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Stabilizing and understanding the interface between nickel-rich cathode and PEO-based electrolyte by lithium niobium oxide coating for high-performance all-solid-state batteries

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ABSTRACT

The pursuit of high energy density and safe lithium ion batteries (LIBs) is a urgent goal for the development of next-generation electric vehicles (EVs). All-solid-state batteries (ASSBs) with the combination of poly(ethylene oxide) (PEO)-based solid polymer electrolyte (SPE) and Ni-rich lithium nickel manganese cobalt oxide LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode are promising candidates for EVs due to their improved energy density and safety. However, the low electrochemical oxidation window of PEO-based SPE and the instability of NMC811 at the charge/discharge process seriously restrict the battery performance. Herein, a high voltage stable solid-state electrolyte layer lithium niobium oxide (LNO) is coated on the NMC811 electrode surface by atomic layer deposition for stabilizing NMC811-PEO solid polymer batteries. Electrochemical tests show that LNO coating can stabilize the NMC811 active materials and mitigate the decomposition of SPE upon the cycling process, rendering a good performance of NMC811-SPEO solid polymer battery. Mechanism studies by SEM, STEM, XAS, and XPS disclose that the uncoated NMC811 suffers from chemomechanical degradations along with oxygen release triggering the decomposition of SPE, which results in unstable cathodic electrolyte interphase. With LNO coating, chemomechanical degradations and oxygen release are inhibited and the decomposition of SPE is mitigated. This work renders a stable and high-performance high-energy-density SSB for high voltage application, which paves the way toward next-generation solid-state LIBs.

1. Introduction

The rapid development of electric transportation and grid-scale energy storage systems require the batteries with high energy density and reliable safety properties [1–3]. However, conventional lithium-ion batteries (LIBs) with liquid electrolytes cannot meet this requirement due to its potential safety issues such as leakage of liquid electrolyte, fire, and even explosion if batteries are short-circuited or over-heated. Compared to conventional LIBs, solid-state batteries (SSBs) with solid-state electrolytes (SSEs) have received more and more research attention due to their improved safety. Among the SSEs, poly(ethylene oxide) (PEO)-based solid polymer electrolyte (SPE) is one of the most promising candidates for the applications in high energy density SSBs because of its high ionic conductivity and low interfacial resistance toward electrodes, along with its low mass density, low cost, facile fabrication process, and environmental-friendly properties [4–8]. Besides, to achieve high energy density SSBs, cathodes with high specific capacity or/and high discharge voltage are favorable [9]. Therefore, many novel

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lithium transition metal oxide cathodes such as lithium nickel oxide, lithium manganese oxide, and lithium nickel manganese cobalt oxide (NMC), with high theoretical specific capacity were developed and received plenty of research concerns [10–17]. Among these cathode materials, Ni-rich lithium nickel manganese cobalt oxide, such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NMC811), is one of the most promising candidates for the near future application in electric transportation.

However, the incorporation of PEO-based SPE with Ni-rich NMC cathode experiences serious challenges. Firstly, the electrochemical oxidation voltage of PEO-based SPE is lower than 4 V (vs.Li/Li⁺) [18, 19]. Although PEO-based SPE can deliver a good performance in LiFePO₄ SSB in a voltage window of 2.5–4.0 V [20], its performance in 4 V class cathode such as LiCoO₂ and Ni-rich cathode is still very poor [21, 22]. At high charge voltage of 4.3 V requested by NMC811 electrode, a serious electrochemical decomposition of PEO-based SPE will happen. The second challenge roots from the instability of Ni-rich NMC811 cathode that causes problems including voltage fading, transition metal dissolution, surface phase reconstruction, and chemomechanical degradations upon cycling, significantly hindering the wide applications of Ni-rich NMC811 cathode in SSBs [12,15,17,23–26].

To enhance the stability of PEO-based SPE at high voltage for coupling with high voltage and high specific capacity cathode materials, protecting the SPE/cathode active material interface with a stable coating layer is proved to be an effective strategy [21,27-30]. An alternative approach is applying different lithium salts for complexing with PEO-based polymer to stabilize the cathodic electrolyte interphase for enhancing the performance of high voltage solid polymer batteries [31,32]. A double-layer polymer electrolyte also has been developed for high performance LiCoO₂ SSBs. As reported by W. Zhou et al. [33], who used a double-layer polymer electrolytes consisting of an anode-stable PEO-based SPE and a high-voltage-stable poly(N-methyl-malonic amide)-based SPE at cathode side, the performance of LiCoO2 SSB was greatly enhanced compared to the SSB with single layer PEO-based SPE. Also some studies show that conductive carbon in the electrode can accelerate the electrochemical decomposition of SSEs [18,34,35], and coatings at carbon/SSE interface can alleviate the electrochemical decomposition of SSEs at high voltage [29,36].

As for enhancing the stability of Ni-rich NMC cathodes, surface coating and element doping are two main strategies [12,17,37–42]. For example, NMC cathode with Li₃PO₄ surface coating was presented with significant improvement in the electrochemical performance due to the effects of Li₃PO₄ coating in avoiding the liquid electrolyte induced corrosion of the NMC particle grain boundary and maintaining the structural stability of NMC particles [17]. Therefore, combining the strategies for stabilizing SPE/electrode interface and the approaches for stabilizing Ni-rich NMC cathode, it seems that coating NMC811 electrode sheet with a good Li⁺ ion conductive, poor electronic conductive layer can not only maintain the stability of NMC811 cathode but also protect the SPE from the decomposition at high voltage.

Herein, an atomic layer deposition (ALD) derived lithium niobium oxide (LNO) solid-state electrolyte thin film is applied to tailor the interface between NMC811 cathode electrode and PEO-based SPE. The advantages of ALD process include the uniformity of coating thickness and low temperature deposition process over other coating techniques, which enable ALD non-destructed for electrode coating. LNO is chosen for engineering the electrolyte/cathode interface because it is electrochemically stable towards high voltage as predicted by the results of first-principles calculations [43,44]. The good stability and high Li⁺ ion conducting of LNO can be a favorable coating material. Furthermore, the low electronic conductivity of LNO is expected to alleviate the electrochemical decomposition of the electrolyte. With the optimized thickness of LNO coating on electrode, compared to LNO coating on NMC811 active material particle, SSBs show much more performance enhancement. The LNO coating on the electrode is demonstrated to not only stabilize the NMC811 particles under high temperature and high-voltage cycling but also reduce the decomposition of PEO-based SPE. As a result,

even though the specific discharge capacity of the bare NMC811 SSB dramatically drops from 204.8 mAh/g to 73.9 mAh/g in 50 cycles, ALD LNO coated NMC811 SSB maintains a high specific discharge capacity of 175.5 mAh/g after 50 cycles, showing significant improvement in the electrochemical performance. Mechanism studies suggest that besides the electrochemical decomposion of SPE at high voltage, the uncoated NMC811 suffers from chemomechanical degradations along with oxygen release triggering the decomposition of SPE, which results in unstable cathodic electrolyte interphase and serious decay in electrochemical performance, while with LNO coating, chemomechanical degradations and oxygen release problems of NMC811 are inhibited and the decomposition of SPE is mitigated, rendering a high performance high energy density SSBs.

2. Experiential

2.1. Preparation of PEO-based SPE

PEO with a molecule weight of 600,000 (Sigma-Aldrich), lithium perchlorate (LiClO₄) with a purity of 99.9% (Sigma-Aldrich), and the solid-state electrolyte Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) with garnet structure were used as fillers to prepare PEO-based solid-polymer electrolyte (SPE). LLZTO was synthesized by solid-state reaction method and the experimental details are described in the previous study [45]. The size of LLZTO is around 3 µm according to the SEM images (Fig. S1). LLZTO fillers were used for enhancing the ionic conductivity of SPE and the stability towards lithium anode. Firstly, 0.24 g of LLZTO was mixed with 50 mL acetonitrile (AN) using ultrasound for 5 h. Secondly, 0.19 g LiClO₄ and 1.2 g PEO were added to this mixture and stirred overnight to get a homogeneous mixture, which was casted onto the Teflon substrate and dried at room temperature overnight to firstly evaporate the AN slowly. Then, the SPE was further heated at a 60 $^\circ C$ vacuum oven for 2 days to obtain PEO-based SPE membranes. Finally, these membranes were immediately transferred into argon filled glovebox and stored over 3 days before they were used for solid-state batteries assembling.

2.2. Preparation of ALD LNO coating NMC811 electrodes

Bare NMC811 electrodes were prepared as followed: Firstly, 80 wt % NMC811 particles, 10 wt % carbon-black (Acetylene Black) and 10 wt% poly(vinylidene) fluoride (PVDF) binder were mixed together in the N-methylpyrrolidinone (NMP) solvent. Secondly, the mixture was coated on an Al foil that serves as the current collector by the doctor blade method. Third, NMC811 electrode was dried in a vacuum at 100 °C for 24 h. The loading of NMC811 is around 2 mg/cm². Atomic layer deposition (ALD) Li–Nb–O (LNO) coated NMC811 electrode was prepared by directly coating LNO on the as-prepared NMC811 electrodes or on the NMC811 particles in an ALD reactor (Savannah 100, Cambridge Nanotechnology Inc., USA). Lithium tert-butoxide [LiOtBu, (CH₃)₃COLi, Alfa Aesar, >99.9%] and niobium ethoxide [Nb(OEt₁₅, Et = –CH₂CH₃, Strem Chemicals Inc., >99.9%] and H₂O were used as the precursors and the deposition temperature was set as 235 °C. The details of ALD process are described in our previous study [46].

2.3. Electrochemical performance testing

All-solid-state NMC811 batteries were assembled in the 2032 type coin cells with anode/electrolyte/cathode sandwich structure, in an argon filled glovebox (Vacuum Atmosphere Company, moisture and oxygen level less than 1 ppm). The PEO-based SPE was used as the electrolyte in the SSBs. Lithium metal was used as the anode and the NMC811 electrode was used as the cathode. No solvent or liquid electrolyte was added into NMC811 SSBs. Charge/discharge characteristics were tested between 2.8 and 4.3 V in a temperature controllable oven using a LAND Battery Tester, the batteries were kept at 60 °C over 30 h before testing. For liquid-based NMC811 batteries, the liquid electrolyte



Fig. 1. (a) Schematic showing the ALD-LNO coating on NMC811 electrode. (b) TEM image of ALD-LNO coated cathode active material particle. Comparison of Nb L₃-edge XAS between ALD-LNO and standard LiNbO₃ sample at (c) TEY and (d) FLY.

contains 1 M LiPF₆ in ethylene carbonate (EC): ethylmethyl carbonate (EMC): diethyl carbonate (DEC) solvents with 1:1:1 of volume radio, and a Celgard separator was used to prevent the shut-circuit. CV of the NMC811 batteries was tested between 2.8 and 4.3 V at 60 °C. Electrochemical impedance spectroscopy (EIS) was performed on the versatile multichannel potentiostat 3/Z (VMP3) by applying an AC voltage of 10 mV amplitude in the 500 kHz to 0.01 Hz frequency range.

2.4. Physical characterization

A Hitachi S-4800 field emission scanning electronic microscopy (FE-SEM), equipped with energy dispersive X-ray spectroscopy (EDX) was used to study the morphologies and the composition of the samples. Pristine LLZTO, NMC811 particles were directly and carefully taped onto the sample holder using a conductive carbon tape for SEM and EDX characterization. NMC811 electrode was cut into small pieces and loaded to sample holders for SEM and EDX characterization. The cycled NMC811 samples were obtained by cutting the anode/electrolyte/ cathode sandwich to expose the interface. The cross-section view of the cycled NMC811 samples were obtained by SEM and EDX characterization.

Synchrotron X-ray absorption (XAS) was carried out at the Canadian Light Source (CLS). X-ray photoelectron spectroscopy (XPS) was conducted by ESCALAB 250 spectrometer, PerkinElmer. Uncycled NMC811 electrodes were used as the bare NMC811 samples for XPS and XAS study. Cycled NMC811/SPE samples were obtained from the cycled SSBs (53 °C, 0.02C current density, 5 cycles). After cooling down the cycled SSBs, the cycled NMC811 samples and PEO-based SPEs sample were peeled off from the SSBs in the glovebox. Then, the cycled NMC811

electrodes were used for XPS and XAS study. And the cycled PEO-based SPE was used for Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) study. The TOF-SIMS were performed using TOF-SIMS IV (ION-TOF GmbH, Germany) with a 25 keV bismuth liquid metal ion source with a base pressure at $\approx 10^{-8}$ bar in the analysis chamber. The negative secondary ions were induced by the primary ion beam bombardment on the surface of the sample.

For the preparation of transmission electron microscopy (TEM) samples, the cycled NMC811 particles were obtained from the cycled SSBs (60 °C, 0.2C current density, 50 cycles) by removing the SPE layer from the disassemble cell using acetonitrile solvent. Cross-sectional view of samples were prepared by focused ion beam method using Thermo-Fisher Helios Nanolab DualBeam. HAADF-STEM images and STEM-EDX elemental maps were acquired with Thermo-Fischer Talos F200X at an accelerating voltage of 200 kV.

3. Results and discussion

ALD derived LNO (ALD-LNO) was deposited directly on the surface of NMC811 electrode using Savannah 100 ALD system following the method that we reported previously [46]. Fig. 1a schematically shows the process of ALD coating on NMC811 cathode electrode. TEM image in Fig. 1b presents the NMC811 particle with 50 cycles of ALD-LNO coating, where the thickness of LNO is around 10 nm, indicating the growth rate of ALD LNO is 0.2 nm/cycle. SEM coupled with energy-dispersive X-ray (EDX) confirmed the coverage of ALD-LNO coating on NMC811 electrode surface (Fig. S3 and Fig. S4) as indicated by the uniform Nb mapping. Synchrotron-based XAS at Nb L₃-edge was used to characterize the chemical environment of the ALD-LNO.



Fig. 2. Discharge voltage profiles of (a) Li/SPE/bare NMC811 SSB and (b) Li/SPE/ALD-LNO coated NMC811 SSB after different cycles. (c) The midpoint voltage evolution of two SSBs over 200 cycles. (d) Comparison of long cycling performance of the Li/SPE/bare NMC811 SSB and the Li/SPE/ALD-LNO coated NMC811 SSB. The cycling performance was evaluated by galvanostatic discharge/charge cycling at a current density of 0.2C at 60 °C (with 0.1C at first three cycles). (e) Comparison of the first-cycle Coulombic efficiency and average Coulombic efficiency of 200 cycles for two SSBs. (f) Comparison of the energy density of 4 V class cathodes in SSBs with dry SPEs published in different years at the first cycle, and (g) the energy density after different cycles [21,22,27,28,31,47–55]. The energy density is calculated based on the cathode only due to the limited data about the thicknesses/weights of anode and SPE.

Fig. 1c-d are the XAS spectra collected under total electron yield (TEY) and fluorescence yield (FLY) mode, respectively. TEY mode collected the information from the top few nanometers of the sample surface, while FLY mode was considered to reflect the bulk property. Both peak position and spectral features of the ALD-LNO spectra are highly relevant to those of standard LiNbO3 in TEY and FLY modes. The ALD-LNO and the standard LiNbO3 sample show the same peak A position at 2372.8 eV without energy shift, which indicated the same oxidation state of Nb in ALD-LNO as in the standard LiNbO₃ sample (Nb⁵⁺). Peak B is related to the ligand field splitting of d-orbitals originating from the local coordination structure of Nb⁵⁺ [46]. The minor shift of peak B in ALD-LNO compared to standard LiNbO3 sample indicates that there is a difference in the local coordination of Nb⁵⁺ in ALD-LNO, which is possibly original from the ALD synthesis process. For ALD-LNO, the Nb L3-edge XAS spectra are almost the same in both FLY and TEY modes (Fig. S5b). This is due to the intrinsic thin film property of ALD-LNO, which results in minor differences in bulk and surface properties since the thickness of 50 cycles of ALD-LNO is only around 10 nm.

The cycling stabilities of the SSBs with bare NMC811 cathode or ALD-LNO coated NMC811 cathode were evaluated at a current density of 0.2C at 60 °C. The results are presented in Fig. 2. The ALD-LNO coating thickness was optimized based on galvanostatic cycling performance, and the results are showed in Fig. S6. The NMC811 electrodes with 20–100 cycles of ALD-LNO coatings all showed significantly improved cycling stability compared to the bare NMC811 electrode,

where 50 cycles of ALD-LNO was picked up for the rest of the study and discussion since it delivers the highest specific discharge capacity and stable cycling performance. The lowered specific capacity by a thicker ALD-LNO coating (100 cycles) is probably due to the significantly restricted ionic/electronic transport through the coating. As a comparison to electrode coating, ALD coating on NMC811 particles is also studied, the results are shown in Fig. S7, where it indicates that particle coating has also improvement in electrochemical performance but not as superior as electrode coating. The significant improvement achieved by electrode coating is probably due to the both protection of NMC811/SPE and carbon/SPE interfaces, which stabilize the NMC811 active materials and inhibit the electrochemical decomposition of SPE at high voltage. Therefore, ALD-LNO coating of 50 cycles was chosen for mechanism studies. Fig. 2a and b are the discharge voltage profiles of the SSBs using bare NMC811 and ALD-LNO coated NMC811 cathodes, respectively. Clearly, the bare NMC811 SSB shows obvious capacity fading along with enlarging overpotential upon cycling, which suggests the continuous formation of the cathodic electrolyte interphase (CEI) and the decay of the NMC811 active materials. In contrast, the SSB with ALD-LNO coated NMC811 electrode demonstrates stable cycling performance with good capacity retention, which indicates the formation of a favorable CEI. The evolutions of the midpoint voltage of these two SSBs over 200 charge/ discharge cycles are compared in Fig. 2c. At the initial cycle, the midpoint voltage of both SSBs are similar at around 3.78 V. However, after 200 cycles, the midpoint voltage of the bare NMC811 SSB



Fig. 3. A STEM image of (a) a bare NMC811 secondary particle after 50 cycles of charge/discharge and its (b) A HAADF-STEM image and corresponding STEM-EDX maps. (c) A STEM image of ALD-LNO coated NMC811 particle after 50 cycles of charge/discharge and its (d) A HAADF-STEM image and corresponding STEM-EDX maps. Scale bars are 2 μm for (a) and (c), 400 nm for (b) and (d).

dramatically fades to 3.02 V while the ALD-LNO coated NMC811 SSB still maintains a high midpoint voltage of 3.52 V. The stabilization of discharge voltage by the ALD-LNO coating is beneficial for preserving high energy density.

The long cycling stabilities of the NMC811 SSBs with or without ALD-LNO coating are compared in Fig. 2d. The specific discharge capacity of the bare NMC811 SSB dramatically decreases from 204.8 to 73.9 mAh/g (i.e. 63.9% loss in capacity) within only 50 cycles. However, the ALD-LNO coated NMC811 SSB can maintain a high specific discharge capacity of 175.5 mAh/g after 50 cycles with 84.1% capacity retention. At 200 cycles, the ALD-LNO coated NMC811 SSB delivers about 5 times higher discharge capacity than the SSB without coating. Meanwhile, the ALD-LNO coated NMC811 SSB shows a high average Coulombic efficiency of 99.2% over 200 cycles, which is significantly higher than 92.3% of the bare NMC811 SSB (Fig. 2e). This result again indicates a more stable cathodic interphase between the PEO-based SPE and the ALD-LNO NMC811 electrode than the non-coated electrode. The energy density of the as-studied NMC811 SSB is compared to the energy densities of SSBs with dry polymer electrolytes from other reported works and the result are shown in Table S1 and Fig. 2f and g. Clearly, SSBs of this work deliver the highest energy density compared to the previous studies not only for the first cycles but also for the extensive cycles.

Ni-rich NMC811 cathode materials are well known to be unstable upon charging/discharging cycles not only at liquid-based batteries but also in solid-state polymer batteries [17,22]. The performance fading of Ni-rich cathode materials is intimately related to the chemomechanical degradation such as the crack [17,22,56] and the surface phase reconstruction [15]. The role of ALD-LNO coating in enhancing the cycling stability of NMC811 electrodes in PEO based SSBs was studied comprehensively by focused ion beam (FIB), STEM, SEM, synchrotron-based XAS.

The cycled NMC811 particles were collected from the cycled SSBs and cut by FIB for structural and morphological analyses. STEM image and corresponding EDX elemental mappings for the bare NMC811 are shown in Fig. 3a–d. The bare NMC811 particle exhibits severe intergranular and intragranular cracks after 50 charge/discharge cycles in SSBs at 60 °C (Fig. 3a and b), which is consistent well with the reported results [22,57]. The significant mechanical cracks were possibly a combined consequence of the internal pressure resulting from material phase heterogeneity and oxygen release [57]. The deep delithiation and lithiation processes under 60 °C can trigger the surface reconstruction by the transition of the layered structure to spinel phases and rock-salt phases with the release of oxygen (Eq. (1) and (2)) [57].

$$Li_{1-x}MO_2 \rightarrow (1-x) \cdot LiM_2O_4(spinel) + (2x-1) \cdot MO(rocksalt) + (2x-1)/2 \cdot O_2$$
(1)

$$Li_{1-x}MO_2 \rightarrow (1-x)/2 \cdot Li_2O + MO(rock salt) + (1+x)/2 \cdot O_2$$
 (2)

where M = Mn, Co, and Ni, and x is the extracted lithium (0 < x < 1). The surface phase reconstruction resulting in inhomogeneous



Fig. 4. Ni L-edge synchrotron-based XAS at TEY mode (a, b) and FLY mode (c, d) for bare NMC811 and ALD-LNO coated NMC811 electrodes before/after 5 charge/ discharge cycle at discharge state. (b), (d) Normalized peak A intensity in comparison with varied peak B intensity.

lithium distribution causes mismatched chemical strain, leading to stress concentration near the crack tip. The released oxygen was trapped in the cracking gap, resulting in a big driving force for intergranular/intragranular cracking. Surprisingly, with ALD-LNO coating, no/less intergranular or intragranular cracks are found (Fig. 3c and d), indicating that ALD-LNO coating can significantly enhance the stability of NMC811 cathode particles during long charge/discharge cycles. Presumably, the ALD-LNO coating inhibits the surface phase reconstruction for the formation of spinel and rock-salt phases, and eliminates the chemical strain caused by inhomogeneous lithium distribution and the oxygen release, thus enhancing the cycling stability of SSBs. Similar results were obtained from SEM observations (Fig. S8).

Synchrotron-based soft XAS was conducted to study the variation of surface chemical properties of NMC811 after charge/discharge and the results are presented in Fig. 4. Spectra were collected at two detection modes (TEY and FYL) simultaneously on the pristine electrode surface and cycled electrodes surfaces with or without ALD-LNO coating at discharge state. The valence state of the Ni can be evaluated by the ratio of two splits (low energy state and high energy state [58,59], which are marked as peaks A and B, respectively in Fig. 4a and b, Ni L-edge synchrotron-based XAS spectra. The ratio of B/A is positively related to

the Ni valence state. Fig. 4a and c are the Ni L-edge XAS spectra at TEY and FLY modes of bare NMC811, ALD-LNO coated NMC811, bare NMC811 after cycling and ALD-LNO coated NMC811 electrodes after cycling at SSBs with PEO-based SPE, respectively. The spectra exhibit similar features in TEY and FLY modes. However, the ratios of B/A of L₃ splits are clearly different among these samples as shown in Fig. 4b and d. For TEY information, the bare NMC811 sample shows the lowest B/A value indicating low oxidation of Ni in pristine NMC811. For bare NMC811 electrode after cycling at the discharge state, the B/A ratio shows a significant increase compared to that of the pristine NMC811 sample, indicating the Ni oxidation state is higher than that of pristine NMC811. In other words, the Ni redox reaction was not fully reversible at the bare NMC811 particles surface during cycling. This result indicates the formation of high oxidation state snipel LiM₂O₄ or NiO₂ phase on the NMC811 particle surface, which is consistent with STEM results. The ALD-LNO coated NMC811 shows a high B/A ratio, which is probably due to the interaction between NMC811 particle surface and ALD precursor (H₂O). While NMC811 electrode with ALD-LNO coating shows less increase in the B/A ratio after cycling at discharge state compared to bare NMC811 electrode after cycling, which means ALD-LNO coating can enhance the reversibility of NMC811 particles. For



Fig. 5. XPS C 1s spectra of (a) bare NMC811 electrode, (b) bare NMC811 electrode after 5 charge/discharge cycles at the discharge state, and (c) ALD-LNO coated NMC811 electrode after 5 charge/discharge cycles at the discharge state. (d) XPS spectrum of Nb 3d of ALD-LNO coated NMC811 electrode after 5 charge/discharge cycles at discharge state.

FLY information, these four samples show almost the same value of B/A ratio (Fig. 4d), which means ALD precursor only react with NMC811 particles surface but not into the bulk, and ALD-LNO coated NMC811 electrode has high reversibility in the bulk NMC811 particle during charge/discharge cycling. Differently, bare NMC811 electrode after cycling presents a much higher B/A ratio in FLY mode compared to the pristine NMC811 electrode, which indicates poor reversibility of bare NMC811 cathode upon cycling not only at the surface but also in the bulk.

In summary, STEM, SEM, and XAS analyses disclosed the instability of NMC811 electrode in PEO-based SSBs, and the ALD-LNO coating can effectively enhance the stability of NMC811 upon long cycles. Co and Mn XAS under FLY mode were also obtained (Figs. S9–S10). The Co and Mn XAS spectra of these four samples showed no obvious difference. These results are consistent with the report by X. Liu et al. who found that the oxidation states of Co and Mn were unchanged in Ni-rich cathode with PEO-based SPE [59].

PEO-based SPE is known to be unstable under high voltage (>4 V) [18,19]. Therefore, the effects of ALD-LNO coating on the interfacial stability between NMC811 electrode and SPE were analyzed by X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). XPS C 1s results of bare NMC811 electrode, and ALD-LNO coated NMC811 electrode before and after 5 cycles charge/discharge at discharge state are shown in Fig. 5a–c, respectively. The C 1s XPS spectrum of bare NMC811 electrode (Fig. 5a) shows the peaks of C=C at 284.3 eV, C–C(C–H) at 284.8 eV, C–OH (C–O–C) at 286.0 eV, and CF₂ at 290.5 eV [60,61]. An increase in the C–OH (C–O–C) (286.0 eV) peak intensity and area is observed in bare NMC811 electrode (Fig. 5c) after being cycled in SPE-based SSBs, which can be attributed the adhesion of PEO-based SPE on the surface of NMC811 electrode after SPE was peeled off from the electrodes. An increased CF₂ peak is also observed in the

ALD-LNO coating NMC811 electrode compared to the bare NMC811 electrodes. The increase of CF2 XPS peak in the cycled LNO-coated NMC811 electrode is possibly due to the ALD process. ALD process is conducted under the vacuum environment with purging procedures, which will probably remove some surface carbon particles (as supported by Fig. 5c, there is a decrease in C=C peak for ALD-LNO coating NMC811 electrode), and expose more PVDF binder for XPS beam probing, so that the CF₂ XPS peak intensity is slightly increased. A new peak corresponding to O-C=O group (288.8 eV) [60] emerged in the bare NMC811 electrode (Fig. 5b). PEO has repeating units of -(O-CH₂-CH₂)-, where there is no O-C=O group in pristine PEO. This O-C=O peak can be attributed to the decomposition products of SPE, as supported by the previous theoretical studies and the nuclear magnetic resonance (NMR) studies which showed that the decomposed products of PEO contain O-C=O group [62-64]. To further confirm the existent of O-C=O group as the decomposed products, ToF-SIMS were acquired from the cycled PEO-based SPE surface from bare cycled NMC811 SSB and the result is presented in Fig. S11. The peaks corresponding to O-CH=O fragments clearly supports the XPS result.

The decomposition of SPE at the NMC811 electrode/SPE interface can form an unstable cathode electrolyte interphase (CEI), and result in low Coulombic efficiency (Fig. 2d) and high cell internal resistance, this proposal is consistent with the EIS results (Fig. S12a). The overall cell resistance of bare NMC811 SSB is over 4 K Ω after 30 cycles of charge/ discharge and increases to around 10 K Ω after 200 cycles of charge/ discharge. The continued increase of cell impedance is the result of accumulated discomposed products from SPE at the interface. With ALD-LNO coating, the C 1s spectrum shows no O–C=O peak, which means ALD-LNO coating on NMC811 electrode surface can effectively palliate the decomposition of PEO-based SPE. This is also supported by the EIS study of ALD-LNO coated NMC811 SSB after different cycling (Fig. S12b). The over-all resistance of ALD-LNO coated NMC811 SSB J. Liang et al.



Fig. 6. Schematically showing the ALD-LNO coating effect on the NMC811 SSBs with PEO-based SPE. (a) bare NMC811 particle. Crack emerged in the NMC811 particle after cycling, along with oxygen released, triggering the severe chemical decomposition of SPE. The decay of NMC811 particle, chemical decomposition of SPE and the electrochemical decomposition of SPE result in an unstable CEI in SSBs; (b) ALD-LNO coated NMC811 particle preserves structural integrity and without (with less) oxygen release, and alleviates the decomposition of SPE.

after 30 cycles is about 1.5 k Ω , which is lower than half of the bare NMC811 SSB. After 200 cycles, the overall resistance slightly increases to 2.8 k Ω , lower a quarter than that of the bare NMC811 SSB.

Combining the XPS, STEM results and previous study [15,57,65]. bare Ni-rich NMC active material undergos phase transition of the layered structure to the spinel and rock-salt phase after charging/discharging, which will release peroxo-like oxygen species or singlet oxygen $({}^{1}O_{2})$ [65,66]. The singlet oxygen is a very strong oxidant for PEO-based SPE, they will trigger the chemical decomposition of SPE similar to its effect to trigger the decomposition of liquid organic electrolyte [67,68]. Therefore, (1) the chemomechanical degradations of NMC811 active materials along with (2) the oxygen release triggering the chemical decomposition of PEO-based SPE, (3) the electrochemical decomposition of PEO-based SPE at high voltage charge process SPE would be the three main reasons for the serious performance decay of Ni-rich NMC811 SSBs. LNO is a good Li⁺ ion conductor but a poor electronic conductor and it has a high electrochemical oxidation window. These properties make LNO a good coating material for stabilizing NMC811/SPE interface. As a result of this, ALD-LNO coating can effectively inhibit the surface reconstruction of NMC811, thus reduce the oxygen release, creating a friendly operation environment for PEO-based SPE. Moreover, the low electronic conductive LNO coating layer can reduce the electrochemical decomposition of PEO-based at high voltage. As a result, ALD-LNO coating helps the NMC811 SSBs achieve a stable long cycling performance. Fig. 6 schematically illustrates the ALD coating mechanism for improving the electrochemical performance of NMC811 SSBs.

4. Conclusions

In conclusion, ALD derived LNO was applied for enhancing the electrochemical performance of SSBs with PEO-based SPE and Ni-rich NMC811 cathode for high energy density. The role of ALD-LNO coating on the NMC811 electrode surface was disclosed by STEM, SEM, XAS, XPS, ToF-SIMS and EIS. The results showed that ALD-LNO coating can (i) stabilize the NMC811 active materials by preventing them from chemomechanical degradation upon cycling, and inhibit the oxygen release, and (ii) minimize the chemical oxidation and electro-chemical decomposition of PEO-based SPE under high voltage charge/

discharge processes. The stabilized NMC811 active materials and cathode electrode/SPE interface rendered a stable and high performance SSB. This study provides a strategy for stabilizing Ni-rich cathode in solid polymer batteries and inhibiting/ameliorating the decomposition of SPE at high voltage, lighting up the way towards next-generation safe and high energy density ASSLIBs.

CRediT authorship contribution statement

Jianneng Liang: Conceptualization, Formal analysis, Investigation, Validation, Writing- original draft. Sooyeon Hwang: Methodology, Formal analysis, Investigation, Writing. Shuang Li: Methodology, Formal analysis, Investigation. Jing Luo: Writing - review & editing, Formal analysis. Yipeng Sun: Methodology, Formal analysis. Yang Zhao: Formal analysis. Qian Sun: Formal analysis. Weihan Li: Methodology, Formal analysis. Minsi Li: Methodology, Formal analysis. Mohammad NorouziBanis: Methodology, Formal analysis. Xia Li: Formal analysis, Ruying Li: Formal analysis. Li Zhang: Project administration, Funding acquisition, Formal analysis. Shangqian Zhao: Project administration, Funding acquisition, Formal analysis. Huan Huang: Project administration, Funding acquisition, Formal analysis. Uservision. Xueliang Sun: Conceptualization, Formal analysis, Supervision. Xueliang Sun:

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2020.105107.

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