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Lithium Vanadium Oxide ($\text{Li}_{1.1}\text{V}_3\text{O}_8$) Coated with Amorphous Lithium Phosphorous Oxynitride (LiPON): Role of Material Morphology and Interfacial Structure on Resulting Electrochemistry

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In the present work, lithium vanadium oxide ($\text{Li}_{1.1}\text{V}_3\text{O}_8$) particles synthesized at two different temperatures were coated with an amorphous lithium phosphorous oxynitride (LiPON) film for the first time, and the effects of the LiPON coating on the electrochemistry of the $\text{Li}_{1.1}\text{V}_3\text{O}_8$ materials with different morphologies were systematically investigated by comparing uncoated $\text{Li}_{1.1}\text{V}_3\text{O}_8$ and $\text{Li}_{1.1}\text{V}_3\text{O}_8$ coated with LiPON of various thicknesses. Galvanostatic discharge-charge cycling revealed increased functional capacity for the LiPON-coated materials. Post-cycling electrochemical impedance spectroscopy showed that LiPON-coated $\text{Li}_{1.1}\text{V}_3\text{O}_8$ materials developed less interfacial resistance with extended cycling, rationalized by vanadium migration into the LiPON coating seen by electron energy loss spectra. Post-mortem quantitative analysis of the anodes revealed more severe vanadium dissolution for the more irregularly shaped $\text{Li}_{1.1}\text{V}_3\text{O}_8$ materials with less LiPON coverage. Thus, this study highlights the specific benefits and limitations of LiPON coatings for stabilizing a moderate voltage $\text{Li}_{1.1}\text{V}_3\text{O}_8$ cathode material under extended cycling in liquid electrolyte, and describes a generally applicable approach for comprehensive characterization of a composite electroactive material which can be used to understand interfacial transport properties in other functional systems.

Introduction

Driven by the increasing energy demand worldwide, intensive efforts concerning energy and power density, longevity, safety and cost are being made to advance Li-ion battery systems. Among the alternative lithium intercalation materials to LiCoO_2 , vanadium oxide based materials such as V_2O_5 , (1) $\text{Na}_x\text{V}_2\text{O}_5$, (2, 3) $\text{Na}_x\text{V}_3\text{O}_8$, (4) $\text{Na}_x\text{V}_6\text{O}_{15}$, (5) $\text{Li}_x\text{V}_2\text{O}_5$, (6) V_6O_{13} , (7), VOPO_4 , (8, 9) and $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (10) have been extensively investigated because of their high specific capacity and low cost. $\text{Li}_{1+x}\text{V}_3\text{O}_8$ ($x = 0.0 - 0.2$) has attracted attention in particular due to its high capacity and excellent rate capability. This material has a layered structure with layers comprised of VO_6

octahedrons and VO_5 distorted trigonal bipyramids with Li^+ residing in octahedral sites in the interlayer space.(11) The lithiation process of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ has been investigated in detail via x-ray diffraction techniques and the following steps were found: a single-phase reaction between 3.6 - 2.6 V, a two-phase transformation at ~ 2.6 V, and a single reaction at ~ 2.35 V.(11-14) The multi-step reaction translates to a theoretical capacity of $362 \text{ mAh}\cdot\text{g}^{-1}$ assuming insertion of 3.9 equivalents of Li^+ .

Conventionally, $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is synthesized via a solid-state method which is carried out at high temperature ($>680^\circ\text{C}$) for extended heating times (>10 h).(10, 15) More facile and environmentally-benign approaches have been developed in recent years including microwave,(16) sol-gel,(17-20) freeze-drying,(16) spray-drying,(21) hydrothermal,(22-24) and rheological phase reaction methods(25). The specific electrochemical performance can be significantly affected, by the preparation and post-synthesis conditions. The sol-gel synthesis typically produces material of smaller particle size, providing more facile access for Li^+ diffusion. For example, the sol-gel preparation route for LiV_3O_8 has demonstrated higher initial capacity relative to the solid state preparation route ($300 \text{ mAh}\cdot\text{g}^{-1}$ versus $180 \text{ mAh}\cdot\text{g}^{-1}$).(19)

Heat-treatment temperature during the synthesis of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ influences the specific surface area, morphology and crystal structure of the product, which consequently affects the electrochemistry.(23, 26, 27) $\text{Li}_{1+x}\text{V}_3\text{O}_8$ prepared at $\sim 500^\circ\text{C}$ usually shows higher crystallinity, larger particle size, more regular particle morphology and lower surface area, compared to lower temperature products which are more poorly crystallized. For example, hydrothermally prepared 300°C $\text{Li}_{1+x}\text{V}_3\text{O}_8$ demonstrated higher initial discharge capacity but poorer cyclic stability compared to 500 and 550°C heat-treated products.(23)

Despite its high theoretical capacity, a significant drawback of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is the capacity fade which originates from the structural changes upon lithiation and subsequent cathode dissolution in organic electrolytes.(19) The solubility of the active cathode material contributes to increased capacity fade in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ cathodes discharged to lower voltages (≤ 2.0 V). In particular, quantitative chemical and electrochemical Li^+ insertion methods on $\text{Li}_{1+x}\text{V}_3\text{O}_8$ have shown partial solubility of $\text{Li}_{4-5}\text{V}_3\text{O}_8$ compounds.(19) After storage of $\text{Li}_{4.0}\text{V}_3\text{O}_8$ and $\text{Li}_{5.0}\text{V}_3\text{O}_8$ in organic electrolyte, samples with the formula of $\text{Li}_{5.0}\text{V}_3\text{O}_8$ showed measureable dissolution of vanadium, while $\text{Li}_{4.0}\text{V}_3\text{O}_8$ samples did not. Consequently, the dissolution was attributed to the presence of V(III), which is partially soluble in electrolyte. A possible mechanism is that ion exchange takes place between V(III) and Li^+ from the electrolyte, which is similar to the first step of Mn dissolution from the LiMn_2O_4 material.(28) Another proposed mechanism is that formation of Li_2O results in O^{2-} extraction from the solid and the original phase will change on the surface.(19) Studies of other V_xO_y and $\text{V}_x\text{O}_y\text{P}_z$ based cathode materials have indicated similar relative solubility trends for V(V), V(IV), and V(III).(29-32) At the bulk level, composite

nanoarchitectures,(33) and mixtures with other stable vanadium based phases(34) have been studied to improve electrochemical stability of LiV_3O_8 containing cathodes.

At the material level, amorphous coatings of nanometer scale thickness have been used in various research fields to alter the interfacial properties and meet the application requirements of materials, devices and systems. Surface coatings such as Al_2O_3 , (35) AlPO_4 , (36) AlF_3 , (17) $\text{Co}_3(\text{PO}_4)_2$, (37) poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO), (38) polypyrrole (39) and ZnO (40) have been adopted by researchers to modify the $\text{Li}_{1+x}\text{V}_3\text{O}_8$ cathode and enhance cycling stability in lithium based batteries. It is generally believed that such surface coatings can alter the electrode-electrolyte chemistry, minimize undesired side reactions, and suppress the increase in charge transfer resistance, thereby improving cycling stability. Amorphous lithium phosphorous oxynitride (LiPON) has been widely studied as a thin-film electrolyte material for solid-state batteries because of its high Li ion conductivity of $\sim 10^{-6} \text{ S}\cdot\text{cm}^{-1}$, low electronic conductivity of $\sim 10^{-14} \text{ S}\cdot\text{cm}^{-1}$ and high voltage stability up to 5.5 V vs. Li metal. (41) LiPON thin films can be prepared by high temperature solid state methods (42) or radio frequency magnetron sputtering of a crystalline Li_3PO_4 target under a N_2 atmosphere. (43) The incorporation of small amounts of nitrogen into the film during the sputtering process enhances Li-ion conductivity and electrochemical stability over films made of pure Li_3PO_4 . (44)

In addition to the application of LiPON in all-solid-state thin film batteries, its potential application as a protective layer in conventional cells which employ liquid electrolytes has been studied in recent years. Due to the electrochemical stability of LiPON (up to 5.5 V vs. Li), LiPON-coated cathode materials can withstand higher voltages compared to uncoated materials. (45-48) For example, LiCoO_2 particles coated LiPON films of $\sim 1 \text{ nm}$ thickness showed significantly improved capacity retention after 40 cycles to 4.4 V compared to uncoated LiCoO_2 particles. (46) Similarly, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials with $\sim 0.6 \text{ nm}$ thick LiPON film delivered much higher capacity with less increase on interfacial resistance upon extended cycling compared to uncoated material when charged to high voltage of 4.9 V. A corresponding reduction in the Mn dissolution was noted with the LiPON-coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials, particularly at higher temperatures. (45) While these prior studies focused on extending the cycling performance for cathodes cycled to higher voltages where electrolyte starts to decompose, our goal here is to examine the benefits of LiPON on moderate voltage cathode materials from the perspective of improving the cycle life, stabilizing the electrode-electrolyte interphase and impeding the dissolution of transition metals. To the best of our knowledge, use of LiPON coating as a protective layer on $\text{Li}_{1+x}\text{V}_3\text{O}_8$ cathode materials has not been previously explored.

In this study, $\text{Li}_{1.1}\text{V}_3\text{O}_8$ active material powders with irregular and regular morphology, prepared at 300 and 550°C, respectively, were coated with LiPON of various thickness, and characterized using x-ray powder diffraction (XRD), inductively coupled plasma optical emission spectrometry

(ICP-OES) scanning electron microscopy (SEM), and transmission electron microscopy (TEM). These materials were then used to prepare electrodes and galvanostatic discharge-charge cycling was conducted in two-electrode cells versus lithium to assess rate capability, and evaluate function under different voltage windows. Electrochemical impedance spectroscopy was performed to evaluate the interfacial resistance after cycling, and the impact of LiPON on the electrochemistry of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ materials of different morphologies was compared. Post mortem, destructive analysis of the lithium anode surfaces was undertaken to quantitatively compare the vanadium deposits on the anode surfaces from the cells constructed with the uncoated and LiPON-coated $\text{Li}_{1.1}\text{V}_3\text{O}_8$ materials. These results will contribute to understanding the impact of LiPON coating on the interfacial chemistry of a moderate voltage electroactive material.

EXPERIMENTAL

Material synthesis

$\text{Li}_{1.1}\text{V}_3\text{O}_8$ synthesis was conducted using a sol-gel method similar to a previously reported procedure.⁽⁴⁹⁾ Stoichiometric amounts of vanadium pentoxide ($\alpha\text{-V}_2\text{O}_5$) and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$), maintaining a Li to V ratio of 1.1 to 3 were used as starting materials. While V_2O_5 was suspended in DI water with stirring, $\text{LiOH}\cdot\text{H}_2\text{O}$ was added to the suspension. The solution was stirred at 50°C under N_2 atmosphere, then freeze-dried and heat-treated at 300 or 550°C to generate the different products, designated as LVO300 and LVO550, respectively.

The LiPON coating was deposited by radio frequency magnetron sputtering while agitating the particles for uniform coating.⁽⁴⁷⁾ The sputtering conditions were generally: 100 RF power, 20mTorr N_2 process gas, ambient temperature, and ≥ 5 cm distance from the sputter target to the powder bed. For each batch, 1 gram of LVO powder was coated. By varying deposition time, three coated samples with different thickness of LiPON were obtained and designated as A, B, C for LVO300 and LVO550, respectively. While the film thickness can be estimated from the deposition rate, the accessible particle surface area, and mass of the LVO powder, here the average thickness was calculated from the experimental BET surface area and ICP analysis for P, Li and V. Detailed chemical analysis for the coated samples will be shown in **Table 1**.

Material characterization

X-ray powder diffraction (XRD) was collected on a Rigaku Miniflex Diffractometer using $\text{Cu K}\alpha$ radiation. Rietveld refinement of LVO300 and LVO550 non-coated materials were performed on GSAS II software. Elemental composition was measured on a Thermo Scientific iCAP 6000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). X-ray photoelectron

spectroscopy (XPS) was performed on a PHI 3056 spectrometer with an Al anode source operated at 15 kV and an applied power of 350 W. Indium was used as a powder support for XPS since the C1s binding energy, from adventitious carbon, was used to calibrate the binding energy shifts of the sample (C1s = 285 eV). Brunauer-Emmett-Teller (BET) surface area was measured on a Quantachrome Nova e3000 Surface Area Analyzer. LiPON film thickness was estimated based on LiPON weight content from ICP-OES results, LiPON density and BET surface area of LVO materials assuming full coverage of the LVO material surface. Scanning electron microscope images (SEM) were measured on a JEOL 7600 Field Emission Scanning Electron Microscope at 10 kV. High resolution transmission electron microscopy (HRTEM) images were acquired on JEOL JEM 2100F and JEOL JEL2011 instruments operating at 200 keV. The presence or absence of the amorphous coating was established by tilting the sample over a wide range of angles (typically 30 degrees); if the sample showed an absence of diffraction contrast at the surface region over the full range of tilts, the LiPON coating was determined to be present. However if at some tilts, diffraction contrast extended all the way to the surface, it was determined that the coating was absent. Since the LiPON coating of LVO300-A and LVO550-A was too thin to be resolved by TEM, the TEM data of these two samples will not be shown. Electron energy loss spectroscopy (EELS) was acquired on the JEOL JEM 2100F.

Preparation of cathodes and cells

To prepare cathodes, mixtures of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ powder (LiPON coated or uncoated), carbon, and polyvinylidene fluoride (PVDF) were dispersed in 1-methyl-2-pyrrolidone (NMP) and casted onto aluminum foil using a doctor blade. Each electrode was $\sim 50\text{ }\mu\text{m}$ in thickness and 1.27 cm in diameter. The loading of active materials was $\sim 4\text{ mg}\cdot\text{cm}^{-2}$. Coin cells were built in an argon-filled glove box using lithium metal anode, two layers of TONEN polypropylene separator and about 0.25 mL of 1 M LiPF_6 in dimethyl carbonate (DMC) and ethylene carbonate (EC) (7:3) electrolyte. Galvanostatic charge-discharge tests were performed on a Maccor battery test system in the voltage ranges of 3.8 - 2.4 V and 3.8 - 2.0 V at 30°C and 50°C using various C rates as described in the below. Electrochemical impedance spectroscopy was measured at 30°C on a BioLogic potentiostat from 1 MHz to 10 mHz.

Results and Discussion

Materials characterization

Figure 1 shows the crystallographic structures of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ and the Li_3PO_4 , the crystalline form of LiPON. The composition of as-synthesized LVO300 and LVO550 powders were both determined to be $\text{Li}_{1.1}\text{V}_3\text{O}_8$ by ICP-OES. Based on the typical composition of LiPON (varies from $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.24}$

to $\text{Li}_{3.6}\text{PO}_{3.3}\text{N}_{0.69}$),(47) the weight content of LiPON in the LiPON-coated materials were determined. LiPON deposition condition, weight content and estimated LiPON thickness of each LiPON-coated sample is tabulated in **Table 1**. Based on deposition conditions (rate, flux, time and powder mass), the film thickness of A, B and C were estimated to be 1, 5 and 10 nm, respectively, for both LVO300 and LVO550 material. The BET surface areas were measured to be 0.74 and 0.71 $\text{m}^2\cdot\text{g}^{-1}$ for LVO300 and LVO550 respectively. The average film thickness is also estimated based on the weight content of LiPON and measured BET surface area of LVO300 and LVO550, **Table 1**. For porous materials such as LVO300, LiPON does not penetrate into the deeper pores of the agglomerates, which results in discrepancy between the estimated and observed film thickness. TEM images which will be shown in **Figure 3** provide more information about the actual film thickness. **Figure 2(a-b)** shows the XRD spectra of LVO300 and LVO550 with different amounts of LiPON coating. LVO550 showed stronger peak intensity and with smaller full width of half maximum intensity (FWHM), indicating higher crystallinity. All diffraction peaks could be assigned to $\text{Li}_{1.1}\text{V}_3\text{O}_8$ phase with a monoclinic structure (PDF#01-073-8145). The LiPON coating process does not change the crystalline structure of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ or introduce new vanadium containing phases.. Rietveld refinement revealed that LVO550 material tends to orient along *b* axis, with a fitted March-Dollase(50) ratio of 1.093, while no preferential orientation was found for LVO300 material. This finding is consistent with the particle shape of LVO300 and LVO550 which will be shown in **Figure 3**.

Electron microscope images of LiPON-coated $\text{Li}_{1.1}\text{V}_3\text{O}_8$ particles are displayed in **Figure 3**. The as-synthesized LVO300 material showed aggregates of irregular blocks without well-recognized boundaries, indicating a small crystallite size and low crystallinity for this material, consistent with the lower temperature used for the heat-treatment (**Figure 3a**). The LiPON coating of LVO300-A and LVO550-A was very thin (less than 1 nm based upon ICP-OES results), and difficult to resolve conclusively by TEM, therefore the TEM images of these samples are not shown. As shown by the TEM images in **Figure 3b-c**, the LVO300-B sample shows an uneven amorphous layer attached onto the surface of the LVO agglomerate, where the thickness values vary typically from 5 to 10 nm. The LiPON film of the LVO300-C appears more continuous with typical thickness 10 to 20 nm on the agglomerates (**Figure 3d**). The as-prepared LVO550 material appears more crystallized with a rod-like shape (**Figure 3e**). The crystals have an estimated size of 1000 nm, 100 nm and 10-100 nm for the three dimensions. The coating on the surfaces of LVO550 particles appear to be more continuous, where about 5 nm thick coating was observed on the LVO550-B sample and about 10-15 nm coating was observed on the LVO550-C sample (**Figure 3f-h**). The observed LiPON film thickness of LVO550 is close to the estimated values in **Table 1**. Compared to the LVO300 materials, LVO550 materials have a smoother surface, and may be free of pores or crevices; consequently the LiPON deposition was more evenly distributed. For LVO300 powders that are particularly porous, however, LiPON

does not penetrate into the deeper pores of the agglomerates. This explained the discrepancy between the observed LiPON thickness and the estimated average values.

X-ray photoelectron spectroscopy (XPS) was used for selected samples to provide further confirmation of the presence of LiPON coating for samples with thinner coating and more irregular morphology, and conformation of retention of the V(V) oxidation state of the parent $\text{Li}_{1.1}\text{V}_3\text{O}_8$ after LiPON coating. XPS was measured using small samples of the powders pressed onto In and load locked from the glove box to the XPS chamber (**Figure 4**). The N1s signal showed clear evidence of the presence of LiPON on the surface of the LVO300-A and LVO300-B materials (**Figure 4a**), where the peak intensity increased as the deposition time increased. The V3p signal (**Figure 4b**), showed no evidence of side bands, and no difference between the uncoated LVO300, LVO300-A and LVO300-B materials, indicating no vanadium oxidation state change resulting from the LiPON deposition.

Electrochemical tests

Discharge-charge cycling of LVO300 Discharge capacities of uncoated, A, B and C of the LVO300 materials cycled at C/10 rate in two different voltage windows (3.8 - 2.4 V and 3.8 - 2.0 V) is shown in **Figure 5(a-b)**. In the voltage window of 3.8 - 2.4 V (**Figure 5a**), the uncoated cell delivered a first discharge capacity of 209 $\text{mAh}\cdot\text{g}^{-1}$ and a second discharge capacity of 243 $\text{mAh}\cdot\text{g}^{-1}$. Capacity of 204 $\text{mAh}\cdot\text{g}^{-1}$ was maintained after 35 cycles. Whereas in the case of LVO300-A, capacity of 248 and 267 $\text{mAh}\cdot\text{g}^{-1}$ was delivered for the first and second discharge, respectively, with 217 $\text{mAh}\cdot\text{g}^{-1}$ maintained after 35 cycles. The B cell showed comparable discharge capacity in the first and several cycles as the A cell, but the capacity fade was more severe than the A. The C cell showed a lower capacity in the initial cycles, however, the capacity gradually increased and the maintained capacity was 223 $\text{mAh}\cdot\text{g}^{-1}$ after 35 cycles. As shown in **Figure 5b**, cycling in the voltage window of 3.8 - 2.0 V, the capacity fade of the uncoated is more severe. Similar trends were observed - the A cell demonstrated better cycling efficiency in the initial cycles, while the C cell showed the highest capacity retention over 35 cycles.

Figure 5(c-d) presents the voltage profiles of Cycle 2 and Cycle 35 of cells cycling from 3.8 to 2.0 V. From **Figure 5c**, the difference in discharge capacity among the four samples can be ascribed to the ~ 2.6 V plateau, where the $\text{Li}_{\sim 3}\text{V}_3\text{O}_8$ and $\text{Li}_4\text{V}_3\text{O}_8$ phase coexist, with a decrease in lattice parameter a and an expansion in b to accommodate the intercalating Li ions.(51, 52) The A cell clearly displayed a longer 2.6 V plateau on Cycle 2. After 35 cycles, the 2.6 V plateau disappeared for the uncoated cell as a result of structural degradation and increased cell resistance. The C cell showed the longest 2.6 V plateau with less polarization observed from the charge curve, which is an indication of better electrochemical stability and structural integrity.

Rate capability and cycling stability of LVO300 and LVO550 The investigation of electrochemical behavior of cathode materials at elevated temperature is of great importance for applications of lithium-ion batteries in wider temperature range. Despite the extensive study of $\text{Li}_{1-x}\text{V}_3\text{O}_8$ materials at room temperature, study of this material at higher temperatures has been rare to date. A rate capability study was performed on LVO300 and LVO550 at 30 and 50°C, respectively, as shown in **Figure 6**. For the LVO300 materials (**Figure 6a-b**), the LVO300-C containing cell with thick LiPON coating demonstrated improved cycling efficiency at C/2, 1C and 2C rate relative to the other three samples. At 50°C, 50-100 $\text{mAh}\cdot\text{g}^{-1}$ more capacity was delivered at C/2, 1C and 2C rates with 50 $\text{mAh}\cdot\text{g}^{-1}$ by the LVO300-C containing cell with improved capacity retention on Cycle 50 compared to the uncoated LVO300 containing cell. Shown in **Figure 6c-d**, the LVO550 materials showed less fade in each C rate step compared to LVO300 materials, indicating improved stability of LVO materials prepared at higher temperature. Different from the LVO300 materials where thicker LiPON was more advantageous in capacity retention, the thinner LiPON coating in LVO550-A was more beneficial. This result is consistent with some of the findings from prior studies of other materials – thinner LiPON coating allows sufficient electron transfer while minimizing side-reactions, and thicker LiPON blocks electron transfer and jeopardizes the rate capability.(45)

LVO300 and LVO550 materials were cycled at 2C at both 30 and 50°C to evaluate their stability after extended cycling at a higher current, **Figure 7**. For the LVO300 materials (**Figure 7a-b**), the LiPON-coated materials showed $\sim 100 \text{ mAh}\cdot\text{g}^{-1}$ more delivered capacity on the initial discharge compared to the non-coated material. Notably, the cycling stability was dramatically improved with the presence of LiPON, especially with the thicker LiPON coating of the LVO300-C material. The difference in cycling stability between the LVO300-uncoated cell and LVO300-C cell at 50 °C was striking – the capacity of the uncoated cell deteriorated rapidly in the first several cycles, where the LVO300-C containing cell maintained more than twice of the capacity of the uncoated after 50 cycles. The LVO550 materials (**Figure 7c-d**) demonstrated better capacity retention relative to the LVO300 series. The LVO550-A containing cell showed improved cycling efficiency relative to the LVO550 uncoated material, but the improvement in the presence of LiPON was not as significant as that for the corresponding LVO300 materials. Notably, the LVO550-B materials with moderate LiPON coating did not show further improvement relative to the LVO550-A material with thin LiPON coating, and the LVO550-C with thick LiPON showed more significant fade.

The discharge profiles of LVO300 and LVO550 cycled at 2C provide insights into the effects of LiPON on the two different materials, **Figure 8**. Similar curve shapes were observed for the materials cycled at 30 and 50°C, indicating similar reaction mechanisms. Compared to the corresponding LiPON-coated samples, the uncoated LVO300 material showed more sloping discharge/charge curves, indicating more electrode polarization, **Figure 8a**. After 50 cycles, the

LVO300-C maintained the voltage shape better than the other three samples and showed less polarization, **Figure 8b**, consistent with the impedance results discussed below. For the LVO550 materials, the four samples displayed very similar curve shapes both on the initial discharge cycles, **Figure 8c**, and after extended cycling, **Figure 8d**.

The thicker LiPON coating (LVO300-C) was the most beneficial in improving the cycling stability and rate capability for the $\text{Li}_{1.1}\text{V}_3\text{O}_8$ material prepared at lower temperature (LVO300). This could be attributed to the more effective coverage of particle/agglomerate surface of the porous LVO300 material, as witnessed by TEM images. Ineffective coverage of LiPON on the cathode particles may give rise to inadequate protection from undesired electrode/electrolyte side reactions. Higher temperature usually causes the side reactions and electrolyte decomposition to happen faster so the electrode degrades faster. The LVO300-C substantially improved cycling stability by suppression of side reactions and the alleviation of electrode polarization, as well as the protection on structural integrity by LiPON. As a comparison, the thinner LiPON of LVO550-A was proven to be the most effective in enhancing the cycling efficiency for the LVO550. As LVO550 has a more regular shape and smoother surface, more continuous coverage could be achieved by LiPON coating. As mentioned before, LiPON has low electronic conductivity. LiPON films applied to the cathode $\text{Li}_{1.1}\text{V}_3\text{O}_8$ powders could contribute to increased resistance and therefore reduce delivered capacity.^{20,21} The data suggested that the thinner LiPON of LVO550-A allows sufficient electron transfer and is the most effective in maximizing the cycling efficiency by suppression of side reactions and stabilization of electrode-electrolyte interphase. As the LiPON layer grows thicker, more electron transfer pathways are blocked. Thus, the LVO550-B and C samples have lower initial discharge capacity.

Post-cycling characterization

Electrochemical Impedance Spectroscopy EIS spectra of LVO300 and LVO550 after cycling at 2C are displayed in **Figure 9**. All the spectra were fitted with the equivalent circuit model in **Figure 9a**.

In the equivalent model, R_s represents the solution resistance; R_{sl} and CPE1 represents the resistance of Li^+ migration through a surface-passivating layer at high frequency and non-ideal surface capacitance, respectively; R_{ct} and CPE2 represents the resistance of charge transfer at electrolyte/electrode interphase at high-to-medium frequency and its non-ideal capacitance, respectively; and W_0 represents the Warburg element which is related to the diffusion of Li^+ ions in the bulk electrode.^(35, 53-57) The fitting results are tabulated in **Table 2**.

The R_{ct} of LiPON-coated samples of LVO300 are significantly lower than the LVO300-uncoated sample, this is in good agreement with the cycling results shown above. And this illustrated with that with the presence of LiPON, the growth of the detrimental electrode/electrolyte

interphase could be effectively impeded by minimizing side reactions. The R_{ct} of LVO550-A is slightly lower than the other LVO550 samples, which is also consistent with the electrochemistry of LVO550 materials.

Vanadium deposition on Li anodes The amount of vanadium deposition on Li anodes of the LVO300 and LVO550 after cycling at 2C was analyzed quantitatively by ICP-OES, and the results are shown in **Figure 10**. For both LVO300 and LVO550 samples, cycling at elevated temperature of 50 °C led to higher vanadium dissolution than cycling at 30 °C. And LVO300 showed higher vanadium dissolution than LVO550, which is due to the poorer crystallinity, as reported previously.⁽¹⁹⁾ The data of LVO300 suggests that the LiPON coating inhibits the vanadium dissolution process, and the effect of LiPON is more significant at 30 °C. However, the barrier effect of LiPON for LVO300 at 50 °C and for LVO550 is marginal.

EELS of LiPON coating EELS spectra were collected on the coating and bulk of the LVO550-C sample before and after 2C cycling for 50 cycles, respectively, as shown in **Figure 11**. The V-L₃ and V-L₂ edge appear at 515 and 521 eV in the spectrum, respectively. The peak at 539 eV corresponds to O-K edge.⁽⁵⁸⁾ The oxygen 2p states hybridize with the 3d states of vanadium in vanadium oxides where the vanadium has the valence of 5⁺, and split in the ligand field into two states, therefore there is another O-K peak at 528 eV with the presence of V-L peaks.⁽⁵⁸⁾ It is clearly seen that the LiPON coating before cycling does not contain vanadium, and vanadium was detected in or on the coating after cycling, **Figure 11b** and **11d**. This result indicates that the vanadium in the Li_{1.1}V₃O₈ bulk can either migrate into the LiPON coating during cycling, or perhaps dissolved V is deposited onto the LiPON from the electrolyte solution. This helps to rationalize the reduced R_{ct} of LiPON-coated samples after cycling, as LiPON itself is insulating and adds to interfacial resistance. The vanadium found in the LiPON coating also explained the limited protective effect of LiPON from vanadium dissolution after cycling. Vanadium dissolution might be hindered under certain conditions, as in the case of LVO300 cycled at 30 °C, but the EELS data indicate that vanadium can migrate through the LiPON layer.

Conclusion

For the first time LiPON-coated Li_{1.1}V₃O₈ powders were prepared and the impact of LiPON on the electrochemistry of liquid electrolyte containing Li/Li_{1.1}V₃O₈ cells was systematically investigated. Heat-treatment temperature during the Li_{1.1}V₃O₈ synthesis could significantly influence the morphology and crystallinity of the material, allowing the impact of LiPON coating on the Li_{1.1}V₃O₈ materials of two different morphologies to be compared. The LiPON layer could generally enable the Li_{1.1}V₃O₈ cathode particles to deliver higher capacity with better capacity retention by acting as a protective layer and reducing electrode-electrolyte side reactions. The thicker LiPON coating of LVO300-C was more favorable for the electrochemistry of LVO300 material, likely due to the more effective coverage on the particle/agglomerate surface. The

improvement by the LVO300-C coating was more remarkable at elevated temperature (50 °C) due to the stabilization of the electrode - electrolyte interphase in the presence of LiPON. However, for the rod-shaped LVO550 materials where LiPON deposition was more continuous, thinner coating of LVO550-A was more effective in enhancing the cycling efficiency. Thicker coating of B and C resulted in additional interfacial resistance due to the insulative nature of LiPON. Post-cycling EIS scans revealed that the presence of LiPON could reduce interfacial resistance by preventing unfavorable electrode-electrolyte side reactions. EELS data proved the presence of vanadium in or on the LiPON layer after cycling, which explained the reduced interfacial resistance with LiPON-coated samples after cycling and validated the vanadium dissolution results.

It is acknowledged that a stable electrode-electrolyte interphase with lower polarization is critical for the cathode material to realize high capacity and good capacity retention. The cycling of cathode materials with coatings is a complex process where multiple characterization techniques are needed to understand the mechanism. With a systematic study of coating thickness, role of material morphology, and related electrochemical characteristics, we shed light on how the LiPON affects electrochemical behavior and interfacial stability, and provided insight for future research probing the LiPON-Li_{1.1}V₃O₈ system in particular and other solid electrolyte-electroactive composite materials in general.

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Figure 1 Crystallographic structures of (a) $\text{Li}_{1+x}\text{V}_3\text{O}_8$ and (b) Li_3PO_4

Table1 LiPON deposition condition and elemental analysis result of LiPON-coated samples

LVO300					LVO550				
Sample	LiPON deposition time (h)	LiPON weight content (%)	Estimated LiPON thickness based on surface area (nm)	Estimated LiPON thickness based on deposition condition(nm)	Sample	LiPON deposition time (h)	LiPON weight content (%)	Estimated LiPON thickness based on surface area (nm)	Estimated LiPON thickness based on deposition condition(nm)
A	1.7	0.06	0.3	1	A	1.5	0.15	0.9	1
B	7.0	0.24	1.3	5	B	6.5	0.69	3.9	5
C	23.0	1.08	5.8	10	C	16.5	2.63	15	10

Figure 2 (a) XRD spectra of the LVO300-uncoated, A, B and C materials with reference pattern (PDF# 01-073-8145); (b) XRD spectra of the LVO550-uncoated, A, B and C materials with reference pattern (PDF# 01-073-8145); (c) Rietveld refinement of LVO300 ($R_{wp} = 8.86\%$); (d) Rietveld refinement of LVO550 ($R_{wp} = 8.83\%$).

Figure 3 (a) SEM image of LVO300-uncoated; (b) TEM image of LVO300-B; (c) TEM image of LVO300-B; (d) TEM image of LVO300-C; (e) SEM image of LVO550-uncoated; (f) TEM image of LVO550-B; (g) TEM image of LVO550-B; (h) TEM image of LVO550-C.

Figure 4. XPS spectra of (a) N1s and (b) V3p emission of LVO300-uncoated, LVO300-A, and LVO300-B powder samples.

Figure 5 Discharge capacity versus cycle number of cells with LVO300 materials cycled at 30 °C at C/10 rate (a) in the voltage range of 3.8-2.4 V and (b) in the voltage range of 3.8-2.0 V. Discharge profiles of LVO300 of (c) Cycle 2 and (d) Cycle 50 in the voltage range of 3.8-2.0 V at C/10.

Figure 6 Discharge capacity versus cycle number of LVO300 and LVO550 materials cycled at various C rates in the voltage range of 3.8-2.0 V (a) LVO300 at 30°C; (b) LVO300 at 50°C; (c) LVO550 at 30°C; (d) LVO550 at 50°C.

Figure 7 Discharge capacity versus cycle number of LVO300 and LVO550 materials cycled at 2C in the voltage range of 3.8-2.0 V (a) LVO300 at 30 °C; (b) LVO300 at 50 °C; (c) LVO550 at 30°C; (d) LVO550 at 50°C.

Figure 8 Discharge profiles of LVO300 and LVO550 materials of Cycle 2 and 50 at 2C cycling at 30 °C. (a) Cycle 2 of LVO300; (b) Cycle 50 of LVO300; (c) Cycle 2 of LVO550 and (d) Cycle 50 of LVO550.

(a) Equivalent Circuit

Figure 9 (a) Equivalent circuit; (b) LVO300 after cycling in the voltage range of 3.8-2.0 V at 2C rate for 50 cycles; (c) LVO550 after cycling in the voltage range of 3.8-2.0 V at 2C rate for 50 cycles.

Table 2 EIS fitting results

	R _{sl} (Ω)				R _{ct} (Ω)			
	uncoated	A	B	C	uncoated	A	B	C
(b)LVO300	18.3 $\pm$ 3.9	14.1 $\pm$ 0.6	13.0 $\pm$ 0.6	11.3 $\pm$ 0.3	48.2 $\pm$ 1.2	14.8 $\pm$ 3.1	13.9 $\pm$ 2.9	12.3 $\pm$ 2.9
(c)LVO550	5.5 $\pm$ 1.5	7.2 $\pm$ 2.1	3.7 $\pm$ 0.5	6.9 $\pm$ 3.0	65.7 $\pm$ 2.0	50.8 $\pm$ 2.5	58.9 $\pm$ 0.5	82.9 $\pm$ 3.9

Figure 10 Vanadium concentration measured on Li anodes recovered from Li/Li_{1.1}V₃O₈ electrochemical cells containing LiPON-coated and uncoated LVO300 and LVO550 powders after cycling at 2C for 50 cycles at 30 and 50°C. (a) LVO300 and (b) LVO550.

Figure 11 (a) HRTEM image and (b) EEL spectrum of the coating and the bulk of the LVO550-C sample before cycling; (c) HRTEM image and (d) EEL spectrum of the coating and the bulk of the LVO550-C sample after cycling at 2C. The red and black circles in (a) and (c) indicate where each spectrum was collected.

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