the microscopic analysis revealed a spinel atomic arrangement throughout, this observation indicates the possible presence of Mn²⁺ defects in the tetrahedral site of the spinel framework of the shell of the nanocrystals.



Figure 2-4. (a) LAADF images, (b) EDX maps, (c) EDX line scan, and (d) EELS line scanned image of CS-LMO 3 single nanocrystal. (e) EELS spectrum across the nanoparticle and (f) main peak position of Mn L_{III} edge in each spectrum.



Figure 2-5. (a) High resolution LAADF and (b) ABF images of bare LMO.

2.3.1.3 X-ray absorption spectroscopy

Mn LII, III- and O K-edge X-ray absorption spectroscopy (XAS) were measured using both a total electron yield (TEY) detector, sensitive to ~5 nm into the powder surface, and fluorescence yield (FY) detector, which probes ~100 nm deep and, thus, dominated by the bulk of the sample. FY data were affected by self-absorption of the escaping fluorescent photons by the material, which results in different intensity ratios of the signals compared to TEY, without corresponding chemical changes. Like EELS, the Mn L_{II, III}-edge spectra were relatively intense due to the electronic dipole allowed $2p \rightarrow 3d$ transition, but the higher energy resolution revealed two groups of multiplets with very fine structure (Figure 2-6 (a)).²⁰ The overall shape of the spectra for bare and CS-LMO 3 was comparable when collected with the same detector. Therefore, both samples had Mn in similar oxidation states, consistent with the similar unit cell volumes. In contrast, the fraction of intensity of the signals in the TEY spectra positioned at absorption energies around 638.5 eV, which is associated with the presence of Mn²⁺ ions,²¹ was always greater than in TFY spectra for the same sample, confirming a slightly reduced state of Mn of the surface in both bare and modified spinels, and consistent with the EELS analysis. Since the intensity ratio, I $(L_{III})/I (L_{III} + L_{II})$, is related to the 3d metal spin states, the branching ratio of L-edge intensity is indicative of the electronic environment of Mn ions. In the case of CS-LMO 3 nanocrystals, the ratios were 0.657 and 0.542 in TEY and TFY mode, respectively, which were higher than the values of bare spinel (0.628 and 0.527) in a significant manner. The large branching ratio corresponds to high spin states of Mn ions with decreasing formal valences of Mn ions in both TEY and TFY spectra. The results suggest that, compared to the bare material, CS-

LMO 3 may be in a slightly reduced state in the bulk and on the surface. O K-edge XAS (Figure 2-6 (b)) represents the transition of a 1s electron in oxygen to a 2p level hybridized with the 3d orbitals of Mn ions with a low spin electronic configuration. A pre-edge absorption at ~529 eV was predominant in all samples, which represents the transition of a 1s electron in oxygen to a 2p hybridized with the 3d orbitals of Mn ions. The signal around 531 eV was found to be subtly higher in the TFY spectra of bare spinel compared to TEY. Comparison with reference O K-edge spectra for Mn²⁺/Mn³⁺ and Mn⁴⁺ in a spinel structure further suggests a more reduced state of Mn in the surface than the bulk.²² The difference was much smaller for CS-LMO 3, which would imply that the surface reduction is slightly more pronounced without the presence of the shell, since Al-O bonds do not contribute in this region of the spectrum due to the absence of low lying dstates. In addition, the two broad peaks above 535 eV in the O K-edge were assigned to the transition to hybridized states between O 2p and Mn 4s/4p and Li 2s bands, as well as mostly ionic O states arising from any aluminum oxides in the shell or at the interface. The broad bands of modified spinel in TEY were more intense than the bare, which likely contains a contribution from any aluminum oxides on the surface.



Figure 2-6. (a) Mn L-edge and (b) O K-edge of bare LMO and CS-LMO 3 nanocrystals collected in TEY and TFY mode.

2.3.1.4 Solid-state nuclear magnetic resonance spectroscopy

Further insight into the structural changes induced by the introduction of Al shells, especially locally, was gathered with solid state magic angle spinning nuclear magnetic resonance (MAS NMR). Previous studies on spinel manganese oxides reported that lithium ions in the tetrahedral site give rise to ⁷Li MAS NMR peaks in the 400-900 ppm range, with higher oxidation states leading to greater shifts.²³ These large shifts are ascribed to hyperfine (or Fermi-contact) interactions, so they are measures of the unpaired electron spin density that is transferred from the paramagnetic ion to the lithium s-orbital. As seen in Figure 2-7 (a), the ⁷Li NMR spectrum of bare $Li_{1+x}Mn_{2-x}O_4$ was dominated by a resonance at ~ 523 ppm with three additional peaks observed at ~ 568, 604, and 660ppm. Consistent with previous reports, the most intense peak in all samples was assigned to tetrahedral lithium environment in the ideal tetrahedral (8a) position of

corresponding domains of spinel structure where the Li/Mn ratio was ¹/₂.²³ The additional peaks in the bare sample have intensity ratios consistent with the Li_{1.05}Mn_{1.95}O₄ composition extracted from analysis of the unit cell parameter by XRD.²⁴ Therefore, they were assigned to the preference for the formation of local Li⁺-Mn⁴⁺ clusters associated with the excess of these ions in the material, based on literature reports.²⁴ A very small peak was detected around -1 ppm for CS-LMO 1. Such peak is assigned to Li domains with diamagnetic environments, and, thus, no Mn in the coordination sphere. It is assigned to a small amount of Li in the shell surrounded by Al. No similarly clear signals around ~0 ppm could be resolved for all other samples due to overlap with the broad spinning sidebands of the hyperfine signals in this spectral region (Figure 2-7).

Significant changes were observed in the ⁷Li NMR spectra of the core-shell nanocrystals. As seen in Figure 2-7 (a), the introduction of the thinnest Al shell, in CS-LMO 1, resulted in the collapse of the small resonances into a single broad shoulder, concomitant to the broadening of the main signal, which also shifted downfield, to 509 ppm. Introduction of additional Al induced further broadening of the main ⁷Li resonance, at 515 ppm, which was asymmetric toward high fields. No other signals could be resolved in these samples. Comparison of relative peak intensities when the data was normalized to the mass of the sample showed that the lithium resonances associated with defects driven by Li excess (observed at 568, 604 and 660 ppm for bare Li_{1+x}Mn_{2-x}O₄) disappeared and/or shifted to lower frequencies, merging with the main resonance. CS-LMO 2 and 3 showed very similar spectra.



Figure 2-7. (a) ⁷Li MAS NMR spectrum, magnified (b) paramagnetic and (c) diamagnetic region in the spectrum of bare LMO and core-shell LMO series. Asterisks indicate spinning side bands.

The formation of a broad and featureless peak is ascribed to the existence of increased atomic disorder, for instance through lithium substitution into the vacancy and defect sites. This disorder broke the tendency for Li⁺-Mn⁴⁺ clustering in bare Li_{1.05}Mn_{1.95}O₄. The formation of Al-rich shells could contribute to the observed structural disorder. As Al incorporates into the shell, it intermixes with Mn within a spinel oxide framework, leading to new surface and subsurface domains where varying concentrations of diamagnetic Al³⁺ are introduced in the coordination sphere of Li at different depths into the particle. This change would reduce the magnitude of the hyperfine shift of the corresponding Li environments. No unique peaks associated Al³⁺-rich environments could be resolved, suggesting that it is located randomly in the structure, not through formation of clusters around Li. A collection of coordination spheres with gradual variations in Al-Mn ratio around Li would result in a broad distribution of resonances,

consistent with the broad peak observed experimentally. The smaller shift in core-shell than bare samples could also reflect subtle changes in local bond geometries around Li as a result of disorder, with a minor contribution of the slightly lower overall oxidation state of Mn in the core-shell than bare nanocrystals as suggested by XAS. The changes certainly cannot be ascribed to an increased excess of Li in $Li_{1+x}Mn_{2-x}O_4$ when going from bare to core-shell, since the ⁷Li signals have been found to shift to higher fields with *x*, to as much as 840 ppm, because of the increased oxidation state of Mn in the bulk.²⁵



Figure 2-8. ²⁷Al MAS spectrum of CS-LMO 3 nanocrystals with (a) wider range of spectra and (b) magnified diamagnetic region. (Asterisks indicate spinning side bands)

The nature of the aluminum environments within CS-LMO 3 nanocrystals was studied by ²⁷Al MAS NMR, as the concentration of this element was high enough for detection. As shown in Figure 2-8, the spectrum showed a broad, distorted signal spanning from 100 ppm to -50ppm, which was a combination of multiple Al resonances.

Modelling of the data required at least four different peaks at ~ 8, 15, 45 and 76 ppm (Figure 2-9). Comparison of the individual line shapes, simulated quadrupole coupling constants and chemical shift values to the literature indicated the existence of Al in 6-fold coordination sites of Al_2O_3 (8 ppm) and $LiAlO_2$ (15 ppm), as well as 5-fold coordination in Al₂O₃ (45 ppm) and tetrahedral Al in LiAlO₂ (76 ppm).²⁶ The existence of LiAlO₂ would confirm that some of the ⁶Li intensity around 0 ppm (Figure 2-7 (c)) in all coreshell samples is indeed due to Li in Mn-free portions of the Al-rich shell. A large spinning sideband manifold was also observed in the ²⁷Al MAS NMR spectrum (Figure 2-8). These spinning sidebands are partially due to electron dipolar interaction containing information on the interaction of these aluminum environments with the paramagnetic Mn centers in the material. Therefore, the broad and intense manifold reflects the close physical proximity between Al species and these Mn centers, as expected from the formation of shells on the spinel cores.²⁷ Similar to ⁷Li MAS NMR, any Al in the spinel lattice would have paramagnetic Mn in the first or second coordination shell, which should give rise to signals at large shifts due to the hyperfine interaction. No such resonances were observed in the sample within the wide spectrum ranges studied. It cannot be discounted that signals exist below the detection limit of the measurement, based on the low Al content in a narrow region of co-existence of Mn and Al observed in the EDX line scans (Figure 2-4 (c)), coupled with the expectation of large signal broadening due to the strength of the dipolar coupling between the Al nucleus and the unpaired electron density of Mn centers.



Figure 2-9. Deconvoluted ²⁷Al MAS NMR data of CS-LMO 3.

2.3.2 Electrochemical performance

2.3.2.1 Galvanostatic experiments

The electrochemical performance as cathodes of bare and core-shell nanocrystals were evaluated in half cells with Li metal. At each Al/Mn ratio, the specific capacity of the electrodes decreased with increasing Li/Mn ratio in the reaction mixture (Figure 2-10 (a)), consistent with the increase in *x* in the Li_{1+x}Mn_{2-x}O₄ core revealed by XRD above. Figure 2-10 (a) shows the potential versus specific capacity of the first cycle of cells containing the bare and core-shell samples with highest capacity at each Al/Mn ratio (i.e., CS-LMO 1, 2 and 3), collected in galvanostatic mode at room temperature. Derivative plots, *dqdv*, versus potential (Figure 2-10 (b)) of the bare oxide showed two distinct peaks at ~ 4.02 and 4.14 V upon charging, and 3.98 V and 4.11 V upon discharging, which is typical of Li_{1+x}Mn_{2-x}O₄ with low *x*.²⁸ All charge and discharge potentials gradually increased by introducing Al ions in the shells, with the values being ~0.03 V higher for CS-LMO 3 than bare LMO. The fact that increases were observed both in charge and discharge implies the existence of an increased thermodynamic redox

potential with Al content in the shell. Kinetic overpotentials would shift the redox steps in charge and discharge in opposite directions, increasing the separation in potential between the two anodic and cathodic sweeps. The potential shift was also not consistent with the changes observed when x is increased in $Li_{1+x}Mn_{2-x}O_4$, which involve merging of the two redox steps in the same sweep (charge or discharge).²⁹ This same effect was observed here by comparing the electrochemical profiles of samples with the same Al/Mn, but different Li/Mn ratios, and thus different x in $Li_{1+x}Mn_{2-x}O_4$, as revealed by XRD (Figure 2-10 (c, d)). This enhancement of the thermodynamic redox potential is intriguing because it results in an increase of the energy density of the cell. The origin of this effect is unclear. Since very little, if any, Al is located in the bulk of the crystals, mechanisms derived from alterations of the location of the redox-active O 2p-Mn 3d hybrid bands due to the presence of Al in the lattice, as reported for $LiCo_{1-x}Al_xO_2$,³⁰ are likely not at play. It is tempting to speculate that this observation is related to the changes in local Li structure revealed by NMR (Figure 2-7), since different local environments will alter the chemical potential. The structural disordering observed with the introduction of Al shells would certainly explain the smearing of each redox plateau, and corresponding peaks of dq/dv. The smearing could signify a change in the order of the transformation between pristine and charged states, which will be explored in follow-up work.



Figure 2-10. (a) Potential versus specific profiles, (b) dq/dv curves of bare and core-shell nanocrystals. (c, d) dq/dv plots of CS-LMO 2 and 3 spinels with different Li to Mn ratio.

2.3.2.2 Cycling performance at room temperature and 50 °C

The reversible specific capacities slightly declined with Al content. Bare LMO delivered 108 mAh/g after the first discharge, and the capacities of CS-LMO 1, 2 and 3 were 2.6, 3.5 and 6.4% lower. Similar effects were observed in our previous study.¹³ After 100 cycles at room temperature, the capacity retentions of CS-LMO 1, CS-LMO 2 and CS-LMO 3 nanocrystals was 77.2 % (87.3 mAh/g), 78.9 % (83.1 mAh/g) and 89.5 % (91.6 mAh/g), respectively, compared to 72.8 % (81.9 mAh/g) for bare LMO (Figure 2-

11 (a)). Therefore, the capacity all core-shell samples surpassed the bare material at this point. The degradation in capacity was mirrored by a significant washing out of the electrochemical profiles of bare LMO (see dq/dv plots in Figure 2-12). The profiles were found to be significantly more stable as the Al content increased. CS-LMO 1 also showed significantly enhanced rate capability compared to bare LMO, delivering higher capacity even at rates as high as 10C. While CS-LMO 2 was comparable to the bare material, CS-LMO 3 showed decreased capability (Figure 2-11 (b)), possibly due to the high ratio of Al³⁺ ions in the material, thus affecting electronic conductivity.



Figure 2-11. (a) Evolution of specific capacity (solid symbol) and coulombic efficiency (open symbol) when cycling at C/10, and (b) rate capability measurement at room temperature.



Figure 2-12. The dq/dv plots at first and 100th cycle in (a) bare LMO, (b) CS-LMO 1, (c) CS-LMO 2, and (d) CS-LMO 3.

The trends were aggravated at elevated temperature (50 °C), where side reactions between electrode surface and electrolyte are accelerated. While the voltage profiles in the first cycle were largely the same as at room temperature (Figure 2-13), the capacity degradation accelerated. At 50 °C, bare LMO retained only 65.5 % (69.3 mAh/g) of their initial capacity after 50 cycles at C/10, compared to 69.8 % (73.1 mAh/g), 70.4 % (75.2 mAh/g) and 80.9 % (81.5 mAh/g) retention of CS-LMO 1, 2 and 3, respectively. The

effects of Al-rich oxide shells were more significant in this harsh environment than room temperature after only 50 cycles. Evidence that the improved electrochemical performance was associated with enhanced interfacial stability was provided from elemental microanalysis of multiple areas of the surface of the lithium anode electrode after cycling at C/10 using SEM-EDX (Figure 2-14). Roughly four times lower atomic contents of Mn were found on the Li metal assembled with CS-LMO 3 electrode compared to bare LMO ($0.48 \pm 0.08 \text{ vs } 2.1 \pm 0.6 \text{ at\%}$). The presence of Mn on the anode is associated with the dissolution of the transition metal ions upon degradation of the cathode-electrolyte interface during cycling, for instance, through degradation mediated by Mn disproportionation in the presence of acidic impurities.³¹ These dissolved ions can migrate toward the anode and deposit on its surface.³² It is noteworthy that low levels of Mn dissolution were found for CS-LMO 3 despite evidence of Mn²⁺ in some particle surfaces, as evidenced by STEM-EELS (Figure 2-4 (e, f)). The result suggests that the Al-rich shells were effective in passivating the active crystal surface toward interfacial degradation.



Figure 2-13. (a) Potential versus specific profiles, and (b) evolution of capacity (solid symbol) and coulombic efficiency (open symbol) when cycling at C/10 at 50 $^{\circ}$ C.



Figure 2-14. Elemental analysis of Mn ions on the Li metal assembled with (a) bare LMO and (b) CS-LMO 3 cathodes, after operating 50 cycles at 50 °C. The Mn content was averaged by measuring SEM-EDX in three different areas.

2.4 Summary

The concept of core-shell architecture of Li_{1+x}Mn_{2-x}O₄ battery cathodes using a colloidal synthetic route was extended to larger core-to-shell ratios than in previous reports. The effect of shell thickness was evaluated by synthesizing samples with varying Al contents. The passivating layers were found to be epitaxial with the core in all samples, with gradients of Al/Mn ratio from surface to bulk. The core in all samples was tailored to result in the same amount of electrochemically active Mn³⁺ to assess the effect of different shells. The modified spinel enhanced cycling durability with respect to materials where a shell was not present. Evidence was gathered that the differences

between samples was driven by the role of the protecting surface sites in contact with electrolyte. An enhancement in the redox potential was observed with Al content, which could not be explained by conventional bulk effects. This intriguing effect warrants further investigation, as it suggests avenues to enhance energy storage in the materials in addition to introducing interfacial stabilization.

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CHAPTER 3

3. NANOCRYSTAL HETEROSTRUCTURES OF LiCoO₂ WITH CONFORMAL PASSIVATING SHELLS

3.1 Introduction

The market of electrical vehicles has clearly identified the development of Li-ion batteries with higher energy and power density than today as a bottleneck for widespread expansion. In these devices, enhancements in energy density necessarily require improving the performance of electrodes, which contain the active materials.^{1,2} Layered oxides are leading candidates for the active material of the positive electrode due to their high capacity and potential of operation, which increase the energy storage. Among them, $LiCoO_2$, which also offers good electronic conductivity upon cycling, was employed in the first devices brought to the market.^{3,4} Despite the move to variants where ions such as Ni replace Co, LiCoO₂ continues to be dominant in several applications, while also epitomizing the fundamental challenges of high energy Li-ion batteries. The high operating potential (> 3.9 V vs Li^+/Li^0) leads to spurious reactions at the electrodeelectrolyte interface, which involve decomposition of the electrolyte and dissolution of active ions from the oxide.^{5,6} These processes contribute to a rapid degradation of performance. The challenges are further exaggerated when the size of the primary particles is reduced to the nanoscale, which would promote short diffusion lengths for the charge carriers in the final dense architecture.⁷ The concomitant high surface area also

accelerates degradation at electrode-electrolyte interfaces,⁸ which ultimately limits the applicability of nanomaterials. Careful tailoring of electrode/electrolyte interfaces to suppress unwanted side reactions while promoting electrode operation is an essential strategy to produce energy storage technologies that surpass the current performance.

Since interfacial stability in battery electrodes is linked to the redox activity of transition metal ions at the cathode surface,⁹ partially replacing them with inactive ions could improve interfacial stability and capacity retention. Such surface replacement should be in the form of ultra-thin passivation layers to minimize losses in the storage capacity of the bulk.^{10,11} Various candidates, such as metal oxides, polymer and carbon have been investigated as possible coating materials on active electrodes, by applying physical vapor deposition, wet-chemical techniques and atomic layer deposition (ALD).¹²⁻¹⁴ But these post-synthetic methods are typically applied on aggregated powders or even electrodes, which poses restrictions on the conformality and homogeneity of the protective layers, aggravated by the subsequent anneals to remove residual precursors.¹⁵ The result is a lack of complete control over the physical and chemical features of the passivating layers, which creates inefficiencies in the form of incomplete passivation of buried interfaces and excessive use of inactive materials that reduce the energy density of the cell. Therefore, efforts continue to build multifunctional electrode architectures where passivating layers are present in optimal amounts to promote durability without affecting storage capability.

Ideally, all possible surfaces of active powder should be covered by passivation layers that are controlled in composition, thickness and structure. Advances in nanotechnology methodologies over the past two decades have brought about the ability

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to manipulate individual, dispersible primary particles to deposit shells of the desired properties, thus building precise heterostructures. The ability to form nanocrystalline heterostructures have been demonstrated in the synthesis of quantum dots,¹⁶ magnetic structures¹⁷ and catalysis,¹⁸ but has yet to be fully exploited in battery applications. The compositional complexity of the oxides of interest, with transition metals in fairly high oxidation states (e.g., Co³⁺, Mn⁴⁺) creates significant challenges with existing recipes based on organic environments that are easily oxidized. Recently, we designed a strategy to produce nanocrystals of spinel-type $Li_{1+x}Mn_{2-x}O_4$ with a 1~2 nm epitaxial shell that was rich in Al³⁺.¹⁹ The coated electrode materials showed an improved cycling durability while maintaining a stable specific capacity, even when subject to harsh environments, such as high temperature cycling. Given the current move away from spinel oxides as electrodes due to their low storage capability,²⁰ increasing the value of this strategy of active material protection required demonstrating versatility in other compositional spaces, such as layered transition metal oxides. Here, we advance toward this goal by demonstrating a novel recipe for the synthesis of core-shell (CS) nanocrystals based on LiCoO₂, a cathode material that enables Li-ion batteries with higher energy density than Li_{1+x}Mn_{2-x}O₄. To control the heterostructures, colloidal chemistry was employed to grow a thin shell rich in Al^{3+} in the same reaction environment where the particles were formed and dispersed, ensuring effective coverage of all surfaces. Post-synthetic annealing was used to produce the final heterostructure and tailor the specific chemistry of the shell. An improved understanding of the chemical identity and specific location of core and shell components was confirmed by a combination of X-ray absorption spectroscopy (XAS), solid state nuclear magnetic resonance (NMR) spectroscopy and scanning transmission electron microscopy (STEM). The core-shell nanocrystals improved electrochemical properties compared to their bare counterparts. The improvements were linked to specific chemical signatures to chart the path forward for this synthetic approach.

3.2 Methods

3.2.1 Synthesis of heterostructure LiCoO₂ nanocrystals

The precursor CoO nanocrystals were prepared by following a colloidal synthetic method. First, 4 mM cobalt (III) acetylacetonate (Product No. 494534, Sigma-Aldrich) was dissolved in a 40 mL of oleylamine (OAm) solution (Product No. 07805, Sigma-Aldrich) at room temperature (RT) under a nitrogen blanket in a Schlenk line. In order to remove water and impurities, the mixture was degassed at 100 °C for 20 minutes under vacuum. The slurry was then heated at 185 °C and maintained it for 1 hour under strong magnetic stirring in an atmosphere of nitrogen gas. Subsequently the temperature was raised to 220 °C and kept for 30 minutes. Aluminium oxide shells were formed on the surface of CoO by a dropwise addition of 20 mL of OAm solution containing 0.8 mmol of aluminum acetylacetonate (Product No. 208248, Sigma-Aldrich) into the CoO colloidal solution at 220 °C. The solution was further annealed for 20 minutes at 220 °C. The resulting nanocrystals were cooled to room temperature in the form of a brown suspension. To remove the oleylamine residues and unreacted products, the nanoparticles were collected by centrifugation for 5 minutes at 10000 rpm, re-dispersed in 15 mL of hexane and washed with ethanol five times. After washing the particles, the powder was dried overnight at 60 °C. In order to prepare LiCoO₂, the nanocrystals were thoroughly mixed with LiOH H₂O (Product No. 43171, Alfa Aesar) at stoichiometric ratios of Li and Co ions and, calcined at 500 °C for 1 or 30 hours in air. Throughout the paper, Bare and CS-LiCoO₂ are used as labels for the products without and with Al shells, respectively. LiCoO₂ nanocrystals presenting the low temperature, spinel polymorph were prepared from the same precursors, using a different synthetic protocol. Co_3O_4 was obtained by calcining the CoO precursor at 300 °C for 4 hours, and it was subsequently reacted with LiOH at 300 °C for 72 hours.

3.2.2 Characterization

Powder X-ray diffraction was performed on a Bruker D8 Advance using Cu Ka $(\lambda_{avg} = 1.5418 \text{ Å})$ radiation. Scan rates were $0.04 \circ \text{s}^{-1}$ from 15° to $80^{\circ} (2\theta)$. Fitting of the patterns to calculate lattice parameters of the different samples was carried out using GSAS-II.

TEM images at low magnification were obtained using a JEM 3010 (JEOL) operated at 300 kV. The images were analyzed to extract the distribution of particle size and population of different morphologies, by measuring approximately 300 nanocrystals using the ImageJ program. Complementary information was collected using scanning electron microscopy (Hitachi S-3000N) fitted with energy dispersive X-ray spectroscopy. All STEM imaging and EDX spectroscopy were performed on an aberration-corrected JEOL JEM-ARM200CF operated at either 200 or 80 kV. Images were acquired in angle annular dark field (ADF) mode, wherein the resulting image intensity is proportional to Z^2 . The ARM200CF is equipped with an Oxford X-Max 100TLE windowless silicon drift EDX detector.

Soft X-ray absorption measurements were carried out at beamline 4-ID-C at Argonne National Laboratory (ANL, Lemont, IL). Data was obtained at a resolution of

~0.1 eV and collected at the O K- and Co $L_{II, III}$ -edges at room temperature, under ultrahigh vacuum conditions (below 10⁻⁸ Torr). A silicon drift diode detector (Vortex) was used to collect the fluorescence yield (FY) and electron yield (EY) positioned near the sample surface. Contributions from visible light were carefully minimized before the acquisition, and all spectra were normalized by the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber. The spectra were aligned using the beamline reference, and a basic normalization using a linear background and edge normalization was performed.

⁷Li and ²⁷Al MAS NMR spectra were acquired at a magnetic field of 7.02 Tesla (300 MHz) on a Bruker Advance III HD spectrometer operating at a Larmor frequency of 116.64 MHz and 78.20 MHz, respectively. A rotor synchronized echo pulse sequence ($\pi/2 - \tau - \pi - acq.$), where $\tau = 1/v_r$ (spinning frequency), was used to acquire the ⁷Li MAS NMR spectra with a 3.2 mm probe at a spinning speed of 20 kHz. A pulse width of 3.5 µs and a pulse delay of 5 seconds were used. The spectra were referenced to 1M LiCl at 0 ppm. For ²⁷Al MAS NMR experiments, a single pulse sequence was used with a pulse width of 1µs and a pulse delay of 2s. The spectra were referenced to 1M Al(NO₃)₃ at 0 ppm. All experiments were performed at a constant temperature of 283K.

3.2.3 Electrochemical measurements

The electrochemical properties were measured on composites containing the nanocrystals as working electrodes. Electrode slurries were prepared by mixing nanocrystals, carbon black (Denka), and 6 wt% of a solution of polyvinylidene difluoride (PVDF, Kynar) in N-methylpyrrolidone (NMP, Sigma-Aldrich). The ratio of components

was set to 80:10:10 wt %. Then, the slurry was casted on electrochemical-grade aluminum foil using a doctor blade, and dried under vacuum at 70 °C overnight to evaporate NMP moieties. The loading level in the dry electrodes was around 3.0 mg/cm². Circular pieces with a diameter of 1/2 inch were punched and assembled in two-electrode coin cells in a glovebox filled with Ar gas (the level of contents of water and oxygen were ≤ 0.1 ppm). Three coin cells in each material were prepared to calculate average and standard deviation of capacities of the cells. High purity lithium foil (Product No. 10769, Alfa Aesar) and 25 µm-thick polypropylene membrane (Celgard 2400) were the counter/reference electrode and separator, respectively. The electrolyte consisted of 1 M LiPF₆ in a 3:7, v/v, mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), produced by BASF. Electrochemical measurements were performed on a Biologic BCS-805 at room temperature. The cut-off potentials were set at 4.3 V and 2.0 V, all potentials in this chapter being referenced to the Li⁺/Li⁰ couple. The values of specific capacity and coulombic efficiency were the result of averaging three different cells to assess reproducibility and error. The rate, C/n, was defined as the current density required to achieve a theoretical capacity of C = 274 mAh/g in n hours. The rate capability was measured by fixing the charge current to C/10 while discharge currents were varied from C/10 to 10 C.

3.3 Structural, electronic and electrochemical properties of heterostructure LiCoO₂ nanocrystals

- 3.3.1 Materials characterization
- 3.3.1.1 X-ray diffraction analysis

Colloidal CoO nanocrystals were prepared by thermal decomposition of Co (III) acetylacetonate (4 mmol, 1.42504 g) in oleylamine, which plays a role as surface-stabilizing ligand and high boiling point solvent.²¹ The passivating layer on the surface was grown by injecting an oleylamine solution of Al (III) acetylacetonate (0.8 mmol, 0.25945 g) into the colloidal suspension of CoO at 220 °C. X-ray diffraction verified the phase purity and structure of the as-made nanocrystals (Figure 3-1). Both bare CoO and core-shell (CS) CoO presented a cubic rock-salt structure (JCPDS card number: 43-1004).



Figure 3-1. X-ray diffraction patterns of (a) CoO and (b) core-shell CoO nanocrystals

To synthesize electrochemically active, Li-containing nanocrystals, the rock-salt oxide precursors were mixed with LiOH and calcined at 500 °C in air. The XRD patterns in Figure 3-2 matched the layered LiCoO₂ structure, qualitatively (JCPDS card number: 01-070-2685). In order to minimize grain growth and core-shell inter-diffusion, a reaction time of 1 hour was used. However, small peaks assigned to a Li₂CO₃ impurity were

observed, especially for CS-LiCoO₂-1h. Its presence is likely due to the insufficient length of the thermal treatment to complete the reaction. It is possible that some Co₃O₄ (JCPDS card number: No. 00-042-1467) was present as well, since it also presents a peak at ~32°, but all other reflections overlap with LiCoO₂. In contrast, no significant impurities were observed when the synthetic step was carried out in 30 hours. The diffraction peaks were broad, indicative of small particle sizes, and presented asymmetries, as exemplified in the zoomed view between 36.5 and 38°. The asymmetry was ascribed to the presence of both polymorphs of LiCoO₂, layered and spinel, which share diffraction peaks.²² The electrochemical properties of the spinel polymorph are worse than the layered variant.²³⁻²⁵



Figure 3-2. XRD patterns of (a) LiCoO₂-1h, (b) CS-LiCoO₂-1h, (c) LiCoO₂-30h and (d) CS-LiCoO₂-30h nanocrystals. Miller indices corresponding to the layered polymorph of LiCoO₂ are provided. Solid circled marks indicate Li₂CO₃ impurities.

Fits of the XRD patterns assuming a layered orthorhombic structure revealed similar values of a dimension for all samples (Table 3-1). In the case of the interlayer spacing, defined by c, an increase was observed with annealing time, both in the presence and absence of Al. CS-LiCoO₂-1h presented the lowest value of all samples, which could be linked to incomplete reactions, and the noticeable presence of Li_2CO_3 . The c/a ratios of the samples mirrored the trends in c, with the highest values associated with the longest annealing times. The layered structures are defined by c/a ratios close to 5.00, with lower ratios being indicative of a cubic spinel polymorph.^{26,27} All the c/a values further support the presence of the low temperature, spinel polymorph in co-existence with the high temperature, layered form of LiCoO₂. Such polymorphism is common when materials are synthesized at low temperature.²⁸ The increase in c/a with reaction time is indicative of an increase of the ratio of layered polymorph. The similarity in cell parameters for LiCoO₂-30h and CS-LiCoO₂-30h suggest that the introduction of Al³⁺ did not significantly affect the bulk structure of the material, as substitution of Co^{3+} in LiCoO₂ by Al³⁺ causes an expansion of the *c* axis.²⁹

	<i>a</i> (Å)	<i>c</i> (Å)	c/a
LiCoO ₂ -1h	2.83	13.96	4.93
LiCoO ₂ -30h	2.82	14.01	4.96
CS-LiCoO ₂ -1h	2.84	13.86	4.87
CS-LiCoO ₂ -30h	2.83	13.99	4.95

Table 3-1. Unit cell parameters and *c/a* ratio of all the nanocrystals.

3.3.1.2 Electron microscopy

Figures 3-3 (a) shows the morphology of the CoO precursors, which formed agglomerates of ~70 nm composed of nanocrystals of ~7 nm and all secondary particles presented similar size. It is worth noting that growth of the Al shells was carried out on these secondary particles, while highly dispersed in the reaction solution. After the reaction with LiOH, the primary particles fused to form objects with a single crystalline appearance, with morphology varying from spherical to faceted, with an appearance of plate (Figures 3-3).³⁰ Minor grain growth was measured after the reaction at 500 °C, as denoted in the histogram in Figure 3-3 (g), which resulted from measuring more than 300 nanocrystals per sample. The ratio of spherical to faceted nanocrystals in bare LiCoO₂ was calculated by selecting nine different areas randomly. The population of each morphology, plotted in figure 3-3 (h), indicates an increase in the ratio of platelets with reaction time. In some cases, transition between morphologies was not complete and the particles appeared to present a void in their interior. The same trend can be qualitatively noticed in the samples with shells. This observation is consistent with the increase in the ratio of layered polymorph, which is known to favor this morphology.³¹



Figure 3-3. Representative TEM images of (a) CoO precursor, (b) LiCoO₂-1h, (c) LiCoO₂-30h, (d) CS-CoO, (e) CS-LiCoO₂-1h and (f) CS-LiCoO₂-30h nanocrystals (All scale bars are same); (g) average particle size of each material with error bars; (h) % plate vs spherical particles in LiCoO₂-1h and LiCoO₂-30h nanocrystals.

Energy dispersive X-ray (EDX) spectroscopy was conducted in a scanning electron microscope (SEM) to measure the ratio of Al/Co in a large portion of the sample. The values were around 0.16 in both core-shell materials. These values correspond to approximately 84% of Al precursor having reacted to form a coating on the colloidal cobalt oxide particles. The core-shell nature of the nanocrystals was directly confirmed by spatially locating Al and Co atoms via EDX spectroscopy in a high-resolution scanning transmission electron microscope (STEM), operated, at 80 kV primary electron energy. The EDX maps and line scan curves provide information on elemental

distribution and concentration throughout the nanocrystals. In all cases, they show a core of Co atoms (Figures 3-4 (a, d)), with Al atoms predominantly located on the surface (Figures 3-4 (b, e)). Additional information was extracted by analyzing line scans conducted along a single particle. Specifically, the concentration of Al in CS-LiCoO₂-1h showed a sharp slope upwards approaching the surface region (Figure 3-4 (c)), while that of CS-LiCoO₂-30h reveals a slightly more gradual slope from the surface (Figure 3-4 (h)). The fact that Co concentrations where higher on the surface after 30 h than 1 h implies the formation of a Al/Co concentration gradient moving from surface to bulk. The measurements indicate that, while the synthetic step at 500°C was not too harsh to wash out the core-shell structure, it did result in a different extent of inter-diffusion, which could affect the electrochemical properties. Atomic resolution STEM imaging (Figure 3-5) show a nanocrystal consisting of multiple crystalline domains, probably due to intergrowths of spinel and layered phase, without local inhomogeneity on the surface, implying epitaxy with the core.



Figure 3-4. EDX mapping of (a) Co and (b) Al atoms in CS-LiCoO₂-1h nanocrystals and corresponding line scans. EDX mapping of (d) Co and (e) Al atom in CS-LiCoO₂-30h nanocrystals and (c), (h) corresponding line scans.



Figure 3-5. (a) LAADF and (b) ABF images of CS-LiCoO₂-30h nanocrystals.

3.3.1.3 Solid-state nuclear magnetic resonance spectroscopy

Solid state NMR experiments were performed to study the lithium and aluminum local environments in the samples prepared. ⁷Li MAS NMR data for all four samples show a main isotropic resonance at around -1 ppm, typical of lithium in a diamagnetic local environment, as would be expected by the presence of low spin (t_{2g}^{6}) Co³⁺ ions in stoichiometric LiCoO₂.³² Both bare LiCoO₂ nanocrystals (1 and 30h) had a small shoulder at around 30 ppm suggesting existence of a slight excess of lithium in the structure (Figures 3-6).³³ For comparison purposes, the low temperature, spinel polymorph of LiCoO₂ was also synthesized and its ⁷Li MAS NMR spectrum was collected (Figure 3-6 (a)). It also presented a resonance close to -1 ppm, again indicative of the presence of Co³⁺, making it impossible to use NMR to resolve layered from spinel components.



Figure 3-6. (a) Mass normalized and (b) alternative view of the ⁷Li MAS NMR spectra of bare and core-shell LiCoO₂ nanocrystals. (Asterisk mark (*) indicates spinning side band)
The nature of the local environments of Al in the core-shell particles was studied with ²⁷Al MAS NMR (Figure 3-7). The data for both samples showed at least 6 different aluminum peaks between 20 to 60 ppm, each separated by ~7 ppm. Upon comparison with previous ²⁷Al MAS NMR spectra of LiAl_xCo_{1-x}O₂ solid solutions and LiCoO₂ coated with Al³⁺ species at high temperatures,³⁴ the signals can be assigned to octahedral Al^{3+} environments with varying amounts of Co^{3+} in the neighboring coordination shell. In other words, they are indicative of presence of LiAl_xCo_{1-x}O₂ solid solution within the structure. Based on the high resolution elemental maps in Figure 3-4, this solid solution is most likely located at the interface between core and shell, and reflects the outward gradient in Al/Co ratios. The similar intensities observed in this region for the two coreshell samples reveals that the solid solution formation is driven by annealing temperature but does not depend on annealing time. The major difference between the two samples was found in the region from 0 to 15 ppm, corresponding to octahedral Al^{3+} environments in an oxide without the transition metal.³¹ CS-LiCoO₂-1h showed a peak around 6 ppm typical of environments in Al₂O₃. This observation suggests the sample also has an oxide layer on the surface, consistent with the very low amount of Co found close to the surface (Figure 3-4 (c)). This peak shifted to 14 ppm and broadened as the annealing time increased to 30h, ascribed to interfacial phases such as a distorted Al₂O₃ structure and/or LiAlO₂, with octahedral Al³⁺. The subtle but significant difference in Al^{3+} species present in the shell of the nanocrystals was expected to affect the electrochemical properties of the materials, based on previous studies.³⁴



Figure 3-7. ²⁷Al MAS NMR spectra of core-shell LiCoO₂ with different annealing hours. (Asterisk mark (*) indicates spinning side band)

3.3.1.4 X-ray absorption spectroscopy

Soft X-ray absorption spectroscopy (XAS) was performed to examine the electronic environment of Co and O atoms, and the effect of the introduction of Al ions or different annealing time. Spectra were measured using both a total electron yield (TEY) detector, sensitive to the surface, and a fluorescence yield (FY) detector, suitable for characterization of the bulk. Data in FY are affected by absorption of the fluorescent photons by the material, which results in a different, anomalous intensity ratio of the signals compared to TEY. The Co L_{II} , III edge in all cases showed main absorption peaks at ~791 and ~776 eV and weak shoulder peaks at ~792 and ~778 eV, respectively (Figure 3-8). These signatures are indicative Co³⁺ with a low spin configuration.³⁵ The electronic structures of Co were essentially the same in all LiCoO₂ materials, which reveals that the redox state of the transition metal was not affected by introducing Al ions on the surface.



Figure 3-8. Co $L_{II, III}$ -edge XAS, collected in (a) TEY and (b) TFY mode, of LiCoO₂-1h (black), CS-LiCoO₂-1h (red), LiCoO₂-30h (green), and CS-LiCoO₂-30h (blue) nanocrystals.

The two broad peaks above 535 eV in the O K-edge XAS were assigned to the transition to hybridized states between O 2p and Co 4s/4p and Li 2s bands (Figure 3-9), as well as mostly ionic O states arising from any aluminum oxides in the shell.³⁶ The small signal observed at 532.3 eV observed in some samples is consistent with the presence of Li₂CO₃ (C=O bonds) in the samples, as shown by XRD, based on comparisons with the literature.³⁷ A pre-edge absorption peak at ~527 eV was prominent in all samples. It represents the transition of a 1s electron in oxygen to a 2p level hybridized with the 3d orbitals of Co³⁺ with a low spin electronic configuration (t_{2g}⁶, ${}^{1}A_{1g}$). The main peak corresponds to a final state of O 1s¹c + Co 3d⁷ electronic configuration, where c is the oxygen 1s core hole.³⁸ No Al-O interactions arise at these energies. In the presence of Al³⁺-rich shells, the intensity of the peak at 527 eV decreased

compared to a new signal at 530.5 eV, accompanied by a very small peak at 534 eV, especially for CS-LiCoO₂-30h. The higher energy peak becomes more intense in the bulk (FY) spectrum. This effect cannot be accounted for by spectral distortions inherent to FY detection, suggesting a difference in O electronic states between bulk and surface. The appearance of this peak cannot be due to changes in the oxidation state of Co, since the corresponding Co L-edge spectroscopic results show no changes. It is possible that these states are created by the replacement of some of the Co³⁺ by Al³⁺ in the coordination shell of O²⁻, which would occur in the LiCo_{1-x}Al_xO₂ gradient. It is expected that Al-O interactions will be more ionic than Co-O. Calculations of density of states are required to verify this hypothesis. They were beyond the scope of this study.



Figure 3-9. O K-edge XAS, collected in (a) TEY and (b) TFY mode, of LiCoO₂-1h (black), CS-LiCoO₂-1h (red), LiCoO₂-30h (green), and CS-LiCoO₂-30h (blue) nanocrystals.

3.3.2 Electrochemical properties

3.3.2.1 Galvanostatic charge-discharge study

The electrochemical performance as electrodes of CS-LiCoO₂ nanocrystals with different annealing time were evaluated in Li metal half cells, and compared with bare LiCoO₂. Figure 3-10 (a) shows the voltage versus specific capacity profiles collected in galvanostatic mode during the first cycle at room temperature. Derivative plots, dq/dv, versus potential (Figure 3-10 (b)) uncovered two distinct peaks at approximately 3.76 V and 3.92 V during charging, and 3.47 V and 3.89 V during discharging. The two redox potentials were related to the spinel and layered forms of LiCoO₂, respectively.³⁹



Figure 3-10. (a) Representative voltage versus specific capacity profiles and (b) corresponding dq/dv plots of bare and core-shell LiCoO₂ nanocrystal electrodes when cycled at C/20.

A comparison with the electrochemical response of $LT-LiCoO_2$ nanocrystals made at 300 °C from the same CoO precursor confirmed this assignment. It is worth noting that the redox potential of the spinel component increased by around 50 mV upon introduction of Al in the sample, whereas the layered component remained constant. The exact origin of this observation is unclear, but could be related to the extensive transformation of spinel domains on the outer domains of the particles to LiCo_{1-x}Al_xO₂, which is known to show a shifted potential with respect LiCoO₂.⁴¹ The relative concentrations of HT- and LT-phase in all samples were qualitatively established by comparing the values of specific charge capacity above and below 3.8 V during the first charge, as shown Table 3-2. The comparison suggested a minor increase in electroactivity of the spinel phase only in CS-LiCoO₂-30h compared to the bare counterpart, whereas no quantitative difference was found in the capacity values for the samples made at 1 h.

	Charge capacity above 3.9 V (mAh/g)	Charge capacity below 3.9 V (mAh/g)	% capacity of LT		
LCO 1h	84.1 ± 0.3	59.6 ± 2.1	41.5 ± 0.8		
CS-LCO 1h	70.6 ± 1.4	<i>41.4</i> ± <i>2.6</i>	<i>36.9</i> ± <i>1.7</i>		
LCO 30h	93.6 ± 1.8	58.6 ± 3.7	38.5 ±1.6		
CS-LCO 30h	73.4 ± 0.4	<i>49.3</i> ± <i>0.8</i>	40.2 ±0.3		

Table 3-2. Specific capacities below and above 3.9 V during the first charge. These values are considered qualitatively representative of the ratio of HT- and LT-phase in the nanocrystals. Percent capacities of LT-phase were calculated as (LT*100/(HT+LT)). All values were taken by averaging three cells.

The anodic signals were washed out upon subsequent reduction, with this effect being pronounced for the spinel component, and suggesting its early degradation. Overall, the discharge capacity of both CS-LiCoO₂ samples was slightly lower compared to bare LiCoO₂, likely due to the presence of electrochemically inactive Al^{3+} species. While bare LiCoO₂-1h and -30h had similar first discharge capacities (~120 mAh/g), the specific capacity of CS-LiCoO₂-30h (~108 mAh/g) was higher than CS-LiCoO₂-1h (~95 mAh/g). It is possible that the kinetics of charge transfer, which promotes utilization, was enhanced by the absence of Li₂CO₃ and a change in the electrical properties of the shell, through the formation of LiAlO₂ and an extensive LiCo_{1-x}Al_xO₂ gradient, as indicated by TEM-EDX.

3.3.2.2 Cycling performance

Figure 3-11 (a) presents the capacity retention after 100 cycles in the 4.3-2 V window, for all materials. The values were normalized to the capacity in the first cycle in order to evaluate the effect of the shells, which should be reflected in the retention of electrochemical activity shown in the first cycle. Three replicas were made for each electrode to ensure the significance of the trends. CS-LiCoO₂-1h and 30h showed enhanced cycling durability, with 65.7 % and 61.3 % retention (63 and 66 mAh/g), respectively, compared to 50.8 % (60 mAh/g) for LiCoO₂-1h and 56.4 % (68 mAh/g) for LiCoO₂-30h. A significant portion of capacity loss is due to the presence of spinel LiCoO₂ domains. Analysis of the voltage profiles revealed that losses were more apparent in the process associated with the presence of spinel domains, consistent with its reportedly poor electrochemical performance. This phase degrades rapidly (Figure 3-11 (d)), with 60% of the capacity lost after just 20 cycles. The loss of activity in the spinel component was much less pronounced in the presence of a shell. Despite the equal or even higher contents of spinel phase that could cause rapid degradation, CS-LiCoO₂

showed higher retention of capacity, which hints at the beneficial role of the shell in stabilizing the interface between electrode and electrolyte. The more stable performance of CS-LiCoO₂-1h compared to CS-LiCoO₂-30h would indicate that the surface chemistry of this phase was more beneficial, likely due to the lower concentration of redox-active Co^{3+} , as indicated by TEM-EDX, since Li₂CO₃ would irreversibly decompose during the first charge.



Figure 3-11. (a) Evolution of normalized specific capacity (solid symbol) and coulombic efficiency (open symbol) of bare and core-shell LiCoO₂ nanocrystal electrodes when cycled at C/20. (b) Discharging rate capability at room temperature. Errors bars in c result from the averaging of three cells. (c) Voltage versus specific capacity profiles and (d) evolution of normalized capacity of spinel LiCoO₂ nanocrystals.

Failure at the bulk was more prominent without the shell, as well; whereas clear redox processes were still discernible after 100 cycles in the core-shell materials, the profiles of bare LiCoO₂ were significantly washed out (Figure 3-12). The discharge rate capability of CS-LiCoO₂ was also more robust than bare counterparts (Figure 3-11 (b)). The ratio of capacity at 5 C vs C/10 was 52.5 % and 55.6 % for CS-LiCoO₂-1h and 30h, respectively, compared to 37.4 % and 39.8 % for LiCoO₂-1h and 30h, respectively. This result implied that charge transfer kinetics is not perturbed by the existence of Al-rich shell, and the lower interfacial degradation maintains it more efficiently.



Figure 3-12. dq/dv plots of (a) LiCoO₂-1h, (b) CS-LiCoO₂-1h, (c) CS-LiCoO₂-30h, and (d) CS-LiCoO₂-30h in the 1st (black) and 100th cycle (red), corresponding to the cells in Figure 3-11a.

2.4 Summary

This study expands our ability to build and manipulate core-shell heterostructures of complex oxides with relevance to energy storage, by demonstrating a colloidal synthetic route toward Al-rich layers grown on individual LiCoO₂ nanocrystals. Growth of the heterostructure occurred in a single reaction vessel, followed by modification with Li. The composition of the layer was tailored by thermal annealing, which induces Co/Al inter-diffusion. Detailed insight into the chemistry of core and shell provided by spectroscopy and microscopy suggests a significant level of tunability of the architectures, which provides room to identify critical descriptors to properties. Despite a decrease in the electronic conductivity at the surface, the presence of the shell around individual nanocrystals enhanced the electrochemical performance as Li battery cathodes. The similarity in the pristine bulk structure of all materials strongly suggests a role of the passivation of surface sites in contact with electrolyte on the differences in performance. The compositional versatility of this synthetic procedure is currently being expanded to phases with even more complex compositions, in order to create new avenues for the design of functional electrode materials for Li-ion batteries.

CHAPTER 4

4. CORE-SHELL NANOCRYSTALS OF LAYERED OXIDES WITH STABLE CATHODE PERFORMANCE IN LITHIUM BATTERIES

4.1 Introduction

The sustained improvement in energy density and cycle life of Li-ion batteries is a requirement for their future widespread application in electric vehicles.¹⁻³ Lavered lithium transition metal oxides have extensively been investigated as cathodes due to their ability to store large amounts of charge at high potential. The alternate stacking of Li and transition metal-rich layers can also enable fast Li-ion diffusion and, thus, cell kinetics.⁴ The best known layered oxide, LiCoO₂, is one of the most popular choices as cathode. However, its low practical capacity (~150 mAh/g) and the high cost of Co have motivated the search for alternative layered materials with lower contents of this transition metal.⁵ Replacement of Co³⁺ by Ni²⁺ and Mn^{3+, 4+} has led to the development of a large class of materials with general composition LiNi_xMn_yCo_{1-x-y}O₂ (also known as NMC). These oxides crystallize in the same hexagonal, layered structure as LiCoO₂. While Ni is introduced as a redox active center to maintain a high capacity, the introduction of mostly inactive Mn ions enhances thermal stability and, thus, safety. However, upon de-intercalation of Li⁺ ions, the oxidation of Co and Ni results in thermodynamically unfavorable formal Co⁴⁺ and Ni⁴⁺. In the oxidized (charged) state, these species have a driving force to reduce irreversibly when in contact with electronrich species in the electrolyte, at the surface of the particles. This process of reduction results in the decomposition of the electrolyte, accompanied by a structural reorganization of the surface from the original layered structure to a spinel and/or rocksalt framework showing cationic disorder, and which is rich in Co²⁺ and Ni^{2+,6-7} This process is complex and can sometimes involve concomitant corrosion of the surface, leading to metal dissolution. Aside from reducing the amount of oxidized transition metal available to compensate for the reverse process of Li intercalation (discharge), the structural disorder increases the barrier for hopping of Li⁺ ions, introducing kinetic limitations into the electrochemical reaction.^{8,9} Macroscopically, these interfacial reactions result in severe fading of the capacity of the electrode to store charge. They get aggravated above ambient temperature, as in real-life applications depending on geographic location, and when nanomaterials with high surface area are employed to enhance the power density of the electrode. Thus, controlling the interfacial reactions is key to enhance the durability of an electrode targeted for applications in high energy batteries.

Coating the surface of a cathode with electronically insulating components has long been a strategy to stabilize its electrochemical properties. These coatings are designed to act as an electronic barrier to the contact between the electrolyte and the redox-active ions in the oxide surface. Although this approach has led to excellent improvements in durability of high voltage cathodes, complete passivation against deleterious irreversible processes has not been achieved.¹⁰ Many methods of surface modification are applied on pre-made electrode powders or architectures, post-synthesis. Furthermore, typical coatings are not matched with the atomic structure of the active materials. The mismatch between bulk and surface gets aggravated by the volume changes undergone by the cathode during cycling, resulting in stresses that can lead to delamination and voids of a few nanometers.¹¹ These voids block the transfer of both ions and electrons, resulting in the degradation of the kinetics of the reaction and, ultimately, capacity loss. To overcome the drawbacks, secondary particle architectures with a builtin concentration gradient of transition metals within the same underlying atomic framework have been explored to fabricate high performance cathodes with chemically stable outer shells.¹¹ However, in all these cases, inner boundaries and buried interfaces in secondary and higher-order structures remain unprotected. This can lead to persistent exposure to the electrolyte, especially in the presence of particle shuffling and cracking during repeated cycling of the electrode.^{12,13} To achieve interfacial stabilization more effectively, it would be ideal to introduce concentration gradients at the level of primary particles, whereby transition metal ions are replaced with redox-inactive ions in thin shells. Recipes of colloidal chemistry have recently been developed that produce nanocrystals of battery materials, such as Li_{1+x}Mn_{2-x}O₄ and LiCoO₂, conformally covered with epitaxial shells.¹⁴⁻¹⁶ The resulting core-epitaxial shell (C-ES) heterostructures showed considerably higher cycling durability, and they were effective in limiting the dissolution of metal ions.¹⁶ However, the level of chemical complexity required to produce NMC cathodes remains to be accomplished. The substitution of Co in $LiCoO_2$ by Ni and Mn is expected to impart structural stability in the nanocrystal core. Furthermore, the substitution of transition metal ions by Al^{3+} in the surface and sub-surface of the layered oxide nanocrystals could introduce both interfacial and structural stabilization.¹⁷

In this work, a colloidal synthetic route was employed to build core-epitaxial shell (C-ES) nanocrystals of $LiCo_{0.5}Ni_{0.25}Mn_{0.25}O_2$ with a concentration gradient of Al^{3+} ions toward the outer layers. The thin Al-rich shells were deposited in the same reaction environment where the primary particles were grown in homogeneous dispersible form to

ensure conformal coverage on all nanocrystals. The concentration gradient across the nanocrystals was manipulated through post-synthetic heat treatments to induce interdiffusion while maintaining the original sizes. The effect of both the initial content of Al and the temperature of treatment was evaluated. The modified NMC crystals enhanced capacity retention, without significant loss of the original values, compared to the bare materials. The effect was particularly pronounced at high temperature or when cycling to high potentials, implying reduced side reactions with the electrolyte. The chemical identity and specific structural identity of both core and shells were characterized by a combination of spectroscopy and microscopy. The outcome of this study is an increased ability to manipulate the assembly of matter into chemically complex nanocrystal heterostructures as battery electrodes, and an enhanced understanding of the features required from passivating layers to enhance cycling durability.

4.2 Methods

4.2.1 Preparation of nanocrystal heterostructures with passivating shells

The precursor nanocrystals were prepared by a colloidal synthetic method. First, 1.9 mmol of manganese (II) acetate (Product No. 330825, Sigma-Aldrich), cobalt (II) acetate tetrahydrate (product No. 208396, Sigma-Aldrich) and nickel (II) acetate tetrahydrate (product No. 379883, Sigma-Aldrich) were dissolved in 30 mL of oleylamine (OAm, Product No. O7805, Sigma-Aldrich) at room temperature, under nitrogen blanket in a Schlenk line. The mixture was degassed at 100 °C for 20 minutes under vacuum to remove water and impurities. The slurry was then heated at 160 °C and maintained it for 15 hours under strong magnetic stirring in an atmosphere of N_2 gas.

Shells were grown on the surface of the transition metal precursor through dropwise addition of 20 mL of OAm solution containing aluminum acetylacetonate (Product No. 208248, Sigma-Aldrich) into the colloidal solution at 160 °C. Two different concentrations of Al in the final material were evaluated. They were produced by setting the amount of aluminum acetylacetonate to 0.28 and 1.1 mmol (0.0922 and 0.3689 g). The resulting colloidal solution was further annealed for 30 minutes at 160 °C to form aluminum oxide, followed by cooling to room temperature. To remove the oleylamine residues and unreacted products, the nanoparticles were collected by centrifugation for 5 minutes at 10000 rpm, re-dispersed in 15 mL of hexane and washed with 20 mL of ethanol four times. After washing the nanocrystals, the powder was dried overnight at 60°C. In order to synthesize Li-contained layered oxide, the nanocrystals were thoroughly mixed with lithium hydroxide hydrate (Product No. 43171, Alfa Aesar) at a stoichiometric ratio of Li to total transition metal ion content (1:1). The powder was calcined at two different temperatures (700 and 800 °C) for 10 hours with a heating rate of 5°C/min in air. Throughout this chapter, bare NMC and CS-NMC are used as labels for the products without and with Al-rich shells, respectively. The labels CS-NMC 1 and 2 indicate the samples resulting from using 0.28 and 1.1 mmol Al in the synthesis.

4.2.2 Characterization

Powder X-ray diffraction was performed on a Bruker D8 Advance using Cu Ka $(\lambda_{avg}=1.5418 \text{ Å})$ radiation. Scan rates were 0.04 ° s⁻¹ from 10° to 80 ° (2 θ). Fitting of the patterns to calculate lattice parameters of the materials was carried out using GSAS-II.

Transmission electron microscopy (TEM) images were obtained using a JEM

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3010 (JEOL) operated at 300 kV. The images were analyzed to extract the distribution of particle size by measuring approximately 200 nanocrystals using ImageJ, a program from the Research Services Branch of NIMH (National Institute of Mental Health) & NINDS (National Institutes of Mental Health, https://imagej.nih.gov/). All scanning transmission electron microscopy (STEM) imaging and energy dispersive X-ray (EDX) spectroscopy were performed on an aberration-corrected JEOL JEM-ARM200CF operated at 200 kV, with a maximum spatial resolution of ~73 pm. High angle annular dark field (HAADF), low angle annular dark field (LAADF), and annular bright field (ABF) images were acquired simultaneously using the corresponding detectors. For EDX spectroscopy, the ARM200CF is equipped with an Oxford X-Max 100TLE windowless silicon drift detector.

X-ray photoelectron spectroscopy (XPS) was performed with a high resolution monochromatic Al-K_{α} X-ray source (15 eV, 25 mA emission current, VSW MX 170 Rowland circle monochromator) and a 150 mm concentric hemispherical analyzer with a multichannel detector (VSW Class 150) operated at constant energy.^{18,19} The photoemission angle is normal to the surface and all core level spectra were calibrated to aliphatic C 1*s* peak fitting component at 284.6 eV and were recorded with a pass energy of either 22 or 44 eV. XPS peak fitting was performed using XPSPEAK (R.W.M. Kwok, v. 4.1, Hong Kong, China, http://xpspeak.software.informer.com/4.1/). Elemental fractions were determined from the integration of peak intensity using established methods, ²⁰ in accordance with the photo-ionized cross section and the escape depth of each core line.²¹

Soft X-ray absorption spectroscopy (XAS) measurements were carried out

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beamline 4-ID-C at the Advanced Photon Source (APS) at the Argonne National Laboratory (ANL, Lemont, IL), and beamline 7D at Pohang Light Source (PLS, Pohang) in Korea. The spectra were collected in fluorescence yield (FY), total electron yield (TEY) and partial electron yield (PEY) modes at room temperature and under ultra-high vacuum conditions (below 10⁻⁸ Torr). The FY spectra were taken from data at the APS and, TEY and PEY spectra were collected at the PLS. Contributions from visible light were carefully minimized before the acquisition, and all spectra were normalized to the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber. The measured spectra were aligned by the beamline reference and a basic normalization using a linear background.

4.2.3 Electrochemical measurements

Electrochemical properties were measured on composites containing the active NMC nanocrystals as working electrodes. Electrode slurries were prepared by mixing active materials and carbon black (Denka) in a 6 wt% solution consisting of polyvinylidene difluoride (PVDF, Kynar) in N-methylpyrrolidone (NMP, Sigma-Aldrich), to total 80:10:10 wt % of oxide, conductive additive and binder. Then, the slurry was cast on electrochemical-grade aluminum foil using a doctor blade, and it was dried under vacuum at 80 °C overnight to evaporate NMP moieties. The loading level in the dry electrodes was set to around 3.5 mg/cm². Circular pieces with a diameter of 1/2" were punched and assembled in two-electrode coin cells in a glovebox filled with Ar, where the level of water and oxygen contents were ≤ 0.1 ppm. High purity lithium foil (Product No. 10769, Alfa Aesar) and a 25 µm-thick polypropylene membrane (Celgard

2400) were the counter/reference electrode and separator, respectively. The electrolyte consisted of 1.2 M LiPF₆ in a 3:7 (wt %/wt %), a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), produced by BASF. Electrochemical measurements in different conditions were performed on a Biologic BCS-805 at room temperature and a VMP3 at 50 °C. The charge/discharge cutoff potentials were selected to 4.3/2.0 V and 4.6/2.0 V depending on the measurement. All potentials in this chapter are referenced to the Li⁺/Li⁰ couple. The rate, *C/n*, was defined as the current density required to achieve a theoretical capacity of LiCoO₂ structure, C = 274 mAh/g, in *n* hours. The rate capability measurement was performed by fixing the charge current to C/10 while discharge currents were varied from C/10 to 20C.

4.3 Analysis of structural and electronic properties of the different materials

4.3.1 Materials characterization

4.3.1.1 X-ray diffraction

The precursor colloidal Ni_xMn_yCo_{1-x-y}O nanocrystals were synthesized by thermal decomposition of transition metal acetates in oleylamine, which plays a role as surfacestabilizing ligand and high boiling point solvent.²² Aluminum oxide layers were grown on the surface of Ni_xMn_yCo_{1-x-y}O colloids at 160 °C by injecting an oleylamine solution of aluminum acetylacetonate at two different ratios (see Methods). Powder X-ray diffraction revealed that both bare and modified nanocrystals presented a disordered cubic rock-salt structure with 4.285 Å cell parameter (Figure 4-1). The existence of a single phase without peak splitting or secondary phases indicates that Ni, Mn and Co ions were uniformly incorporated into a single multi-metal oxide.

The rock-salt oxides were mixed with lithium hydroxide thoroughly and calcined at 700 or 800 °C for 10 hours in air to produce an electrochemically active layered oxide. The resulting XRD patterns matched well with a layered, α -NaFeO₂-type structure (Figure 4-2), consisting of sheets of edge sharing MO_6 octahedra separated from one another by intercalated LiO₆ sheets.²³ The unit cell parameters in table 4-1 were extracted by fitting the diffraction patterns of the nanocrystals. Increasing the reaction temperature from 700°C to 800°C introduced a slight expansion of along the c axis, whereas a stayed largely constant, leading to a slightly higher c/a ratio in the structure. The *a* parameter is mostly only sensitive to changes in composition of the transition metal layer, whereas the c parameter is also modulated by the concentration of defects, such as stacking faults or antisite occupancy.²⁴ Consequently, an increase in the c/a ratio is typically associated with a layered structure with decreased number of such defects, with a ratio close to 5.00 implying a very low density of such defects.²⁵ At both 700 °C and 800 °C, the introduction of the shells had no discernible effect on the unit cell dimensions. The unit cell parameters of all crystals were larger than single crystalline LiCoO₂ (a=2.8161 Å, c=14.0536 Å),²⁶ consistent with the expectation that Co³⁺ is replaced by Ni²⁺ and Mn³⁺ or Mn⁴⁺, which have either larger (Ni²⁺) or, at most, similar ionic radii (Mn⁴⁺).²⁷ All in all, the introduction of Al-rich shells did not have significant effects on the bulk structure of the oxides.



Figure 4-1. XRD patterns of (a) bare rock-salt precursor, (b) core-shell 1 and (c) coreshell 2 precursor nanocrystals. The difference between the core-shell samples was the amount of Al precursor injected during synthesis (see Methods for details).



Figure 4-2. XRD patterns of bare and core-shell nanocrystals synthesized at (a) 700 °C and (b) 800 °C for 10 hours in air. (Bare NMC: black, CS-NMC-1: red, and CS-NMC-2: blue)

	NMC 700	CS-NMC 700-1	CS-NMC 700-2	NMC 800	CS-NMC 800-1	CS-NMC 800-2
а	2.844	2.849	2.840	2.843	2.836	2.836
С	14.137	14.165	14.162	14.183	14.184	14.184
c/a	4.970	4.972	4.987	4.989	5.001	5.001

Table 4-1. Structural parameters of bare and core-shell NMC oxide nanocrystals.



Figure 4-3. TEM-EDX of (a) precursor $Ni_xMn_yCo_{1-x-y}O$, (b) NMC 700, and NMC 800 nanocrystals. The values were averaged with margin of errors by randomly choosing six different regions.

4.3.1.2 Electron microscopy and elemental analysis

Figure 4-3 (a) shows the morphology of the bare rock-salt precursor, which formed agglomerates with ~70 nm composed of primary nanocrystals of ~8 nm, with all secondary particles presenting a similar size. These secondary particles were

functionalized with surfactant molecules, which made them dispersible in the reaction medium. This dispersibility enabled the homogeneous growth of Al-rich overlayers. After reacting with lithium hydroxide, the primary particles fused to form objects with a single crystalline appearance. Slightly greater grain growth was measured after the reaction at 700°C than 800°C, as denoted in a histogram in Figure 4-4, which resulted from counting more than two hundred nanocrystals per sample.

Electron dispersive X-ray spectroscopy (EDX) in a TEM was used to establish the transition metal ratio of both rock-salt precursor and layered NMC nanocrystals. In all cases, Co : Ni : Mn was found to be approximately 0.47 : 0.28 : 0.25, based on the analysis of six different regions in a TEM grid (Figure 4-3 (a)). This molar ratio deviated from the equimolar value injected in the colloidal reaction, most likely due to the different decomposition temperature and kinetics of the three organometallic reagents²⁸, which led to different yields of incorporation of the transition metals into the oxide. Subsequent EDX maps and line scans provided direct information on the distribution of Al, Co, Mn and Ni in CS-NMC 700-2 and 800-2 crystals (Figure 4-5). The maps clearly demonstrated a homogeneous distribution of Al ions over the whole particle. In a single nanocrystal, the atomic ratio of Al^{3+} was detected as ~14 % with respect to the total concentration of metal ions. Through analysis of spectral linescans, a large increase in the Al concentration was observed near the surface of the particles in both CS-NMC 700-2 and CS-NMC 800-2 specimens. However, the material annealed at higher temperature showed a larger gradient in the concentration from the surface to the core of the particle. The change in gradient indicates that there is a different distribution of Al³⁺ in the two specimens, which is expected to provide distinct chemistry in the bulk and on the surface.



Figure 4-4. Particle size distribution of (a) precursor oxide, (b) bare NMC 700 and (c) bare NMC 800 nanocrystals. The average particle size and margin of error in each sample are noted on the graph.



Figure 4-5. EDX mapping of (a) CS-NMC 700-2 and (b) CS-NMC 800-2 crystals. EDX line scans of (c) CS-NMC 700-2 and (d) CS-NMC 800-2 single nanocrystals. (Al: black, Co: red, Mn: green, and Ni: blue)

Annular bright-field (ABF) and high-angle annular dark-field (HAADF) imaging were employed to gain insight into the atomic arrangement of both heavy and light elements in the nanocrystals. The single particles typically consisted of multiple crystalline domains, which could be generated when the primary crystallites fused to form a single particle during calcination. The CS-NMC 700-2 nanocrystals showed a layered structure with some overlap between crystallites in the particle (Figure 4-6 (a)). Despite spectral evidence of high Al concentration near the surface, a change in structure corresponding to an Al₂O₃ or similar phase was not found as compared to NMC 700 nanocrystals in figure 4-6 (b). This observation confirms the existence of epitaxy in the nanocrystals. It implies migration of Al³⁺ into the TM sites in the layered structure, with the outer layers of the particles having a much higher Al content.

The ionic radius of Ni²⁺ is 0.69 Å, which is similar to the ionic radius of Li⁺ (0.76 Å). Their similar size promotes exchange of crystallographic sites between these two ions. Evidence of such exchange was found in some cases. A single-crystal area of a bare NMC 800 particle near the surface without overlap with neighboring crystallites was examined by ABF (sensitive to both light and heavy atoms) and HAADF (only sensitive to heavy atoms) along the [101] direction (Figure 4-7). The images clearly show evidence of heavy atoms, likely Ni²⁺, in the Li layers. In the same images, a vacancy site or Li⁺ substitution appears on a transition metal site (Figure 4-7). The substitution of TM ions onto Li sites blocks the diffusion pathways in the structure, leading to a degradation the kinetics of the (de)intercalation reaction.



Figure 4-6. HAADF STEM image of (a) CS-NMC 700-2 and ADF image of (b) bare NMC 700 nanocrystals.



Figure 4-7. HAADF and ABF STEM images of NMC 800. The atomic resolution images were captured from the edge of the polycrystalline particles.

4.3.1.3 X-ray photoelectron spectroscopy

The chemical properties of the surface of CS-NMC 700-2 and 800-2 nanocrystals were investigated by XPS. The Al 2p core level was composed of two signals, with binding energies of 74.2 and 76.4 eV. The peak at high energy was assigned to Al^{3+} in an oxygen environment corresponding to pure Al_2O_3 (Figure 4-8). In turn, the component observed at lower binding energy was ascribed to Al³⁺ in the structure of a transition metal oxide, such as LiAl_xM_{1-x}O₂ (M=Co, Ni, Mn) solid solutions, based on literature reports.²⁹ The area ratio of the Al 2p peak at high energy over the signal at low energy was 0.86 and 0.54 in CS-NMC 700-2 and 800-2, respectively, indicating that higher reaction temperature promoted the formation of Al-rich surface layers with the same layered structure as the core (Table 4-2). The relative amount of solid solution phase may influence the surface reactivity in the passivation layers over cycling as well as electrochemical properties such as diffusivity of Li ions through the solid-liquid interface.³⁰ A similar trend was observed in the two binding environments observed at the Al 2s core level (Figure 4-8); the signal at lower bonding energy, 119.2 eV, was more predominant in the spectrum of CS-NMC 800-2 nanocrystals than the signal at higher energy, 121.1 eV. A complex Co $2p_{3/2}$ signal was observed in both cases, with two distinct components at ~781.5 and ~783.7 eV, whose ratio decreased from just over 1 to 0.75 (Figure 4-8 and Table 4-2). The spectrum is overall consistent with the presence of Co^{3+} in a layered oxide.³⁰ The change in ratio suggests the existence of subtle distortions of the bonding environment of Co^{3+} in the octahedral sites as LiAl_xM_{1-x}O₂ (M=Co, Ni, Mn) solid solutions are formed on the surface of NMC nanocrystals.³¹



Figure 4-8. XPS spectra of (a) CS-NMC 700-2 and (b) CS-NMC 800-2 nanocrystals.

Area/Ra tio	High BE in Al2p	Low BE in Al2p	Ratio Al2p	High BE in Al2s	Low BE in Al2s	Ratio Al2s	High BE in Co2p	Low BE in Co2p	Ratio Co2p
CS- NMC 700	84.58	97.57	0.86	63.77	64.36	0.99	392.01	368.39	1.06
CS- NMC 800	71.61	132.14	0.54	29.95	67.45	0.44	290.84	387.51	0.75

Table 4-2. Area and ratio of peaks in the Al2p, Al2s, and Co2p spectra of CS-NMC 700-2 and CS-NMC 800-2 nanocrystals from XPS in Figure 4-8.

4.3.2 Electrochemical performance

The electrochemical performance as cathodes of core-shell NMC nanocrystals with different annealing temperatures were evaluated in Li metal half cells and compared with the bare counterparts. Figure 4-9 (a) shows the voltage versus specific capacity profiles during the first cycle of all materials prepared at 700°C, collected in galvanostatic mode at room temperature. Overall, the discharge capacities of CS-NMC samples were lower than bare NMC, likely due to the presence of electrochemically inactive Al^{3+} species. Specifically, while CS-NMC 700-1 had similar first discharge capacities (~156 mAh/g) compared to bare NMC 700 (~162 mAh/g), the specific capacity of CS-NMC 700-2 was notably lower (~134 mAh/g). All profiles presented sloping features with no distinct plateaus. Incremental capacity plots, dq/dv versus potential (Figure 4-9 (b)), uncovered two broad, yet distinct peaks at approximately 3.77 V and 3.87 V during charging of bare NMC, and 3.70 V and 3.88 V during discharging, respectively. Aside from a slight smearing of these broad features, no significant differences were observed between bare and modified NMC 700 electrodes in the incremental capacity plots.

Figure 4-9 (c) presents the evolution of capacity when the electrodes were cycled in the 4.3-2.0 V potential window. The normalized to the capacity in the first cycle, reflect the retention of electrochemical activity according to the effect of Al³⁺-doped shells. CS-NMC 700-1 and 2 showed enhanced cycling durability, with 80.3 % and 84.0 % retention (112 and 125 mAh/g), respectively, compared to 72.1 % (117 mAh/g) for bare NMC 700 (Figure 4-9). With respect to the contents of Al³⁺, the modified nanocrystals improved their durability in Li cells, emphasizing the role of passivating layers. As shown in Figure 4-9 (d), while the discharge rate capability of CS-NMC 700-1 nanocrystals was enhanced compared to the bare material, the rate performance of CS-NMC 700-2 was initially worse, then became comparable at the highest rates. At the highest rates, the decaying response of the bare material could reflect the degradation of the material as a simple result of the multiple cycles that were accumulated.



Figure 4-9. (a) Potential versus specific capacities, (b) dq/dv vs potential curves, (c) evolution of discharging capacities (solid symbol) and coulombic efficiency (open symbol) of electrodes containing NMC 700 (black), CS-NMC 700-1 (red) and CS-NMC 700-2 (blue), when cycling at C/10 in Li metal half cells; (d) discharge rate capability measured at room temperature.

Figure 4-10 (a) shows the voltage versus specific capacity profiles of all materials prepared at 800°C, collected in galvanostatic mode during the first cycle between 4.3 and 2 V, at room temperature. The discharge capacities of NMC 800, CS-NMC 800-1 and CS-NMC 800-2 were 160, 152 and 120 mAh/g, respectively. The voltage profiles remained sloping, with no clear plateaus. Interestingly, the introduction of the shells led

to a displacement of the electrochemical curves to higher potential. Incremental capacity plots (Figure 4-10 (b)) revealed that the average redox potentials of CS-NMC 800-2 were 3.88 and 3.87 V upon charging (oxidation) and discharging (reduction), respectively, compared to 3.78 V and 3.75 V for bare NMC 800. The shift in both reduction and oxidation reactions indicated enhancement of the thermodynamic potentials of each compound. This effect has been observed upon bulk substitution of transition metals by Al³⁺ in layered oxides,³² even at small amounts.³³ It has been ascribed to an increase in ionic character of the transition metal-oxide bonds, which shifts the Fermi level.³⁴ Therefore, it probably signifies the incorporation of small amounts of Al into more domains of the layered transition metal oxide as a result from the more extensive diffusion into the core of the crystal. As shown in figure 4-10 (c), the capacity retentions of CS-NMC 800-1 and -2 after 50 cycles were 86.1 % and 88.7 % (130 and 106 mAh/g), respectively, compared to 82.4 % (131 mAh/g) in the bare material. Both modified nanocrystals enhanced their capacity retention with respect to the contents of Al³⁺ in comparison with the bare. Figure 4-10 (d) presents the rate capabilities of the electrodes cycled in 4.3-2.0 V at different discharging rates while fixing the rate of charge at C/10. The CS-NMC 800-1 nanocrystals show significantly enhanced rate capability with 84 mAh/g at 20C rate compared to 61 mAh/g for bare NMC 800. Moreover, this material showed significantly enhanced capability compared with CS-NMC 700-1 (~34 mAh/g at 20C), which contains same amount of Al^{3+} . To further evaluate their rate performance, the CS-NMC 800-1 electrodes were cycled at various rates between 4.3 and 2.0 V; cells operated at 5C delivered 64 mAh/g after 100 cycles, with minimal losses (Figure 4-11).



Figure 4-10. (a) Potential versus specific capacities, (b) dq/dv vs potential curves, (c) evolution of discharging capacities (solid symbol) and coulombic efficiency (open symbol) of electrodes containing NMC 800 (black), CS-NMC 800-1 (red) and CS-NMC 800-2 (blue) when cycling at C/10 in Li metal half cells; (d) discharge rate capability measured at room temperature.



Figure 4-11. Rate capability of CS-NMC 800-1 nanocrystals at different rate of charge/discharge reactions in coin cells ($vs \text{ Li}^0/\text{Li}^+$).

A second set of tests of the bare and CS-NMC crystals were performed at a C/10rate by raising the charge cutoff to 4.6 V (Figure 4-12). Increased cutoff is known to aggravate capacity decay, especially driven by accelerated electrolyte decomposition and interfacial side reactions.³⁵ The specific capacity of CS-NMC 700-2 sample was ~160 mAh/g, compared to 185 mAh/g for bare NMC, reflecting the effect of introducing an electrochemically inactive species in the material. Incremental capacity plots of bare NMC 700 in Figure 4-12 (b) indicate two broad peaks during charging reaction below 4.3 V, which are similar to the curves performed in the cells with potential cut off at 4.3 V. However, significant anodic signals were detected in all electrodes calcined at 700 °C above 4.4 V, which are not observed to reverse upon discharging, resulting in low coulombic efficiencies, or to reproduce upon subsequent cycles. Figure 4-12 (c) presents the evolution of the discharge capacities. Compared to a retention of 62.9 % (119 mAh/g) for bare NMC 700, CS-NMC 700-2 delivered 85.3 % of its capacity (141 mAh/g) after 40 cycles (Figure 4-12 (c)). The capacities of the electrodes calcined at 800 °C in figure 4-12 (d) showed a similar trend, with initial specific capacities of 164 mAh/g and 158 mAh/g for CS-NMC 800-1 and -2, compared to 191 mAh/g for NMC 800. After 40 cycles, the capacity retention of CS-NMC 800-2, 89.1 % (126 mAh/g), was higher than 76.5 % (146 mAh/g) and 76.5 % (126 mAh/g) for bare NMC 800 and CS-NMC 800-1 electrodes, respectively (Figure 4-12 (f)). Both CS-NMC 700/800-2 oxides showed distinctly improved retention capabilities compared to the bare counterpart, even when operating to higher potentials, where electrolyte decomposition is exacerbated, strongly suggesting a beneficial role of the passivation layers.



Figure 4-12. (a, d) Potential versus specific capacities, (b, e) dq/dv vs potential curves, (c, f) evolution of discharging capacities (solid symbol) and coulombic efficiency (open symbol) of electrodes containing NMC 700/800 (black), CS-NMC 700/800-1 (red), and CS-NMC 700/800-2 (blue), when cycling in the potential between 2.0 V and 4.6 V at C/10 in Li metal half cells.

Operation at conditions above standard temperature, will also accelerate detrimental interfacial reactions, and impose severe challenges to the lifetime of the battery. Figure 4-13 (a, b) shows the voltage versus specific capacity of all oxide electrodes, collected in a galvanostatic mode at 50 °C. Initial discharging capacities of CS-NMC 700, and 800-2 (138 mAh/g and 137 mAh/g, respectively) were slightly increased compared to the capacities (134 mAh/g and 120 mAh/g) of the electrodes

performed at room temperature, while no distinct differences were observed in bare, CS-NMC 700-1 and CS-NMC 800-1 electrodes. As shown in Figure 4-13 (c, d), bare NMC 700 and 800 retained 76.1 % (109 mAh/g) and 82.5 % (131 mAh/g) of their capacities, respectively, when cycling at 50°C, whereas CS-NMC 700-2 and 800-2 showed significantly enhanced performance, with 91.3 % (126 mAh/g) and 96.7 % (133 mAh/g) retention, respectively. Along with the trends in the tests at different conditions, their durability at an elevated temperature intensively supports the function of Al³⁺-rich passivating layers while minimizing their original properties.



Figure 4-13. (a, b) Potential versus specific capacities, and (c, d) evolution of discharging capacities (solid symbol) and coulombic efficiency (open symbol) of electrodes, containing NMC 700/800 (black), CS-NMC 700/800-1 (red), and CS-NMC 700/800-2 (blue) when cycling at C/10 in Li metal cells at 50 °C.

4.3.3 Effects of passivating layers

4.3.3.1 Depth-profiles of nanocrystals at highly oxidized states

To gain insight into the origins of the more robust stability of CS-NMC 700-2 compared to bare NMC 700, O K-edge X-ray absorption spectroscopy (XAS) was collected using partial electron yield (PEY), total electron yield (TEY), and fluorescence yield (FY) detectors, which probe increasing depths into the sample (\sim 1-2, 2-5 and 50 nm, respectively). The incident X-rays are absorbed by the samples through excitation of core-level electrons to unoccupied states above the vacuum or Fermi level.³⁶ Electron yield can be refined into the partial electron yield (PEY) that collects escaped electrons only in a selected energy window, while the total electron yield (TEY) detects all primary photoelectrons, such as Auger and secondary electrons that emerge from the surface of sample, independent of the energy. The broad complex signal at ~527 eV (Figure 4-14), predominant in all samples, represents the transition of the 1s electron in oxygen to a 2p level hybridized with the 3d orbitals of transition metal ions, whereas the broad higher peaks above ~533 eV corresponds to the transitions to hybridized states of oxygen 2p and transition metal 4s and 4p orbitals.³⁶ Although the exact nature of the hole-states depends on the degree of covalence in the TMO₆ octahedral unit, the pre-edge intensity of O exhibits a correlation with the formal oxidation states of transition metal ions.³⁶

The overall O K-edge spectra were very similar between bare and core-shell materials, implying the introduction Al³⁺ ions had little effect on the electronic environment of oxide ions, likely due to their low concentration (Figure 4-14). Significant changes were observed in the pre-edge region upon de-intercalation of Li ions in all samples. The pre-edge peak was shifted to lower energy with an increase of

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integrated pre-edge. The shift to lower energy is contributed by the higher oxidation state of metal ions since the greater effective nuclear charges induce a deeper binding energy to the 1s orbital of oxygen. As shown in Figure 4-14 (a), the O pre-edge broadened significantly, its onset shifting to lower energies as a result of the advent of a shoulder at \sim 527 eV.³⁸ Since these spectra were collected in FY mode, they were representative of the bulk of the nanocrystals. No significant difference was detected in core-shell compared to the bare materials. Similar broadening of the pre-edge was observed in the TEY spectra (Figure 4-14 (b)), but its intensity decreased slightly after charging. Differences were more apparent in PEY mode (Figure 4-14 (c)). While the trend in preedge broadening and intensity ratio before and after charging CS-NMC 700-2 was comparable to TEY, the pre-edge of charged NMC 700 was significantly weakened. The onset of the pre-edge was also subtly shifted to slightly higher energies, closer to the pristine state. Since the post-absorption edge features (i.e., above 532 eV) were similar between samples, the decrease in pre-edge intensity was associated with a decrease in the hybridization of the transition metal-oxygen bonds in the surface of the charged state. This decrease is typically associated with the reduction of the transition metal, which occurs at the surface, while the bulk is oxidized upon charging. The fact that the surface of charged cathodes appears more reduced than the bulk has been observed;³⁹ it is ascribed to the outcome of interfacial reactions. Therefore, the introduction of a shell led to the stabilization of highly charged species on the surface of the cathode, which would provide one explanation of the enhanced cycling stability of the core-shell materials.


Figure 4-14. O K-edge spectra obtained by (a) fluorescence yield, (b) total electron yield, and (c) partial electron yield mode. (NMC 700: black, charged NMC 700: red, CS-NMC 700-2: blue and charged CS-NMC 700-2: cyan)

4.4 Summary

Core $LiCo_{0.5}Ni_{0.25}Mn_{0.25}O_2$ nanocrystals with passivating shells presenting a gradient of Al^{3+} substitution from surface to interior were prepared by a combination of a colloidal synthesis and calcination reactions. The controlled gradient of inactive Al^{3+} ions created distinct chemical environments in the layered structure through an individual particle. The modified nanocrystals improved the capacity retention even in harsh

conditions such as elevated temperature and high potentials with respect to the bare counterparts. The layers stabilized the electronic environment of the surface in highly oxidized states, providing a possible explanation for the enhanced electrochemical performance. The versatility of the concept of core-shell nanocrystal heterostructures has now been extended to the highest levels of complexity of state-of-the-art oxide cathodes, maturing this novel strategy to create stable cathode-electrolyte interfaces through manipulation of surface chemistry homogeneously at the level of individual cathode primary nanoparticles.

CONCLUSION

Coatings designed to passivate the surface of cathode materials reacting at high potentials have gradually improved the performance of Li-ion batteries. These coatings should suppress undesired reactions at these interfaces not only by providing barriers for direct electron transfer between oxide and electrolyte molecules, while allowing ion transport, but also avoiding chemical interactions with the transition metal ions on the oxide surface, especially when they reach high oxidation states during cycling. Interfacial interactions with the electrolyte can lead to undesired dissolution and decomposition reactions, with detrimental re-deposition of unwanted products on the battery components, especially insulating layers that impede both ion and electron transport, and, thus, rapidly degrade the capacity retention of the battery.

Replacing the transition metal ions with inactive ions within protective layers potentially improves interfacial stability, but the main challenge is to minimize their thickness on each individual particle, to minimize losses in theoretical capacity, while ensuring conformality to passivate all interfaces. In this thesis, we extended the approach of core-shell heterostructures originally reported in our group to increase its chemical versatility and to reach the optimum characteristics of the resulting passivating layers. We targeted the presence of Li ions in the passivating layers to ensure the existence of ion carriers to sustain charge transfer kinetics. We also sought to match the structure of the active oxide and the shell, which benefits carrier transport by reducing their strain at the boundaries. Here, we focused on the synthesis of core-shell nanocrystals consisting of high energy cathodes and Al-rich passivating layers, and sought to demonstrate chemical versatility by applying the concept to multiple phase spaces, namely, LiMn₂O₄, LiCoO₂ and LiCo_{0.5}Ni_{0.25}Mn_{0.25}O₂. To control the heterostructures, colloidal chemistry was employed to grow nanoscale shells in the same reaction environment where the particles were formed and dispersed. Post-synthetic annealing was used to produce the final heterostructure and tailor the specific chemistry of the shell. Deep insight into the architectures provided by spectroscopy and microscopy, which revealed a significant level of tunability of the heterostructures. The finely tailored nanostructures enhanced their capacity retentions compared to the bare counter parts, while minimizing losses of kinetics. Stabilization effects were more apparent on the surface than in the bulk of crystals when it was harvested in extreme conditions, implying the suppression of the side reactions. These nanocrystal heterostructures offer extremely fine tunability of surface modification, unreachable by most other methods, while also being potential model objects for the study of the interfacial interactions in Li-ion batteries, which remain to be fully elucidated even to this day.

CITED LITERATURE

Chapter 1

- [1] Yang, Z. G.; Zhang, J. L.; Kintner-Meyer, M. C. W.; Lu, X. C.; Choi, D. W.;
 Lemmon, J. P.; Liu, J. *Chem. Rev.* 2011, *111*, 3577-3613.
- [2] Diouf, B.; Pode, R. Renew. Energy. 2015, 76, 375-380.
- [3] Zu, C. X.; Li, H. Energy Environ. Sci. 2011, 4, 2614-2624.
- [4] Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. *Energy Environ. Sci.* **2011**, *4*, 3243-3262.
- [5] Armand, M.; Tarascon, J. M. Nature. 2008, 451, 652-657.
- [6] Huggins RA. Advanced Batteries Materials Science Aspects, Springer, 2009
- [7] Goodenough, J. B.; Kim, Y. Chem. Mater. 2010, 22, 587-603.
- [8] Kraytsberg, A.; Ein-Eli, Y. Adv. Energy. Mater. 2012, 2, 922-939.
- [9] Whittingham, M. S. Chem. Rev. 2004, 104, 4271-4301.
- [10] Wang, L. Z.; Takada, K.; Kajiyama, A.; Onoda, M.; Michiue, Y.; Zhang, L. Q.;
 Watanabe, M.; Sasaki, T. *Chem. Mater.* 2003, *15*, 4508-4514.
- [11] Shao-Horn, Y.; Croguennec, L.; Delmas, C.; Nelson, E. C.; O'Keefe, M. A. Nat.Mater. 2003, 2, 464-467.
- [12] Nitta, N.; Wu, F. X.; Lee, J. T.; Yushin, G. Mater. Today. 2015, 18, 252-264.
- [13] Wang, G. G.; Wang, J. M.; Mao, W. Q.; Shao, H. B.; Zhang, J. Q.; Cao, C. N. J.Solid. State Electrochem. 2005, 9, 524-530.
- [14] Lee, M. J.; Lee, S.; Oh, P.; Kim, Y.; Cho, J. Nano. Lett. 2014, 14, 993-999.
- [15] Gauthier, M.; Carney, T. J.; Grimaud, A.; Giordano, L.; Pour, N.; Chang, H. H.;
- Fenning, D. P.; Lux, S. F.; Paschos, O.; Bauer, C.; Magia, F.; Lupart, S.; Lamp, P.; Shao-

Horn, Y. J. Phys. Chem. Lett. 2015, 6, 4653-4672.

- [16] Delacourt, C.; Kwong, A.; Liu, X.; Qiao, R.; Yang, W. L.; Lu, P.; Harris, S. J.; Srinivasan, V. J. Electrochem. Soc. 2013, 160, A1099-A1107.
- [17] Jarry, A.; Gottis, S.; Yu, Y. S.; Roque-Rosell, J.; Kim, C.; Cabana, J.; Kerr, J.;Kostecki, R. J. Am. Chem. Soc. 2015, 137, 3533-3539.
- [18] Chen, Z. H.; Qin, Y.; Amine, K.; Sun, Y. K. J. Mater. Chem. 2010, 20, 7606-7612.
- [19] Pieczonka, N. P. W.; Liu, Z. Y.; Lu, P.; Olson, K. L.; Moote, J.; Powell, B. R.; Kim,
- J. H. J. Phys. Chem. C 2013, 117, 15947-15957.
- [20] Lee, K. T.; Jeong, S.; Cho, J. Acc. Chem. Res. 2013, 46, 1161-1170.
- [21] Jung, Y. S.; Cavanagh, A. S.; Dillon, A. C.; Groner, M. D.; George, S. M.; Lee, S.
 H. J. Electrochem. Soc. 2010, 157, A75-A81.
- [22] Qiao, R.; Chin, T.; Harris, S. J.; Yan, S.; Yang. W. Curr. Appl. Phys. 2013, 13. 544-548.
- [23] Kim, C.; Phillips, P. J.; Xu, L. P.; Dong, A. G.; Buonsanti, R.; Klie, R. F.; Cabana, J. *Chem. Mater.* 2015, 27, 394-399.
- [24] Liu, H.; Wolf, M.; Karki, K.; Yu, Y. S.; Stach, E. A.; Cabana, J.; Chapman, K. W.;Chupas, P. J. *Nano Lett.* 2017, *17*, 3452-3457.
- [25] Scott, I. D.; Jung, Y. S.; Cavanagh, A. S.; An, Y. F.; Dillon, A. C.; George, S. M.;Lee, S. H. *Nano Lett.* 2011, *11*, 414-418.
- [26] Yan, P. F.; Zheng, J. M.; Zhang, X. F.; Xu, R.; Amine, K.; Xiao, J.; Zhang, J. G.;Wang, C. M. *Chem. Mater.* 2016, 28, 857-863.

- [27] Kazyak, E.; Chen, K. H.; Wood, K. N.; Davis, A. L.; Thompson, T.; Bielinski, A. R.;
 Sanchez, A. J.; Wang, X.; Wane, C. M.; Sakamoto, J.; Dasgupta, N. P. *Chem. Mater.* **2017**, 29, 3785-3792.
- [28] Vandalon, V.; Kessels, W. M. M. Appl. Phys. Lett. 2016, 108, 011607.
- [29] Hu, L. H.; Bruner, P.; Grehl, T.; Brongersma, H. H.; Cabana, J. Chem. Mater. 2017, 29, 5896-5905.
- [30] Chaudhuri, R. G.; Paria, S. Chem. Rev. 2012, 112, 2373-2433.
- [31] Talapin, D. V.; Shevchenko, E. V. Chem. Rev. 2016, 116, 10343-10345.
- [32] Mahadevu, R.; Yelameli, A. R.; Panigrahy, B.; Pandey, A. ACS Nano. 2013, 7, 11055-11063.
- [33] Yamauchi, T.; Tsukahara, Y.; Yamada, K.; Sakata, T.; Wada, Y. *Chem. Mater.***2011**, *23*, 75-84.
- [34] Zhong, X. H.; Xie, R. G.; Zhang, Y.; Basche, T.; Knoll, W. Chem. Mater. 2005, 17, 4038-4042.
- [35] Zhang, Q.; Yan, B. Inorg. Chem. 2010, 49, 6834-6839.

Chapter 2

- [1] Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. *Energy Environ. Sci.* **2011**, *4*, 3243-3262.
- [2] Tarascon, J.-M.; Armand, M. Issue. Nature 2001, 414, 359-367.

[3] Hosono, E.; Kudo, T.; Honma, I.; Matsuda, H.; Zhou, H. S. Nano Lett. 2009, 9, 1045-1051.

- [4] Xu, G. J.; Liu, Z. H.; Zhang, C. J.; Cui, G. L.; Chen, L. Q.J. Mater. Chem. A. 2015, 3, 4092-4123.
- [5] Aurbach, D.; Zinigrad, E.; Teller, H.; Dan, P. J. Electrochem. Soc. 2000, 147, 1274–1279.
- [6] Bhattacharyya, R.; Key, B.; Chen, H.; Best, A. S.; Hollenkamp, A. F.; Grey, C. P. Nat. Mater. 2010, 9, 504–510.
- [7] J. Cabana, B. J. Kwon, L. Hu, Acc. Chem. Res. 2018, 51, 299-308.
- [8] H. Liu, M. Wolf, K. Karki, Y.S. Yu, E. A. Stach, J. Cabana, K. W. Chapman, P. J. Chupas, *Nano. Lett.* **2017**, *17*, 3452-3457.
- [9] Scott, I. D.; Jung, Y. S.; Cavanagh, A. S.; An, Y. F.; Dillon, A. C.; George, S. M.;
 Lee, S. H. *Nano Lett.* 2011, 11, 414-418.
- [10] Oudenhoven, J. F. M.; van Dongen, T.; Niessen, R. A. H.; de Croon, M. H. J. M.;Notten, P. H. L. *J. Electrochem. Soc.* 2009, *156*, D169-D174.
- [11] Shim, J. H.; Lee, S.; Park, S. S. Chem. Mater. 2014, 26, 2537-2543.
- [12] Kalluri, S.; Yoon, M.; Jo, M.; Liu, H. K.; Dou, S. X.; Cho, J.; Guo, Z. P. Adv. Mater.2017, 29, 1605807.
- [13] Kim, C.; Phillips, P. J.; Xu, L. P.; Dong, A. G.; Buonsanti, R.; Klie, R. F.; Cabana, J.*Chem. Mater.* 2015, 27, 394-399.
- [14] Paulsen, J. M.; Dahn, J. R. Chem. Mater. 1999, 11, 3065-3079.
- [15] Chan, H. W.; Duh, J. G.; Sheen, S. R. J. Power Sources. 2003, 115, 110-118.
- [16] Sun, Y. Chem. Soc. Rev. 2013, 42, 2497–2511.

- [17] Tan, H. Y.; Verbeeck, J.; Abakumov, A.; Van Tendeloo, G. Ultramicroscopy 2012, 116, 24-33.
- [18] Tang, D. C.; Sun, Y.; Yang, Z. Z.; Ben, L. B.; Gu, L.; Huang, X. J. Chem. Mater.2014, 26, 3535-3543.
- [19] Lin, F.; Markus, I. M.; Nordlund, D.; Weng, T. C.; Asta, M. D.; Xin, H. L. L.; Doeff, M. M. Nat. Commun. 2014, 5, 9.
- [20] Liu, R. S.; Jang, L. Y.; Chen, J. M.; Tsai, Y. C.; Hwang, Y. D.; Liu, R. G. J. Solid State Chem. **1997**, *128*, 326-329.
- [21] Risch, M.; Stoerzinger, K. A.; Han, B. H.; Regier, T. Z.; Peak, D.; Sayed, S. Y.;
- Wei, C.; Xu, Z. C.; Shao-Horn, Y. J. Phys. Chem. C 2017, 121, 17682-17692.
- [22] Grush, M. M.; Horne, C. R.; Perera, R. C. C.; Ederer, D. L.; Cramer, S. P.; Cairns, E.
- J.; Callcott, T. A. Chem. Mater. 2000, 12, 659-664.
- [23] Lee, Y. J.; Wang, F.; Grey, C. P.J. Am. Chem. Soc. 1998, 120, 12601-12613.
- [24] Lee, Y. J.; Grey, C. P. J. Electrochem. Soc. 2002, 149, A103-A114.
- [25] Cabana, J.; Johnson, C. S.; Yang, X. Q.; Chung, K. Y.; Yoon, W. S.; Kang, S. H.;
- Thackeray, M. M.; Grey, C. P. J. Mater. Res. 2010, 25, 1601-1616.
- [26] Han, B. H.; Paulauskas, T.; Key, B.; Peebles, C.; Park, J. S.; Klie, R. F.; Vaughey, J.
- T.; Dogan, F. ACS Appl. Mater. Interfaces, 2017, 9, 14769-14778.
- [27] Dogan, F.; Vaughey, J. T.; Iddir, H.; Key, B. ACS Appl. Mater. Interfaces, 2016, 8, 16708-16717.
- [28] Kim, D. K.; Muralidharan, P.; Lee, H. W.; Ruffo, R.; Yang, Y.; Chan, C. K.; Peng,
 H.; Huggins, R. A.; Cui, Y. *Nano Lett.* **2008**, *8*, 3948-3952.
- [29] Gao, Y.; Reimers, J. N.; Dahn, J. R. Phys. Rev. B 1996, 54, 3878-3883.

[30] Ceder, G.; Chiang, Y. M.; Sadoway, D. R.; Aydinol, M. K.; Jang, Y. I.; Huang, B. *Nature*, **1998**, *392*, 694-696.

[31] Jang, D. H.; Shin, Y. J.; Oh, S. M.J. Electrochem. Soc. 1996, 143, 2204-2211.

[32] Lee, K. T.; Jeong, S.; Cho, J. Acc. Chem. Res. 2013, 46, 1161-1170.

Chapter 3

- [1] Croguennec, L.; Palacin, M. R. J. Am. Chem. Soc. 2015, 137, 3140-3156.
- [2] Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. *Energy Environ*.*Sci.* 2011, *4*, 3243-3262.
- [3] Lai, W.; Erdonmez, C. K.; Marinis, T. F.; Bjune, C. K.; Dudney, N. J.; R.
 Wartena, F.; Xu, Chiang. Y. Adv. Mater., 2010, 22, E139-144.
- [4] Nishi, Y. Chem. Record, 2001, 1, 406-413.
- [5] Lee, K. T.; Jeong, S.; Cho, J. Acc. Chem. Res. 2013, 46, 1161-1170.
- [6] Kraytsberg, A.; Ein-Eli. Y. Adv. Energy Mater. 2012, 2, 922-939.
- [7] Bruce. P. G.; Scrosati. B.; Tarascon. J. M. Angew. Chem. Int. Ed. 2008, 47, 2930-2946.
- [8] Yin. Y. X.; Xin. S.; Guo. Y. G. Part. Part. Syst. Charact. 2013, 30, 737-753.
- [9] Matsui. M.; Dokko. K.; Kanamura. K. J. Power Sources, 2008, 177, 184-193.
- [10] Cabana. J.; Kwon. B. J.; Hu. L. Acc. Chem. Res. 2018, 51, 299-308.
- [11] Chen. Z. H.; Qin. Y.; Amine. K.; Sun. Y. K. J. Mater. Chem. 2010, 20, 7606-7612.
- [12] Scott. I. D.; Jung. Y. S.; Cavanagh. A. S.; An. Y. F.; Dillon. A. C.; George. S.
 M.; Lee. S. H. *Nano Lett.* 2011, *11*, 414-418.

[13] Xiong, L. L.; Xu, Y. L.; Tao, T.; Du, X. F.; Li, J. B. J. Mater. Chem. 2011, 21, 4937-4944.

[14] Cho, H. M.; Chen, M. V.; MacRae, A. C.; Meng, Y. S. ACS Appl. Mater. Interfaces, 2015, 7, 16231-16239.

[15] Chen, H.; Zhou, M.; Wang, T.; Li, F.; Zhang, Y. X. J. Mater. Chem. A, 2016, 4, 10786-10793.

[16] Su, L. W.; Jing, Y.; Zhou, Z. Nanoscale, **2011**, *3*, 3967-3983.

- [17] Zhong, X. H.; Xie, R. G.; Zhang, Y.; Basche, T.; Knoll, W. Chem. Mater. 2005, 17, 4038-4042.
- [18] Yamauchi, T.; Tsukahara, Y.; Yamada, K.; Sakata, T.; Wada, Y. *Chem. Mater.***2011**, *23*, 75-84.
- [19] Chaudhuri, R. G.; Paria, S. Chem. Rev. 2012, 112, 2373-2433.
- [20] Kim, C.; Philips, P. J.; Xu, L.; Dong, A.; Buonsanti, R.; Klie, R. F.; Cabana, J. Chem. Mater. 2015, 27, 394-399.
- [21] Whittingham, M. S. Chem. Rev. 2014, 114, 11414-11443.
- [22] Mourdikoudis, S.; Liz-Marzan, L. M. Chem. Mater. 2013, 25, 1465-1476.
- [23] Maiyalagan, T.; Jarvis, K. A.; Therese, S.; Ferreira, P. J.; Manthiram, A. Nat. Commun. 2014, 5, 1-8.
- [24] Kang, S. G.; Kang, S. Y.; Ryu, K. S.; Chang, S. H. Solid State Ion. 1999, 120, 155-161.
- [25] Santiago, E. I.; Bueno, P. R.; Andrade, A. V. C.; Paiva-Santos, C. O.; Bulhoes,
- L. O. S. J. Power Sources. 2004, 125, 103-113.

- [26] Kan, Y. C.; Hu, Y.; Ren, Y.; Bareno, J.; Bloom, I.; Sun, Y. K.; Amine, K.; Chen, Z. H. J. Power. Sources. 2014, 271, 97-103.
- [27] Gummow, R. J.; Thackeray, M. M. Mater. Res. Bull. 1992, 27, 327-337.
- [28] Rossen, E.; Reimers, J. N.; Dahn, J. R. Solid State Ion. 1993, 62, 53-60.
- [29] Antolini, E. Solid State Ionics. 2004, 170, 159-171.
- [30] Shao-Horn, Y.; Hackney, S. A.; Kahaian, A. J.; Thackeray, M. M. J. Solid State Chem. 2002, 168, 60-68.
- [31] Xu, J. X.; Bai, S. D.; Higuchi, Y.; Ozawa, N.; Sato, K.; Hashida, T.; Kudo, M. J.
- Mater. Chem. A. 2015, 3, 21518-21527.
- [32] Kramer, D.; Ceder, G. Chem. Mater. 2009, 21, 3799-3809.
- [33] Grey, C. P.; Dupre, N. Chem. Rev. 2004, 104, 4493-4512.
- [34] Murakami, M.; Noda, Y.; Koyama, Y.; Takegoshi, K.; Arai, H.; Uchimoto, Y.;
- Ogumi, Z. J. Phys. Chem. C. 2014, 118, 15375-15385.
- [35] Han, B.; Paulauskas, T.; Key, B.; Peebles, C.; Park, J.; Klie, R. F.; Vaughey, J.
- T.; Dogan, F. Appl. Mater. Interfaces. 2017, 9, 14769–14778.
- [36] Chen, C. H.; Hwang, B. J.; Chen, C. Y.; Hu, S. K.; Chen, J. M.; Sheu, H. S.;
- Lee, J. F. J. Power. Sources. 2007, 174, 938-943.
- [37] Hetaba, W.; Mogilatenko, A.; Neumann, W. Micron. 2010, 41, 479-483.
- [38] Yogi, C.; Takamatsu, D.; Yamanaka, K.; Arai, H.; Uchimoto, Y.; Kojima, K.;
- Watanabe, I.; Ohta, T.; Ogumi, Z. J. Power. Sources. 2014, 248, 994-999.
- [39] Yoon, W. S.; Kim, K. B.; Kim, M. G.; Lee, M. K.; Shin, H. J.; Lee, J. M.; Lee,
- J. S. J. Phys. Chem. B. 2002, 106, 2526-2532.

[40] Bueno, P. R.; Presquero, N. C.; Ferreira, F. F.; Santiago, E. I.; Varela, J. A.;Longo, E. J. Phys. Chem. C. 2008, 112, 14655-14664.

[41] Ceder, G.; Chiang, Y. M.; Sadoway, D. R.; Aydinol, M. K.; Jang, Y. I.; Huang,B. *Nature*, **1998**, *392*, 694-696.

[42] Su, C. C.; He, M. N.; Peebles, C.; Zeng, L.; Tornheim, A.; Liao, C.; Zhang, L.;
Wang, J.; Wang, Y.; Zhang, Z. C. ACS Appl. Mater. Interfaces, 2017, 9, 30686-30695.

[43] Chen, H. L.; Grey, C. P. Adv. Mater. 2008, 20, 2206.

[44] Tebbe, J. L.; Holder, A. M.; Musgrave, C. B. ACS Appl. Mater. Interfaces, 2015, 7, 24265-24278.

Chapter 4

[1] Hassoun, J.; Lee, K. S.; Sun, Y. K.; Scrosati, B. J. Am. Chem. Soc. 2011, 133, 3139-3143.

[2] Kraytsberg, A.; Ein-Eli, Y. Adv. Energy. Mater. 2012, 2, 922-939.

[3] Goodenough, J. B. Acc. Chem. Res. 2013, 46, 1053-1061.

[4] Shao-Horn, Y.; Croguennec, L.; Delmas, C.; Nelson, E. C.; O'Keefe, M. A. Nat.Mater. 2003, 2, 464-467.

[5] Fu, C. C.; Li, G. S.; Luo, D.; Li, Q.; Fan, J. M.; Li, L. P. ACS Appl. Mater. Interfaces,
2014, 6, 15822-15831.

[6] Sallis, S.; Pereira, N.; Mukherjee, P.; Quackenbush, N. F.; Faenza, N.; Schlueter, C.;
Lee, T. L.; Yang, W. L.; Cosandey, F.; Amatucci, G. G.; Piper, L. F. J. *Appl. Phys. Lett.* **2016**, *108*, 263902.

- [7] Takamatsu, D.; Koyama, Y.; Orikasa, Y.; Mori, S.; Nakatsutsumi, T.; Hirano, T.;
 Tanida, H.; Arai, H.; Uchimoto, Y.; Ogumi, Z. Angew. Chem. Int. Ed. 2012, 51, 11597-11601.
- [8] Koyama, Y.; Arai, H.; Tanaka, I.; Uchimoto, Y.; Ogumi, Z. Chem. Mater. 2012, 24, 3886-3894.
- [9] Kang, K.; Ceder, G. Phys. Rev. B. 2006, 74, 094105.
- [10] Cabana. J., Kwon. B. J., Hu. L. Acc. Chem. Res. 2018, 51, 299-308.
- [11] Hou, P. Y.; Zhang, H. Z.; Zi, Z. Y.; Zhang, L. Q.; Xu, X. J. J. Mater. Chem. A. 2017, 5, 4254-4279.
- [12] Liu. H., Wolf. M., Karki. K., Yu. Y.S., Stach. E. A., Cabana. J., Chapman. K. W., Chupas. P. J. *Nano. Lett.* **2017**, *17*, 3452-3457.
- [13] Miller, D. J., Proff, C., Wen, J. G., Abraham, D. P., Bareno, J. Adv. Energy. Mater.2013, 3, 1098-1103.
- [14] Hu, L. H.; Bruner, P.; Grehl, T.; Brongersma, H. H.; Cabana, J. *Chem. Mater.* 2017, 29, 5896-5905.
- [15] Kwon, B. J.; Phillips, P. J.; Key, B.; Dogan, F.; Freeland, J.; Kim, C.; R.; Klie.;Cabana, J. *Nanoscale*, **2018**.
- [16] Kim, C.; Phillips, P. J.; Xu, L. P.; Dong, A. G.; Buonsanti, R.; Klie, R. F.; Cabana, J. *Chem. Mater.* 2015, 27, 394-399.
- [17] Kim, U. H.; Myung, S. T.; Yoon, C. S.; Sun, Y. K. ACS Energy Lett. 2017, 2, 1848-1854.
- [18] Bolotin, I.L.; Tetzler, S.H.; Hanley. L, J. Phys. Chem. C. 2007, 111, 9953-9960.
- [19] Majeski, M.W.; Bolotin. I.L.; Hanley. L, ACS Appl. Mater. Interfaces. 2014, 6,

12901-12908.

[20] Ratner, B.D.; Castner, D.G, Electron spectroscopy for chemical analysis, in Surface Analysis - Techniques and Applications, J.C. Vickerman and N.M. Reed, Editors. **1993**, *John Wiley & Sons: Chichester*.

- [21] Scofield, J.H, J. Electron Spectros. Relat. Phenomena, 1976, 8, 129-137.
- [22] Mourdikoudis, S.; Liz-Marzan, L. M. Chem. Mater. 2013, 25, 1465-1476.
- [23] Ben Yahia, H.; Shikano, M.; Kobayashi, H. Chem. Mater. 2013, 25, 3687-3701.
- [24] MacNeil, D. D.; Lu, Z.; Dahn, J. R. J. Electrochem. Soc. 2002, 149, A1332-A1336.
- [25] Bueno, P. R.; Pesquero, N. C.; Ferreira, F. F.; Santiago, E. I.; Varela, J. A.; Longo,
- E. J. Phys. Chem. C. 2008, 112, 14655-14664.
- [26] Akimoto, J.; Gotoh, Y.; Oosawa, Y. J. Solid. State Chem. 1998, 141, 298-302.
- [27] Sun, H.; Zhao, K. J. J. Phys. Chem. C. 2017, 121, 6002-6010.
- [28] Afzal, M.; Butt, P. K.; Ahmad, H. J. Therm. Anal. 1991, 37, 1015-1023.
- [29] Verdier, S.; El Ouatani, L.; Dedryvere, R.; Bonhomme, F.; Biensan, P.; Gonbeau, D.*J. Electrochem. Soc.* 2007, *154*, A1088-A1099.
- [30] Lu, Y. C.; Mansour, A. N.; Yabuuchi, N.; Shao-Horn, Y. Chem. Mater. 2009, 21, 4408-4424.
- [31] Appapillai, A. T.; Mansour, A. N.; Cho, J.; Shao-Horn, Y. Chem. Mater. 2007, 19, 5748-5757.
- [32] Hu, S. K.; Chou, T. C.; Hwang, B. J.; Ceder, G. J. Power Sources. 2006, 160, 1287-1293.
- [33] Wilcox, J. D.; Rodriguez, E. E.; Doeff, M. M. J. Electrochem. Soc. 2009, 156, A1011-A1018.

[34] Ceder, G.; Chiang, Y. M.; Sadoway, D. R.; Aydinol, M. K.; Jang, Y. I.; Huang, B. *Nature*. **1998**, *392*, 694-696.

[35] Chen, Z. H.; Qin, Y.; Amine, K.; Sun, Y. K. J. Mater. Chem. 2010, 20, 7606-7612.

- [36] Yoon, W. S.; Balasubramanian, M.; Chung, K. Y.; Yang, X. Q.; McBreen, J.; Grey,
- C. P.; Fischer, D. A. J. Am. Chem. Soc. 2005, 127, 17479-17487.
- [37] Hwang, S.; Kim, S. M.; Bak, S. M.; Chung, K. Y.; Chang, W. Chem. Mater. 2015, 27, 6044-6052.
- [38] Wandt, J.; Freiberg, A.; Thomas, R.; Gorlin, Y.; Siebel, A.; Jung, R.; Gasteiger, H.
- A.; Tromp, M. J. Mater. Chem. A. 2016, 4, 18300-18305.
- [39] Lin, F.; Nordlund, D.; Markus, I. M.; Weng, T. C.; Xin, H. L.; Doeff, M. M. *Energy Environ. Sci.* **2014**, *7*, 3077-3085.

APPENDICES

VITA

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PUBLICATION:

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- 2. Bob Jin Kwon, Baris Key, Jacob Jokisaari, Chunjoong Kim, Soojeong Kim, Hyun Deog Yoo, Sang-Don Han, Igor L. Bolotin, Luke Hanley, Robert F. Klie, and Jordi Cabana, "Structural Evolution of Disordered Manganese Oxide Layers upon Reversible Insertion of Mg ions" manuscript in preparation.
- Bob Jin Kwon, Fulya Dogan, Baris Key, Jacob Jokisaari, Chunjoong Kim, Robert F. Klie and Jordi Cabana, "Effect of Passivating Shells on the Properties of Spinel-Type LiMn₂O₄ Nanocrystal Heterostructures", *Journal of Materials Chemistry A*, submitted.

- 4. Ryan D. Bayliss, Baris Key, Gopalakrishnan Sai Gautam, Pieremanuele Canepa, Bob Jin Kwon, Saul H. Lapidus, Fulya Dogan, Abdullah A. Adil, Andrew S. Lipton, Peter J. Baker, Gerbrand Ceder, John T. Vaughey and Jordi Cabana "Mg Mobility in Spinel Oxides", *Nature Materials*, 2018, in revision.
- Bob Jin Kwon, Patrick J. Phillips, Baris Key, Fulya Dogan, John W. Freeland, Chunjoong Kim, Robert F. Klie and Jordi Cabana, "Nanocrystal Heterostructures of LiCoO₂ with Conformal Passivating Shells", *Nanoscale*, 2018, in press.
- Jordi Cabana, Bob Jin Kwon, Linhua Hu, "Mechanisms of Degradation and Strategies for the Stabilization of Cathode-Electrolyte Interfaces in Li-ion Batteries", *Accounts* of Chemical Research, 2018, 51, 299-308.
- Chunjoong Kim, Abdullah Adil, Ryan Bayliss, Tiffany Kinnibrugh, Saul Lapidus, Gene Nolis, John Freeland, Patrick Phillips, Tanghong Yi, Hyun Deog Yoo, Bob Jin Kwon, Young-Sang Yu, Robert Klie, Peter Chupas, Karena Chapman, Jordi Cabana, "Multivalent Electrochemistry of Spinel Mg_xMn_{3-x}O₄ Nanocrystals", *Chemistry of Materials*, 2018, 30, 1496-1504.
- 8. Bob Jin Kwon, Jong-Young Kim, Sung Jin An "Highly transparent and conducting graphene-embedded ZnO films with enhanced photoluminescence fabricated by aerosol synthesis" *Nanotechnology*, 2014, 25.
- Seung II Park, Bob Jin Kwon, Jeong Hoon Park, Hyun Jung, and Kook Hyun Yu, "Synthesis and Characterization of 3-[¹³¹I]Iodo-L-Tyrosine Grafted Fe₃O₄@SiO₂ Nanocomposite for Single Photon Emission Computed Tomography (SPECT) and Magnetic Resonance Imaging (MRI)" *Journal of Nanoscience and Nanotechnology*, 2011, 11, 1818-1821.
- Jieun Ko, Bob Jin Kwon, and Hyun Jung, "Synthesis and Characterization of the SnO₂-Pillared Layered Titanate Nanohybrid" *Journal of Physics and Chemistry of Solids* 2010, 71, 658-662.
- Sang Wook Kim, Bob Jin Kwon, Jeong Hoon Park, Min Goo Hur, Seung Dae Yang, and Hyun Jung, "γ-ray Radiation Induced Synthesis and Characterization of α-Cobalt Hydroxide Nanoparticles" *Bulletin of the Korean Chemical Society* 2010, 31, 910-914.

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Nanocrystal heterostructures of LiCoO₂ with conformal passivating shells

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