Understanding Atomic Scale Phenomena within the Surface Layer of a Long-term Cycled 5V Spinel Electrode

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Abstract

Lithium-ion batteries utilizing 5V spinel material, $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, have received considerable interest in recent years for their ability to deliver high energy and power densities. In this article, we report an atomic scale analysis of the surface layer of a core-shell 5V spinel structure where a small amount of the manganese lattice sites have been substituted with cobalt in the shell to reach a stoichiometry of $\text{Li}_x\text{Mn}_{1.18}\text{Ni}_{0.55}\text{Co}_{0.27}\text{O}_4$. Our analyses include electrochemical analysis, atom probe tomography (APT) analysis, kinetic analysis of the interfacial reactions, and high resolution scanning transmission electron microscopy (HR-TEM) analysis. The APT analysis is performed on the material before and after long-term cycling at room temperature to provide insights into the atomic scale phenomena within the surface layer of the electrode material. Our APT data reveals a 25 to 30 nano-meter (nm) region which forms after cycling. From our analyses, we believe that the outer few nanometers of this region stabilizes the 5V spinel within the chemical environment of the lithium-ion cell such that its structure is not compromised and thereby enables this material to cycle without significant capacity fading.

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1. Introduction

Given the concern of global climate change and the understanding that carbon dioxide emissions are driving this change, much effort has been invested to lower carbon dioxide emissions. One approach to reduce carbon dioxide emissions is to curtail the carbon dioxide emissions from vehicles through the introduction of hybrid electric vehicles, plug-in hybrid electric vehicles, and electric vehicles¹⁻⁴. Today, lithium cobalt oxide materials are widely used in consumer electronic applications, yet these materials are cost prohibitive for larger scale vehicle applications. As a result, alternative materials with higher energy densities and lower cost are being investigated⁵⁻⁸.

One approach to achieve higher energy densities in Li-ion batteries is to use cathode materials that operate at higher electric potentials versus $\text{Li}^+/\text{Li}_{(\text{s})}$. One such cathode material is the 5V spinel, $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ⁹. When the 5V spinel cathode material is combined with a graphite anode material, an energy density of up to 240 Wh kg^{-1} is possible¹⁰. Given its higher electric potential and three dimensional lithium ion transport capability, the 5V spinel is an auspicious high energy and high power cathode materials for Li-ion batteries. To date, the main issue with the 5V spinel material is the instability of the interface between the electrolyte and the 5V spinel material¹⁰. Researchers have developed zinc oxide coatings¹¹⁻¹⁴ and others researchers have fluorinated electrolytes to address this issue¹⁵⁻¹⁷, yet the issue remains.

In this article, we take a systematic approach to analyze the core-shell 5V spinel material. First, the electrochemical performance of the core-shell 5V spinel is compared to the 5V spinel using half cells. Next, the composition of the surface layer of the core-shell 5V spinel material is characterized at the atomic scale by APT. Subsequently, to determine the impact of the surface layer within the Li-ion cell, kinetic measurements of the interfacial reactions were acquired using Argonne National Laboratory's (ANL) Electrochemical Reaction Kinetics Analysis System (ERKAS). Finally, to assess the structure of the surface layer of the cycled core-shell 5V spinel, high resolution scanning transmission electron microscopy (HR-STEM) was applied.

2. Experimental

2.0. Electrochemical Characterization

To determine the electrical chemical performance of the standard 5V spinel material and the core-shell 5V spinel material, half cells were fabricated using these cathodes and metallic lithium anodes. The standard 5V spinel, NanomyteTM SP-10, was acquired from NEI Corporation headquartered in Somerset, NJ. The core-shell 5V spinel material was synthesized through a co-precipitation method published earlier¹⁸⁻¹⁹. The composition of the standard 5V spinel electrode was: 84 wt% active material, 8 wt% C45, and 8 wt% Kureha 1120 PVDF. The composition of the core-shell 5V spinel follows: 85 wt% active material, 7.5 wt% carbon black, and 7.5 wt% PVDF. The electrolyte for the coin cells was 1.2M LiPF₆ in 30 wt% ethylene carbonate and 70 wt% ethyl methyl carbonate from Tomiyama Pure Chemical Industries, LTD. also known as GEN 2 Electrolyte. Celgard 2325 separators were used for coin cells. The CR2032 coin cells were sealed using an automated crimping machine from Hohsen Corporation in the glove box with an argon atmosphere where the oxygen and water content is less than 1 ppm.

Once half cells were fabricated, coin cells were cycled on a MACCOR Series 4000 Automated Test System at room temperature using a voltage window between 3.5V and 4.9V versus Li⁺/Li_(s). The first three formation cycles applied a charge and discharge rate of C/10. The next hundred cycles utilized a charge rate of C/3 and a discharge rate of C/2.

2.1. Atom Probe Tomography Analysis

The APT technique uses an extremely strong electric field and pulsed UV laser to ionize and desorb atoms from the surface and then a time of flight mass spectrometry for characterization. The APT is useful in determining sub-nanometer structures and concentration gradients. The APT technique requires the specimen to be formed into a sharp nano-scale tip so that a sufficiently large electric field can be achieved. Sharp nano-scale APT specimens from the pristine and long term cycled core-shell 5V spinel electrodes were fabricated utilizing a modified version of the technique published by Thompson²⁰. The only notable change to the published technique is a deposition of 50 nm layer of nickel using Northwestern University's ion beam sputter deposition system, a Model IBS/e from South Bay Technologies, to protect the surface of the material from subsequent milling steps. The nickel deposition has trace amounts of aluminum

which aid in determining the extent of the protective nickel layer in the latter APT analysis. The other modifications were geometric in nature.

Two focused ion beam (FIB) systems were used in this work, namely, the FEI Helios Nanolab SEM/FIB at Northwestern University, and the FEI Dual Beam 235 FIB at the University of Illinois Urbana Champaign. To protect the samples and milled specimens from long exposures to the atmosphere, a PELCO[®] SEM Pin Stub Vacuum Desiccator was used.

Scanning electron microscopy (SEM) images of the surface of the un-cycled core-shell 5V spinel electrode are shown in Figure 1. Within this figure, a crystal with a “soccer-ball” like appearance is seen. This crystal structure was selected for APT analysis since it is free from visible voids and defects which lead to a robust specimen which can handle the extreme electrostatic forces established within the APT system on the specimen.

Figure 1 Surface of uncycled core-shell with Ni deposition

Figure 2 represents sequential points within the nano-tip fabrication process on the “soccer-ball” like crystal.

Figure 2 Scanning electron microscopy (SEM) images of the various stages of fabricating a nano-tip to enable the atom probe tomography analysis technique on the core-shell 5V spinel crystal in Figure 1. In (c), (d), and (e), the uppermost layer is platinum, then nickel, then spinel. In (f), the platinum layer is removed leaving a nickel capping layer on the spinel.

Similar crystals were used to fabricate nano-tip specimens of the cycled core-shell 5V spinel electrode. The nano-scale specimen tips were analyzed in the CAMECA LEAP 4000 XSi tomograph at the Northwestern University Center for Atom Probe Tomography (NUCAPT) in Evanston, Illinois. The APT data was processed using CAMECA’s IVAS™ 3.6.6 data analysis software.

2.2 Kinetic Analysis of the Interfacial Reaction

To perform the kinetic analysis of the interfacial reactions, ANL’s ERKAS was applied. This system is composed of two key components. First, a Tenney Environmental Test Chamber, Model TJR-A-WF4, from Thermal Product Solutions is used to control the operating temperature of the CR2032 coin cells. Second, the Keithley 2401 Source Meter is utilized to precisely control and measure the voltage and current of the coin cells.

The kinetic analysis uses half cells in which the cathode is the standard 5V spinel, core-shell 5V spinel, or carbon black, and the anode is metallic lithium. The carbon black, TIMCAL C45, electrode is used for two reasons. First, it is used to demonstrate that the electrolyte is free from contaminants. Second, since the cathode electrodes typically use C45 as a constituent to improve electrical conductivity, the C45 electrode helps to distinguish between an electrochemical reaction between the C45 and the electrolyte and an electrochemical reaction between the active material and the electrolyte. The compositions of the standard 5V spinel electrode and the core-shell 5V spinel electrode were the same as previously noted in Section 2.0. The C45 electrodes were fabricated using a slurry mixture of 50 wt% C45 and 50 wt% Kureha PVDF in solution of N-Methyl-2-pyrrolidone (NMP). GEN 2 Electrolyte and Celgard 2325 separators were utilized for the coin cells. The CR2032 coin cells were sealed as detailed earlier.

Once the half cells were fabricated, the coin cells completed two and a half formation cycles using a C/10 rate and a voltage window between 3.5V and 4.9V versus $\text{Li}^+/\text{Li}_{(\text{s})}$ at room temperature and were left in a charged state. The coin cells were then placed into custom fixtures within the Tenney Environmental Test Chamber for the kinetic analysis. For the duration of the analysis, the potential of the coin cell were fixed at 4.9V versus $\text{Li}^+/\text{Li}_{(\text{s})}$. Kinetic measurements were taken at 5°C, 10°C, 15°C, 20°C, and 25°C. Each temperature was held constant for varying periods of time ranging from 24 hours for the lower temperatures to up to five days for the higher temperatures. In doing so, there is sufficient time for the current to reach an equilibrium state.

2.3 High Resolution Scanning Transmission Electron Microscopy (HR-STEM) Analysis

To perform the HR-STEM analysis on the surface layer of the room temperature cycled core-shell 5V spinel, the samples were sent to the Evans Analytical Group® (EAG) in Raleigh, NC. To protect the surface layer of the sample from subsequent FIB milling steps, EAG first deposited 130 nm of carbon onto the electrode surface using an electron beam-induced deposition (EBID) technique within their FEI Helios dual beam FIB/SEM system. Then using this system, EAG deposited an additional carbon layer onto the electrode surface using an ion beam-induced deposition (IBID) technique. After the carbon deposition, EAG used a proprietary in-situ FIB technique to lift a specimen from the electrode. EAG then mounted the specimen onto a 200 mesh copper TEM grid using IBID of platinum. Afterwards, EAG applied a gallium ion beam to thin a small section of the specimen to an electron transparency thickness. Lastly,

EAG utilized their aberration-corrected Hitachi HD2700 scanning transmission electron microscope to acquire the HR-STEM images. The electron beam and the spatial resolution of the aberration-corrected Hitachi HD2700 are approximately 0.14 nm.

3. Results and Discussion

3.0 Electrochemical Characterization Results

Through cycling half cells of the standard 5V spinel and the core-shell spinel materials, the benefit of introducing cobalt into the outer shell of the 5V spinel is apparent in Figure 3.

Figure 3 Cycler results for core-shell 5V spinel and standard 5V spinel in half cells

From Figure 3, the substitution of the cobalt into the shell of the 5V spinel dramatically improves the performance of the half cell. To probe further into the half-cell cycler results, the voltage profiles were investigated. The voltage profiles for the first and last cycles of the core-shell 5V spinel and the standard 5V spinel are shown in Figure 4. The first cycles were done with C/10 charge and discharge rates while the hundred and third cycles were done with C/3 charge and C/2 discharge rates.

Figure 4 Voltage profiles: a) 1st cycle for the core-shell 5V spinel, b) 103rd cycle for the core-shell 5V spinel, c) 1st cycle for the standard 5V spinel, d) 103rd cycle for the standard 5V spinel in half cells

Figure 4 reveals a couple of key points. First, the core-shell 5V spinel maintains its voltage profile from the first cycle to the hundred and third cycle which implies that the structure of the core-shell 5V spinel remains intact. Second, the voltage profile of the standard 5V spinel changes dramatically from the first cycle to the hundred and third cycle. This voltage profile clearly shows a dramatic increase in the cell impedance and a massive decrease in capacity that are likely related to structural changes especially within the surface layer of the standard 5V spinel.

To begin to understand the mechanism behind the excellent cycle performance of the core-shell 5V spinel, it is important to understand what is occurring at the atomic scale within the surface layer of this material.

3.1 Atom Probe Tomography Results

To understand the atomic scale phenomena within the surface layer of the core-shell 5V spinel, two types of specimens were investigated by the APT technique specifically the un-cycled and cycled material. By comparing the results from the cycled electrode against the uncycled electrode, the changes within the surface layer of the core-shell spinel can be seen. Figure 5 and Figure 6 illustrate the 1D concentration profiles through the surface layer of the un-cycled and cycled core-shell 5V spinel respectively.

Figure 5 1D concentration profile of un-cycled core-shell 5V spinel

Figure 6 1D concentration profile of cycled core-shell 5V spinel

The leftmost portions of these figures represent the uppermost portion of the nano-tip specimen. The nano-tip specimen starts with a protective nickel deposition and then transitions into the core-shell 5V spinel. The protective nickel deposition is distinguished from the nickel in the spinel by trace amounts of aluminum in the nickel deposition. Therefore, the protective nickel deposition terminates at the same point as does the trace aluminum. This point is also the uppermost portion of the spinel surface. Figure 5 reveals that the surface layer of the uncycled core-shell 5V spinel is identical to the bulk composition which is no surprise since this material

has not been cycled. In stark contrast, Figure 6 reveals a dramatic change within the first 25 to 30 nm of the core-shell 5V spinel surface; afterwards, a bulk concentration is reached.

By further analysis, a more complete atomic-scale picture emerges. In Figure 6, there is an apparent build-up of lithium on the uppermost surface of the spinel which indicates that the lithium-ions are likely tramped within electrolyte reaction products similar to what occurs within solid electrolyte interphase (SEI) on the anode. Following the lithium rich layer, a layer emerges in which the nickel is enriched and the manganese and lithium are depleted. This nickel enriched layer is believed to form as a result of the dissolution of the manganese into the electrolyte (refer to Equation 1 below) and a subsequent diffusion of nickel from the bulk to the surface:

In this reaction, the Mn^{2+} dissolves into the electrolyte while the Mn^{4+} remains on the electrode surface. This reaction for the manganese based cathode materials such as the 4V $\text{Li}_x\text{Mn}_2\text{O}_4$ is widely referenced in the literature²¹⁻²⁷. It should be noted that in a 4V spinel, $\text{Li}_x\text{Mn}_2\text{O}_4$, half of the manganese is in a 3^+ oxidation state, and the other half is in a 4^+ oxidation state. Therefore, the disproportionation reaction is possible. In contrast, in a pure 5V spinel, $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, an oxidation state of 3^+ is not possible for the manganese since all the manganese is in a 4^+ oxidation state. Therefore, the disproportionation reaction is not possible for the standard 5V spinel assuming that the oxidation state of the manganese on the surface is the same as the bulk which may not be the case²⁸. Nickel oxide layers are known to form on the outer most surface of other cathode materials²⁹. Thus, the formation of a nickel enriched layer on the core-shell 5V spinel is not peculiar. It should be noted that within the first two nanometers from the surface, the concentration of oxygen is dramatically lower than at a distance of ten nanometers from the surface. Therefore, within the first two nanometers of the core-shell 5V spinel, a very thin layer similar to a nickel oxide material appears to exist. This material is clearly not a pure nickel oxide phase; however, the predominant constituents of this region are clearly nickel and oxygen. One explanation for the dramatic reduction in the concentration of oxygen is that protons within the electrolyte attack the surface oxygen to form water thereby removing oxygen from the surface of the electrode.

Once the nickel enriched layer is formed, it is believed and demonstrated later in the article that this layer allows the transport of Li-ions yet hinders the chemical reaction between the electrode surface and the electrolyte. As a result, this layer stabilizes the 5V spinel within the chemical environment of the Li-ion battery.

It should be noted that cobalt is not present in the protective nickel coating yet appears to be present in Figure 5 and Figure 6. This represents an artifact in the way the CAMECA software bins the results. For instance, the nickel isotopes are 58, 60, 61, 62, and 63, and cobalt is 59. Therefore, in the region of the protective nickel coating, the tail from the nickel 58 is creating this cobalt artifact which is evident when the mass spectrum data is inspected more closely. Therefore, it is prudent to always cross check the elemental binning against the mass spectrum which was done for this report.

Additional un-cycled and cycled core-shell 5V spinel specimens were analyzed, and similar results were obtained.

3.2 Kinetic Analysis Results of the Interfacial Reaction

To determine if the nickel enriched surface layer of the core-shell 5V spinel impacts the activation energy for the oxidation of R, $\Delta G_b^\ddagger$, or the electron tunneling between the constituents of the electrolyte and the cathode material, κ_{el} , a number of electrochemical reaction kinetic measurements were made at varying temperatures. These measurements are based upon the following backward rate constant relationship which has been established by previous theoretical work³⁰⁻³⁴ and associated current relationship³⁴:

$$k_b = K_{P,R} v_n \kappa_{el} \exp(-\Delta G_b^\ddagger / RT) \quad (2)$$

$$i = nFAk_b C_R(0,t) \quad (3)$$

$$i = nFAK_{P,R} v_n \kappa_{el} \exp(-\Delta G_b^\ddagger / RT) C_R(0,t) \quad (4)$$

$$\ln(i) = -\Delta G_b^\ddagger / RT + \ln(nFAK_{P,R} v_n \kappa_{el} C_R(0,t)) \quad (5)$$

$$\ln(i_0) = \ln(nFAK_{P,R} v_n \kappa_{el} C_R(0,t)) \quad (6)$$

where:

k_b is the backward electrochemical reaction rate constant.

$K_{P,R}$ is the ratio of the reactant concentration in the reactive position at the electrode to the bulk solution concentration.

v_n is the nuclear frequency factor that accounts for the frequency of attempts on the energy barrier.

κ_{el} is the electronic transmission coefficient that is related to probability of electron tunneling.

$\Delta G_b^\ddagger$ is the activation energy for the oxidation of R.

R is the universal gas constant.

T is the absolute temperature in Kelvin.

i is the current from the cathode electrode to the electrolyte which oxidizes the constituents of the electrolyte. Note the direction of current is opposite to the direction of electron flow.

i_0 is the current at the y-intercept of the natural log of the current.

n is the number of electrons transferred during the electrochemical reaction.

F is Faraday's constant.

A is the electrochemical surface area of the electrode.

$C_R(0,t)$ is the surface concentration of R at time t.

From Equation 4, it is clear that the steady-state current in our half cells taken at a fixed potential of 4.9V versus $\text{Li}^+/\text{Li}_{(s)}$ is dependent upon a number of coefficients and variables. The objective of our work is to determine if any significant difference in either $\Delta G_b^\ddagger$ or κ_{el} exists between the core-shell 5V spinel electrode and the standard 5V spinel electrode. Any significant difference in

either of these coefficients will provide evidence that the kinetics of the interfacial reactions are different.

To this end, half cells with standard 5V spinel, core-shell 5V spinel, and C45 cathodes, and metallic lithium anodes were fabricated and placed into the ERKAS for evaluation. To ensure that the electrolyte in these cells is free from impurities, half cells with a carbon black, TIMCAL C45, cathode and a metallic lithium anode were used. The operating temperature of the half cells was stepped through the following sequence: 5°C, 10°C, 15°C, 20°C, and 25°C, and the corresponding currents were measured. The results can be found in Figure 7.

Figure 7 Electrochemical reaction kinetic results: linear fittings for the standard 5V spinel, core-shell 5V spinel, and C45.

Table 1: Fitting results of kinetic study shown in Figure 6.

Material	Slope	Slope Error	y-Intercept	y-Intercept Error
Standard 5V Spinel	-47,876.98	4,743.65	13.27	1.98
Core-Shell 5V Spinel	-47,513.96	5,305.28	12.43	2.22
C45	-60,281.51	3,122.67	16.17	1.30

From Figure 7 and Table 1, three points are evident. First, the C45 electrode is much less active than the other two electrodes. Second, since the slopes of the linear fits for the 5V spinel and the core-shell 5V spinel are comparable, their activation energies, $\Delta G_b^\ddagger$, are comparable. As a result, the nickel enriched layer within the surface layer of the core-shell 5V spinel does not impact the activation energy for the oxidation of R.

Next, the y-intercept points for the standard 5V spinel material and the core-shell 5V spinel material are very close to each other. For instance from Table 1, the y-intercept point for the standard 5V spinel material is 13.27, and the y-intercept point for the core-shell 5V spinel material is 12.43. To investigate the y-intercepts further, it is useful to subtract the y-intercepts using Equation 6. In doing so, the constants drop out, and the following expression remains.

$$\ln(i_{0\ 5V}) - \ln(i_{0\ \text{Core-Shell } 5V}) = \ln(A_{5V}) + \ln(\kappa_{el\ 5V}) - \ln(A_{\text{Core-Shell } 5V}) - \ln(\kappa_{el\ \text{Core-Shell } 5V}) \quad (7)$$

Brunauer Emmett Teller (BET) Surface Area Analysis revealed that the surface area of the standard 5V spinel, A_{5V} , is $3.61\ \text{m}^2/\text{g}$, and that the surface area of the core-shell 5V spinel is $1.069\ \text{m}^2/\text{g}$. The mass of the standard 5V spinel on the electrode is 12.9 mg and the mass of the core-shell 5V spinel on the electrode is 4.75 mg. Given the surface area per gram values, electrodes loadings, and slope intercepts, the difference in the natural log of the electronic transmission coefficients simplifies to the following:

$$\ln(\kappa_{el\ 5V}) - \ln(\kappa_{el\ \text{Core-Shell } 5V}) = -1.37 \quad (8)$$

$$\ln(\kappa_{el\ 5V} / \kappa_{el\ \text{Core-Shell } 5V}) = -1.37 \quad (9)$$

By taking the inverse natural log of Equation 9, the relative value of $\kappa_{el\ \text{Core-Shell } 5V}$ to $\kappa_{el\ 5V}$ is determined:

$$\kappa_{el\ \text{Core-Shell } 5V} = 4\ \kappa_{el\ 5V} \quad (10)$$

Therefore, the electronic transmission coefficient that is related to probability of electron tunneling for the core-shell 5V spinel material is a factor of 4 more than the electronic transmission coefficient for the standard 5V spinel material. This result indicates that the nickel enriched layer of the core-shell 5V spinel does not hinder the tunneling of the electrons from the constituents of the electrolyte to the cathode, but promotes the tunneling of the electrons. The increase in electron tunneling may improve the electrical conductivity among the cathode particles within the electrode thereby enabling more efficient lithiation and de-lithiation of the cathode and thereby contributing to its excellent cycle performance.

However, the nickel enriched surface layer of the core-shell 5V spinel does not hinder the oxidation of the electrolyte. Therefore, given the excellent cycle performance of the core-shell 5V spinel and the kinetic analysis results, the performance can only be explained by a reduction

of undetermined chemical reaction(s) between the surface of the core-shell 5V spinel and the electrolyte induced by the formation of the nickel enriched surface layer of the core-shell spinel. We know that with the introduction of cobalt into the shell of the core-shell 5V spinel, a nickel enriched surface layer forms during cycling. We believe that the nickel enriched surface layer forms in three stages. First, the manganese is depleted from the surface layer via the disproportionate reaction (1) at the interface between the electrolyte and the electrode surface. For instance, the Mn^{2+} dissolves into the electrolyte while the Mn^{4+} remains on the surface. Then, nickel and manganese diffuse to the surface from the bulk. Since the manganese continues to dissolve into the electrolyte, over time the surface layer becomes enriched with nickel. However, the key discovery is a dramatic drop in the concentration of the oxygen at the surface seen in Figure 6. The dramatic drop in oxygen occurs over a 2 nm distance from the surface. This drop is likely do to protons within the electrolyte that attack the oxygen at the surface to form water and thereby remove oxygen from the surface. With a closer look at Figure 6, the predominant constituents of the 2 nm surface layer are nickel and oxygen, and the lesser constituents are lithium, manganese, and cobalt. Thus, we believe that this 2 nm “nickel oxide” like region at the electrode surface enables nickel to stay in an electrochemically inactive oxidation state of 2^+ throughout the cycling process. In the oxidation state of 2^+ , the nickel is less chemically reactive with the electrolyte. As a result, the 2 nm “nickel oxide” like surface layer of the core-shell 5V spinel protects the 5V spinel from undetermined detrimental chemical reaction(s) at the interface between the surface of the core-shell 5V spinel and the electrolyte. Thus, the structure of the core-shell 5V spinel remains intact and thereby enables this material to cycle without significant capacity fading.

3.3 High Resolution Scanning Transmission Electron Microscopy (HR-STEM) Results

To assess the structure of the nickel enriched surface layer of the room temperature cycled core-shell 5V spinel, a high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) technique was used. Figure 8 represents the HAADF-STEM image of the surface layer of the core-shell 5V spinel. Moving from right to left in the image of Figure 8 is the following sequence: the carbon deposition, the surface layer of electrode, and the bulk of the electrode.

Figure 8 High angle annular dark field scanning transmission electron image of the surface layer of the cycled core-shell 5V spinel

From Figure 8, the periodicity of the higher atomic number elements in the core-shell 5V spinel material remains the same from the bulk to within approximately 1 to 2 nm from the surface. Thus, the structure of a significant portion of the 25 nm to 30 nm nickel enriched surface layer is similar to the structure of the bulk. Hence, for a significant portion of the nickel enriched surface layer, the oxygen face centered cubic structure (FCC) remains intact during the room

temperature cycling of the core-shell 5V spinel which helps to explain the excellent cycle performance of this material. However, for the outermost 1 to 2 nm of the nickel enriched surface layer, the HR-TEM analysis is inconclusive due to imperfections in the surface of the core-shell 5V spinel which demonstrates the inherent value of utilizing APT analysis that is able to account for every other atom.

4. Conclusion

To better understand the mechanism for how the substitution of cobalt into the shell of the core-shell 5V spinel structure enables its impressive cycle performance, we applied a systematic approach. First, we measured the electrochemical performance of the standard 5V spinel and the core-shell 5V spinel materials in half cells. The half cells demonstrated that the core-shell 5V spinel is able to cycle with minimal capacity loss over a hundred cycles while the standard 5V spinel fades quickly after only thirty cycles. To gain insights into the composition of the surface layer of the core-shell 5V spinel, we utilized APT analysis. This analysis revealed the development of a 25 to 30 nm nickel enriched surface layer where the outermost 1 to 2 nm layer is a “nickel oxide” like phase. Subsequently, we demonstrated through kinetic measurements that the nickel enriched surface layer of the core-shell 5V spinel does not alter the activation energy for the oxidation of the electrolyte nor does it reduce the tunneling of electrons from the electrolyte to the cathode. Given the kinetic results and the excellent cycle performance of the core-shell 5V spinel, we conclude that the 1 to 2 nm “nickel oxide” layer protects the 5V spinel from undetermined detrimental chemical reaction(s) at the interface between the surface of the spinel and the electrolyte and thereby enabling its impressive cycle life. We speculate that the lower concentration of oxygen at the surface enables the nickel at the surface to remain in an electrochemically inactive oxidation state of 2^+ throughout the cycling process and thereby provides chemical stability. Lastly, we used HAADF-STEM to demonstrate that a significant portion of the nickel enriched layer is similar in structure to the spinel bulk which provides evidence that the 1 to 2 nm “nickel oxide” layer protects the spinel structure.

In summary, we have shown that with the introduction of cobalt into the shell of the core-shell 5V spinel structure, a 1 to 2 nm “nickel oxide” layer forms that protects the 5V spinel from

detrimental chemical reaction(s) at the interface between the electrolyte and the 5V spinel and thereby enables its impressive cycle life.

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