Reduction of Charge-Transfer Resistance at the Solid Electrolyte – Electrode Interface by Pulsed Laser Deposition of Films from a Crystalline $\text{Li}_2\text{PO}_2\text{N}$ Source

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ABSTRACT

Amorphous films deposited by pulsed laser deposition from a crystalline $\text{Li}_2\text{PO}_2\text{N}$ in a N_2 ambient atmosphere (LiPON-PLD) have been examined as an approach to reduce the charge-transfer resistance at the electrode-solid electrolyte interface. Despite the relatively low ionic conductivity of $1.5 \times 10^{-8} \text{ Scm}^{-1}$ ca. at 25°C , the amorphous LiPON-PLD films deposited between a $\text{LiMn}_{1.485}\text{Ni}_{0.45}\text{Cr}_{0.05}\text{O}_4$ (LNM) cathode and LiPON electrolyte resulted in sharply improved electrochemical performance in terms of charge-transfer resistance and CV profiles. Cells without a LiPON-PLD film had a charge-transfer resistance of $4470 \Omega\text{-cm}^2$ compared to 760 and $960 \Omega\text{-cm}^2$ for the sample with 17 nm and 31 nm thick LiPON-PLD films, respectively. The LiPON-PLD amorphous films show no evidence of the continuous planar -P-N-P-N- backbone characteristic of the crystalline target material, but compared with LiPON prepared from radio frequency magnetron sputtering with Li_3PO_4 in a N_2 atmosphere, the LiPON-PLD films were composed of a higher amount of triply coordinated $\text{P} - \text{N} < \text{P}$ with relatively lower contributions of $\text{P}-\text{N}=\text{P}$.

INTRODUCTION

Towards the goal of increasing the specific energy of solid-state and conventional liquid electrolyte lithium ion battery cells, alternative higher voltage cathode materials have been examined from a wide range of compounds that include LiCoPO_4 , $\text{Li}_2\text{CoPO}_4\text{F}$, LiNiPO_4 , $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M}=\text{Mn}, \text{Ni}, \text{Co}$), $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{MxO}_4$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}, \text{ and Ga}$), LiCoMnO_4 among others.^{1,2,3,4,5,6,7} However, cathodes with desirable high operating voltage typically suffer from undesirable anodic oxidation of the electrolytic solvents at the cathode/electrolyte interface. This oxidation of the solvent, if unchecked, can result in a

passive film growth with a concomitant decrease in the specific power of the electrode. In solid-state Li battery cells, this is typically not an issue due to the absence of organic solvents, though in some cases such as the $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{M}_x\text{O}_4$ (LNM) cathode – LiPON interface, an unusually high charge-transfer resistance is observed at voltages associated with the $\text{Ni}^{+2}/\text{Ni}^{+4}$ redox couple near 4.7V. This resistance can be several orders of magnitude or greater than that observed for the 4V-class of cathodes (e.g. LiCoO_2).⁸ Furthermore, crystalline solid electrolytes (e.g. cubic lithium lanthanum zirconium oxide (LLZO)) and most commonly used cathodes (e.g. $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$) will have crystallographic mismatch at the interface that can result in an additional resistance term. An amorphous Li^+ conductive film could serve as a buffer to allow for rapid Li^+ transport between the cathode and electrolyte grains.

In both solid-state lithium cells and conventional Li-ion cells, non-transition metal oxides, fluorides, or phosphates have been widely examined as a passive interlayer between the cathode and electrolyte.⁹ Ideally, this passive film should have high Li^+ conductivity to facilitate fast charge transfer kinetics between the cathode and electrolyte and prevent anodic oxidation of the bulk electrolyte. Thin films of lithium phosphate (e.g. Li_3PO_4 and $\text{Li}_4\text{P}_2\text{O}_7$) are promising candidates for cathode passivation films since they have good oxidative stability albeit with modest ionic conductivity at room temperature relative to non-Li bearing materials such as AlPO_4 . These lithium phosphate films have been shown to reduce interfacial impedance at both liquid electrolyte-solid electrode interfaces as well as for solid electrolyte-solid electrode interfaces.^{10,11} However, these films are prone to deleterious re-crystallization causing point contacts at the electrode-solid electrolyte interface, and have ionic conductivities roughly four orders of magnitude lower than state-of-art fast Li^+ ion conductors such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO).¹² It is expected that by both limiting re-crystallization and increasing the

Li^+ conductivity, thin amorphous films based on lithium phosphorus oxynitride could serve to further reduce the interfacial impedance.

It has been shown that substitution of N for O in Li_3PO_4 results in improved ionic conductivity and electrochemical stability, as well as the increase in devitrification temperature.¹³ The latter property is particularly desirable since amorphous solid electrolytes are usually (but not always) more ionically conductive than crystalline solid electrolytes.¹⁴ As noted above, while N-rich lithium phosphate films (LiPON) prepared by radio frequency (RF) magnetron sputtering are amorphous with good conductivity, when deposited directly on the LNM cathode result in an unusually high impedance electrode/electrolyte interface. In contrast, pulsed laser deposition (PLD) of lithium phosphate films present lower interfacial impedance than RF sputtered LiPON films,¹⁵ yet incorporation of N_2 into lithium phosphate films with PLD (by way of deposition in a N_2 ambient) is difficult given the very strong triple bond for N_2 and poor surface adsorption of N_2 onto the PLD target.^{16,17}

One approach to increasing the N content of PLD-deposited lithium phosphate thin films is to start with a N-rich PLD target. Recently, the modelling and synthesis of a crystalline high N-content lithium phosphate-based compound, $\text{Li}_2\text{PO}_2\text{N}$, was reported.¹⁸ This compound is chemically stable even at high temperatures, making it an ideal target material for PLD processing. In this article, we report the preparation by PLD of thin films in a N_2 ambient from a crystalline $\text{Li}_2\text{PO}_2\text{N}$ target. These amorphous thin films, when deposited between an LNM cathode and the RF magnetron sputtered LiPON electrolyte interface, resulted in sharply reduced charge-transfer resistance and improved electrochemical kinetics. We discuss the film structure and chemistry characterized by a number of different analytical techniques.

EXPERIMENTAL

Synthesis of Crystalline Li₂PO₂N

The Li₂PO₂N microcrystalline powder was synthesized using a previously reported solid-state reaction.¹⁷

The precursors, 1.0000 g Li₂O (33.467 mmol, Alfa Aesar, 99.5%), 0.9501 g P₂O₅ (6.693 mmol, Sigma Aldrich, 99.999%) and 1.3634 g P₃N₅ (8.3667 mmol, received as a gift from Tianyu Chemical Co., Ltd. Zhejiang, China, >99% purity with Mn ≤ 0.001%, Mg ≤ 0.005%, Cu ≤ 0.0001%, Fe ≤ 0.001%, and Si ≤ 0.01), were ground for 30 minutes in an agate mortar in an argon-filled glove box. The mixture was transferred to a quartz tube (6 inches in length and 0.5 inch in diameter) and evacuated for 45 minutes prior to sealing. The mixture was heated to 950°C for 10 hours with a ramp up/down rate of 100°C hour⁻¹. After this first heat treatment, the tube was opened and the product was ground for 30 minutes in an argon-filled glove box, then transferred to another quartz tube with approximately same dimensions and heated to 950°C for an additional 10 hours using the same temperature program. The final microcrystalline product was ball-milled using Y-ZrO₂ ball-milling media in a HDPE vial in a ratio of 1:25 (Li₂PO₂N: ball-milling media). Analysis using Powder X-ray diffraction (PXRD) shows that the ball-milling media and Li₂PO₂N do not react.

Characterization of the Powder and Pellets

A PANalytical X'Pert Pro Powder Diffractometer equipped with a Ni-filtered Cu K_α radiation (λ = 1.5418 Å) was used for phase identification. PXRD patterns were collected at room temperature, and High Score Plus, a software package supplied by PANalytical, was used to complete Rietveld refinement and structural analysis. PXRD data were collected at room

temperature. A Zeiss[®] Merlin SEM was used to collect all scanning electron microscopy (SEM) images of the bulk $\text{Li}_2\text{PO}_2\text{N}$ material at 3.0kV. Prior to collecting SEM images, all samples were placed on carbon conductive tape. Thermogravimetric analysis (TGA) was collected under argon with a flow rate of 10 L min^{-1} and a heating rate of $10^\circ\text{C min}^{-1}$ using TA Instruments SDT Q600 Simultaneous TGA/DSC instrument. Electrochemical Impedance Spectroscopy (EIS) measurements were performed on $0.5''$ diameter pellets of $\text{Li}_2\text{PO}_2\text{N}$ that were cold-pressed at 300 MPa, using Al/C blocking electrodes and sealed inside a pressurized cell. Impedance measurements were obtained using a Solartron SI 1260 Impedance Gain-Phase Analyzer from 1MHz – 1 Hz with 100.0 mV amplitude. Activation energies were determined from the plot of conductivity vs. T^{-1} (fitted by the Arrhenius equation) using a Maccor 4300 System Environmental Chamber with a temperature range from 25 to 100°C . For the preparation of $\text{Li}_2\text{PO}_2\text{N}$ PLD target, 776mg of ball-milled $\text{Li}_2\text{PO}_2\text{N}$ were cold-pressed at 300 MPa to form a $1''$ pellet. Ball-milling $\text{Li}_2\text{PO}_2\text{N}$ allowed for the fabrication of a dense PLD target, achieving $> 75\%$ of the theoretical density (2.63 g cm^{-3}).

Preparation of thin films

Thin films were prepared at room temperature by pulsed laser deposition (PLD) onto silica substrates from the $\text{Li}_2\text{PO}_2\text{N}$ pellet. The light source was a fifth-harmonic neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (213 nm; LOTIS TII LS-2137/4-BBO) with power density of $6.25 - 7.5 \text{ W cm}^{-2}$ and fixed repetition frequency of 10 Hz. The deposition was carried out under a flow of N_2 gas at a pressure inside the chamber of 1 Pa.

Characterization of thin films

In order to better ascertain the crystallinity of the as-deposited films, synchrotron X-ray diffraction was employed for high counting statistics necessitated by the thin films. These

measurements were performed at the Aichi Synchrotron Radiation Center, beamline 8S1 ($\lambda=1.35320$ Å). SEM micrographs were collected with a Hitachi SU8030 at an accelerating voltage of 10 kV. Impedance measurements were performed by depositing thin films on interdigitated Pt electrodes (BAS, IDA-Pt 2 μm) and connecting with a microprobe to an Agilent 4294A impedance analyzer from 110 MHz - 20 Hz, 20 mV excitation. Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy measurements were performed on a Jasco 6200 FTIR system and a Jasco NRS-5100M Raman spectrometer (laser $\lambda = 532$ nm), respectively. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Versa Probe II (Ulvac-Phi) equipped with an Al K α -focused X-ray source. The incident angle of X-rays and take-off angle of photoelectrons were fixed at 90° and 45°, respectively. The incident angles of the monomer Ar ion beam and GCIB were 33° and 55°, respectively. After deposition in a glove box, all samples were transferred under vacuum and had no air exposure before loading into the XPS system.

Binding energies were corrected for instrument offsets by assuming adventitious C at 285 eV. The XPS measurements were obtained on samples prepared and transferred by load lock under argon. Surface measurements as well as measurements following sequential ca. 10 nm deep Ar⁺ etching steps were obtained.

Full cell fabrication and testing

All solid-state cells were fabricated by depositing cathode films of LiMn_{1.485}Ni_{0.45}Cr_{0.05}O₄ (LNM) onto Ti/Pt coated silica substrates by PLD from a target of Li_{1.5}Mn_{1.485}Ni_{0.45}Cr_{0.05}O₄ with a thickness of ca. 30 nm. In some cases the LNM cathodes were coated with a thin film (ca. 10-50 nm) by PLD deposition from Li₂PO₂N target. Thicknesses of these films were estimated based on calibration depositions of much thicker films measured by

surface profilometry. After deposition of these layers, a film of LiPON was deposited by RF magnetron sputtering from a Li_3PO_4 target at a power density of 1.1 W cm^{-2} at 4 Pa N_2 followed by Li anode film deposition by thermal evaporation of Li foil. Typical electrolyte and anode film thickness were $4 \mu\text{m}$ and $1 \mu\text{m}$, respectively. The full cells were tested by cyclic voltammetry at 1 mV s^{-1} from 3-5V, and by electrochemical impedance spectroscopy (EIS) at various potentiostatic conditions using 20 mV excitation from 200 kHz – 10 mHz. Cells were held potentiostatically for 1 hour before commencing EIS measurements.

Results:

Properties of the $\text{Li}_2\text{PO}_2\text{N}$ target

X-ray diffraction measurements confirmed that the $\text{Li}_2\text{PO}_2\text{N}$ powder used for the PLD target crystallized in the orthorhombic space group $\text{Cmc}2_1$ (# 36) with lattice constants $a = 9.0712(4) \text{ \AA}$, $b = 5.4025(7) \text{ \AA}$, and $c = 4.6940(8) \text{ \AA}$ (Figure 3a). This result matched previous reports for crystalline $\text{Li}_2\text{PO}_2\text{N}$, where the crystal structure consists of parallel arrangements of anionic $\{\text{PO}_2\text{N}\}^{2-}$ chains formed of corner sharing (PO_2N_2) tetrahedra.¹⁷ The thermal stability of the $\text{Li}_2\text{PO}_2\text{N}$ powder was verified by TGA to 900°C in Ar (Supplementary Fig. S1).

Structural properties of the amorphous LiPON-PLD film

As discussed in detail below, the composition of the thin films prepared by PLD in N_2 from a crystalline $\text{Li}_2\text{PO}_2\text{N}$ target in N_2 differ somewhat in stoichiometry from the target material. Hereafter, we refer to these films by the acronym “LiPON-PLD” to distinguish them from RF sputtered LiPON or PLD-deposited Li_3PO_4 (LPO) films. The LiPON-PLD films were fully amorphous, with only reflections associated with the Pt underlayer film detected by S-XRD (Figure 3b).

The morphology of thin films prepared by PLD from ceramic targets is often highly dependent on the target conditions. A low density, porous target can result in target spallation rather than ablation and subsequent deposition of a low-density porous film. In our studies, we found that ball milling and cold pressing the as-prepared $\text{Li}_2\text{PO}_2\text{N}$ powder resulted in a dense, well-adhered pellet highly suitable for PLD deposition (Figure 1). Similarly, the morphology of the film can depend on deposition pressure and laser type. For example, as reported by others, a lithium phosphate film deposited by PLD in N_2 ambient atmosphere using the 3rd harmonic of a Nd:YAG laser resulted in relatively porous and rough films.¹⁹ In contrast, for our studies we found that films deposited in N_2 from the $\text{Li}_2\text{PO}_2\text{N}$ target using the 5th harmonic of a Nd:YAG laser in this work resulted in dense, smooth films as shown in Figure 2.

Electrochemical properties of LiPON-PLD films

The ionic conductivity of the amorphous LiPON-PLD films was superior to that of the crystalline $\text{Li}_2\text{PO}_2\text{N}$ target within the measured temperature range of 45-100°C as shown in Figure 4, with an extrapolated room temperature ionic conductivity of the thin film estimated at $1.5 \times 10^{-8} \text{ S cm}^{-1}$ and activation energy of 0.68 eV. The higher conductivity of the amorphous thin film relative to the crystalline parent material may be partially explained by the general trend that crystallized conductors have decreased free volumes available for alkali ion conduction relative to the glassy state, and this in turn leads to a decreased ionic conductivity.²⁰

It is interesting that despite the low ionic conductivity of LiPON-PLD films (relative to RF sputtered LiPON films at ca. $2 \times 10^{-6} \text{ S cm}^{-1}$), interposing a thin film of LiPON-PLD between the LNM cathode and LiPON electrolyte resulted in sharply improved electrochemical performance. Figure 5a shows the CV scans of cells fabricated with 31 nm and 17 nm thick LiPON-PLD films deposited between the cathode and LiPON electrolyte, and a cell without a

LiPON-PLD film. The cell without any LiPON-PLD between the cathode and LiPON electrolyte had no well-defined redox peaks associated with the $\text{Ni}^{+2/+4}$ couple expected at about 4.7V. Instead, the CV showed a broad, poorly defined oxidation wave between ca. 4.3 - 5.0V, and a polarized conjugate reduction wave from 5.0 - 4.2V, with the $\text{Mn}^{+3/+4}$ oxidation peak centered at 4.17V. In contrast, cells with aLiPON-PLD film between the cathode and LiPON electrolyte presented well defined oxidation peaks at 4.74V and 4.83V and reduction peaks at 4.52V and 4.59V. The $\text{Mn}^{+3/+4}$ oxidation peak was much less polarized for these two cells, appearing at 210 mV lower voltage than cells with no LiPON-PLD film. The observation of distinct and predicted $\text{Ni}^{4+/2+}$ redox peaks in the cells with the LiPON-PLD interlayers suggests that this film likely improves the electrochemical stability of the interface.

Similarly, the impedance spectra for cells with LiPON-PLD films between the cathode and LiPON electrolyte indicate significant improvement relative to cells without the LiPON-PLD film. Figure 5b shows the EIS spectra collected at 4.7V, with the inset showing the high frequency low impedance range of the spectra. The high frequency relaxation observed in the inset was assigned to the solution resistance and capacitance of the LiPON electrolyte. The lower frequency x-axis intercept of this relaxation, taken as the area-specific resistance of the electrolyte, was approximately the same for all cells (ca. $160\Omega\text{-cm}^2$) regardless of the presence or absence of the LiPON-PLD layer. The mid-frequency relaxation was assigned to the charge-transfer resistance and double layer capacitance. The lower frequency x-axis intercept was estimated as the sum of the charge-transfer resistance and solution resistance. Clearly, the LiPON-PLD film sharply reduced charge-transfer resistance. The sample without the LiPON-PLD film had a charge-transfer resistance of $4470\Omega\text{-cm}^2$ compared to 760 and $960\Omega\text{-cm}^2$ for the sample with 17 nm and 31nm thick LiPON-PLD films, respectively. To better understand the

remarkable improvement in electrochemical kinetics observed for cells with a LiPON-PLD film between the cathode and electrolyte layers, further study of the chemistry of the LiPON-PLD films was warranted.

Chemical properties of LiPON-PLD thin films

The chemical composition of LiPON-PLD thin films prepared by PLD of a $\text{Li}_2\text{PO}_2\text{N}$ target in N_2 atmosphere was elucidated by a number of techniques including Rutherford Backscattering Spectrometry (RBS), inductively coupled plasma mass spectrometry (ICP-MS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

The $\text{Li}_2\text{PO}_2\text{N}$ precursor is composed of infinite planar -P-N-P-N- chains that show high crystallinity and stability in air.¹⁷ Upon PLD under 1 Pa N_2 atmosphere, the stoichiometry of the resultant LiPON-PLD thin films was estimated from RBS and ICP-MS measurements to be $\text{Li}_{1.69}\text{PO}_{2.86}\text{N}_{0.32}$, which is notably Li- and N- poor relative to the $\text{Li}_2\text{PO}_2\text{N}$ target likely due to volatilization of Li-N species during deposition. It is commonly observed that Li-bearing films deposited by PLD are Li-poor,²¹ which can be mitigated by increasing the Li concentration in the target.²² As a basis of comparison, a LiPON thin film from RF magnetron sputtering of a Li_3PO_4 target in 4 Pa N_2 was also prepared and the stoichiometry was determined using the same techniques. The resultant film composition determined by RBS and ICP-MS yielded a composition $\text{Li}_{3.44}\text{PO}_{3.86}\text{N}_{0.24}$. This LiPON film composition corresponds closely to reported literature values,^{23,24,25} suggesting the RBS/ICP-MS values for both films were reasonable.

The LiPON-PLD film has a larger amount of nitrogen per phosphorus in the thin film as determined by the chemical composition analysis. Figure 6 displays FTIR spectra for a LiPON

thin film (prepared from RF magnetron sputtering of Li_3PO_4 in N_2) and a LiPON-PLD thin film (prepared from PLD of $\text{Li}_2\text{PO}_2\text{N}$ in N_2). Both spectra share stretches at $925\text{-}950\text{ cm}^{-1}$ and $1025\text{-}1050\text{ cm}^{-1}$, which correspond to P-O stretching of the amorphous LiPON thin films. However, an extra mode at 1080 cm^{-1} appears in the FTIR spectrum of LiPON-PLD film when compared to the LiPON film. This extra mode corresponds to P-N stretching in the thin film. In contrast, crystalline $\text{Li}_2\text{PO}_2\text{N}$ has P-N vibrations that occur at 669, 698, 850, 1055, and 1115 cm^{-1} .¹⁷ After PLD, the amorphous thin films made from crystalline $\text{Li}_2\text{PO}_2\text{N}$ only show P-N vibrations around 1055 and 1115 cm^{-1} . The LiPON-PLD thin films do not show vibrations at $600\text{-}875\text{ cm}^{-1}$, which indicates that the planar -P-N-P-N- backbone characteristic of crystalline $\text{Li}_2\text{PO}_2\text{N}$ becomes fragmented, producing an amorphous film without infinite chains.

Raman spectroscopy and XPS support the loss of linear -P-N-P-N- chains when $\text{Li}_2\text{PO}_2\text{N}$ is deposited using PLD. Figure 6b shows the Raman spectrum for LiPON-PLD film where well-defined phosphate stretches appear at $750\text{ cm}^{-1} \nu_s$ (P-O-P), $952\text{ cm}^{-1} \nu_l$ (PO_4), $1000\text{ cm}^{-1} \nu_{as}$ (PO_4), $1036\text{ cm}^{-1} \nu_3$ (PO_4), agreeing with previous literature.^{15,16,26} Also, the Raman spectrum shows stretching at 1275 and 1375 cm^{-1} which correspond to N-O and O-N=O symmetric stretching, respectively. Interestingly, a stretch at 809 cm^{-1} appears in the Raman spectrum, which corresponds to P-N=P stretching and triply coordinated P – N $<^{\text{P}}_{\text{P}}$.^{27,28}

XPS further elucidates the bonding in both LiPON-PLD and LiPON films (Figure 7). After etching the surface by ca. 20 nm, deconvoluted XPS data demonstrate that LiPON-PLD thin films are dominated by triply coordinated P – N $<^{\text{P}}_{\text{P}}$ with relatively lower contributions of P-N=P. As the film was etched, an increasing amount of O-N=O was present, evidencing the presence of LiNO_3 throughout the bulk of the LiPON-PLD film. Deconvoluted O1s peaks show that the film consists of P=O and lower amounts of P-O-P and P-O⁻. In contrast to the LiPON-

PLD film, the LiPON film has a higher concentration of $\text{P}=\text{N}-\text{P}$ with lower contributions of triply coordinated $\text{P}-\text{N} < \text{P}^{\text{P}}$, and even lower $\text{O}-\text{N}=\text{O}$. As evidenced by the O1s peak data, the $\text{P}-\text{O}^-$ bonds have a greater presence in LiPON thin films. LiPON films also show the presence of Li_2CO_3 , whereas integration of CO_2 into the surface is unfavored in LiPON-PLD. Additionally, the Li 1s binding energy was found to be 56.0 eV for LiPON films while the Li 1s binding energy for LiPON-PLD has a binding energy of 55.5 eV (Figure S2). Similarly, the LiPON-PLD P2p peaks is shifted slightly to a lower binding energy, where the $\text{P}2\text{p}_{3/2}$ peak is more dominant than the $\text{P}2\text{p}_{1/2}$ peak (Figure S3); this shift in binding energy correlates to an increase in nitrogen content in the LiPON-PLD thin films. Also, the shift in the binding energy indicates that LiPON-PLD films contain relatively more $(\text{PO}_3)^-$ character when compared to LiPON, which is dominated by $(\text{PO}_3)^{4-}$ and $(\text{P}_2\text{O}_7)^-$ species. These XPS results agree with previous analysis of LiPON thin films.^{26,29,30}

To elucidate how triply coordinated $\text{P}-\text{N} < \text{P}^{\text{P}}$ forms from $\text{Li}_2\text{PO}_2\text{N}$, a scheme is proposed in Figure 8. During PLD processing, P-N bonds are broken, causing nitrogen to evolve out of the structure while simultaneously forming triply coordinated $\text{P}-\text{N} < \text{P}^{\text{P}}$. According to this model, as the amount of nitrogen is increased, the content of triply coordinated $\text{P}-\text{N} < \text{P}^{\text{P}}$ should increase, which is confirmed by comparing XPS results for LiPON-PLD and LiPON.

Amorphous films of LiPON-PLD contain a higher amount of triply coordinated $\text{P}-\text{N} < \text{P}^{\text{P}}$ and lose the infinite -P-N-P-N- backbone characteristic of the crystalline material. In comparison to LiPON thin films, using crystalline $\text{Li}_2\text{PO}_2\text{N}$ as a nitrogen-rich starting precursor for PLD increases the ratio of N/P in the deposited films. Thus, increasing the amount of nitrogen in the LiPON-PLD thin film also increases the amount of triply coordinated $\text{P}-\text{N} < \text{P}^{\text{P}}$.

Despite the detailed elucidation of the chemistry of the LiPON-PLD herein, we have not been able to determine the reason for the marked improvement in electrochemical kinetics by interposing a LiPON-PLD film between the cathode and LiPON solid electrolyte. Further studies are planned to vary the stoichiometry of the pellet and hence the film to better understand the interplay between films' chemistry and its electrochemical performance.

CONCLUSIONS

Phase-pure $\text{Li}_2\text{PO}_2\text{N}$ was synthesized and the resultant powder pelletized for use as a PLD deposition target. Thin amorphous LiPON-PLD films prepared from this target in a N_2 ambient atmosphere have been deposited and used as a passive layer between a thin film LNM cathode and LiPON solid electrolyte. The ionic conductivity of the amorphous LiPON-PLD films was superior to that of the crystalline $\text{Li}_2\text{PO}_2\text{N}$ target with an extrapolated room temperature ionic conductivity of the thin film estimated at $1.5 \times 10^{-8} \text{ S cm}^{-1}$ and activation energy of 0.68 eV. Despite the relatively low ionic conductivity, LiPON-PLD films interposed between the LNM cathode and LiPON electrolyte resulted in sharply improved electrochemical performance in terms of charge-transfer resistance and CV profiles. Cells without a LiPON-PLD film had a charge-transfer resistance of $4470 \text{ } \Omega\text{-cm}^2$ compared to 760 and $960 \text{ } \Omega\text{-cm}^2$ for the sample with 17 nm and 31 nm thick LiPON-PLD films, respectively.

Amorphous films of LiPON-PLD were composed of a higher amount of triply coordinated $\text{P} - \text{N} < \text{P}^{\text{P}}$ with relatively lower contributions of $\text{P}-\text{N}=\text{P}$ and lose the continuous planar $-\text{P}-\text{N}-\text{P}-\text{N}-$ backbone characteristic of the crystalline target material. In comparison to RF sputtered LiPON thin films, using crystalline $\text{Li}_2\text{PO}_2\text{N}$ as nitrogen-rich starting precursor for

PLD increases the ratio of N/P in the deposited films. Thus, increasing the amount of nitrogen in the LiPON-PLD thin film also increases the amount of triply coordinated $P - N < P_p$.

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FIGURE CAPTIONS

Figure 1. SEM images of $\text{Li}_2\text{PO}_2\text{N}$ powder a) before ball milling and b) after ball milling.

Figure 2. SEM image of a thick, dense LiPON-PLD film deposited from the $\text{Li}_2\text{PO}_2\text{N}$ target using the 5th harmonic of a Nd:YAG laser in 1 Pa N_2 . This film is representative of the thin LiPON-PLD films.

Figure 3. a) Powder X-ray diffraction pattern of the $\text{Li}_2\text{PO}_2\text{N}$. The observed (black), calculated (red), and difference (green) patterns are presented with a GOF = 0.0093 ($R_{\text{profile}} = 0.22528$ and $R_{\text{expected}} = 3.80058$) between the calculated and experimental patterns. Indexing results show that the unit cell has dimensions $a = 9.0712(4) \text{ \AA}$, $b = 5.4025(7) \text{ \AA}$, and $c = 4.6940(8) \text{ \AA}$; b) Synchrotron X-ray diffraction pattern of the amorphous LiPON-PLD film on Pt film on silica. Reflections associated with the indices of the Pt underlayer are indicated on the figure.

Figure 4. Ionic conductivity as a function of temperature for the pellet and as-deposited LiPON-PLD film.

Figure 5. a) Cyclic voltammograms of full cell Pt|LNM|LiPON| with and without LiPON-PLD buffer layer coatings between the cathode and LiPON electrolyte. Scan rate was 1 mV s^{-1} ; b) EIS measurements of full cell Pt|LNM|LiPON| with and without LiPON-PLD buffer layer coatings between the cathode and sputtered LiPON electrolyte. Numerals above data points represent $\log(\text{frequency (Hz)})$.

Figure 6. a) FTIR spectra for RF magnetron sputtered LiPON and LiPON-PLD films; b) Raman spectrum for the LiPON-PLD film.

Figure 7. XPS spectra of a) O1s scan and b) N1s for LiPON-PLD, and c) O1s and d) N1s for LiPON. Deconvolutions are noted on the spectrum.

Figure 8. Schematic diagram detailing the formation of triply coordinated $\text{P} - \text{N} < \text{P}$ in LiPON-PLD. P-N bonds are fragmented during PLD (red dotted lines), causing some nitrogen to evolve

out of the structure, while retained nitrogen forms triply coordinated $P - N <_P^P$ and doubly coordinated $P-N=P$. The N_2 atmosphere during PLD processes helps stabilize nitrogen into the LiPON-PLD thin films.

Figure(1)

Figure(2)

Figure(3a)

Figure(3b)

Figure(4)

Figure(5a)

a)

Figure(5b)

Figure(6a)

Figure(6b)

Figure(7)

Figure(8)