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Engineering the Conductive Carbon/PEO Interface to Stabilize Solid Polymer Electrolytes for All-Solid-State High Voltage LiCoO$_2$ Batteries

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All-solid-state lithium batteries (ASSLBs) are promising energy storage devices for applications in electric transportation and large-scale energy storage systems. Polyethylene oxide (PEO)-based solid polymer electrolytes (SPEs) are attractive solid-state electrolytes for ASSLBs due to their high ionic conductivity, light weight, and low cost. However, the low electrochemical oxidation potential window of PEO seriously restricts their implementation with high voltage cathodes for high-energy-density ASSLBs. Effective interfacial engineering between high voltage cathodes and SPE can be a solution. Most of the reported conventional cathode protection approaches have been focused on building coating layers on active material particles, which, however, can be insufficient because the conductive carbon is able to accelerate the decomposition of SPEs. In this work, ALD coating on electrode instead of active material particles realizes a unique method to protect cathode and SPE interface. As a successful example, a thin lithium tantalate coating on high-voltage LiCoO$_2$ electrode by atomic layer deposition demonstrated good compatibility with PEO-based SPEs, significantly enhancing the cycling performance of the ASSLBs. The inner mechanism is attributed to that the protection of conductive carbon/PPO interface helps to reduce the electrochemical oxidation of PEO-based SPE. This work shall give new insights for the interfacial engineering of high voltage cathode and solid polymer electrolytes.

Introduction

All solid-state lithium batteries (ASSLBs) are promising candidates for the application in electric vehicles (EVs) and other large-scale energy storage systems due to their high energy density and enhanced safety. Feasible solid-state electrolytes (SSEs) are a key component to realize ASSLBs. Among of all the solid-state lithium ion conductors, SSE systems including solid polymer electrolytes (SPEs), oxide-based SSEs, sulfide-based SSEs, and hybrid electrolytes received most of the research interests.1-4 To realize the practical applications of ASSLBs, the following challenges of SSEs must be addressed: (i) high interfacial resistance, (ii) low ionic conductivity, (iii) narrow electrochemical window, and (iv) instability with electrodes.2,5-6 SPEs based on polyethylene oxide (PEO) and lithium salt complexes, are promising candidates for ASSLBs, owing to their high ionic conductivity at elevated temperature and low interfacial resistance toward electrodes. More importantly, PEO is commercially available, low cost, light weight, and environmentally friendly.6 However, (1) the low ionic conductivity at room temperature,6-8 (2) the susceptibility to lithium dendrites and (3) the instability at high voltage10 of PEO-based SPEs are the main issues that hinder their wide applications in ASSLBs.

Tremendous research efforts have been dedicated to address challenges (1) and (2) in recent years. For example, Cui’s group enhanced the RT ionic conductivity of PEO-based SPEs from 10$^{-7}$ S/cm to 4.4×10$^{-5}$ S/cm by in-situ formation of nanosized SiO$_2$ particle fillers in PEO matrix.8 Hu’s group created a 3-dimensional garnet-type SSE nanofiber network for PEO to form a hybrid electrolyte that has an ionic conductivity of 2.5×10$^{-4}$ S/cm at RT.11 Plenty of works applying inorganic SSE fillers in PEO matrix to enhance the RT ionic conductivity of PEO-based SPE have also been reported.12,13 On the other hand, many studies were reported to address the lithium dendrite formation problem in ASSLBs with PEO-based SPEs.11-14 For example, Zhao et al. prepared a LLZTO-PEO hybrid electrolyte for ASSLBs and they proposed that anions were tethered in the hybrid electrolyte by the polymer matrix and ceramic fillers, which results in a uniform distribution of space charges and lithium ions, thus, resulting in dendrite-free lithium deposition.14 However, the issue of the instability of PEO-based SPE under high voltage (challenge (3)) received a few research attentions. The instability of PEO under high voltage makes it challenging to couple with high voltage cathode such as LiCoO$_2$. Even though PEO-based SPEs show excellent stability with LiFePO$_4$ cathodes with charging voltage below 4 V (vs. Li/Li$^+$),15 the limited...
theoretical energy density of LiFePO₄ restrains its further application in future electric transportations. Alternatively, layer structured oxide cathodes such as LiCoO₂ have a high specific capacity and high charge/discharge voltage, which makes them promising candidates for high energy density ASSLBs. Since the practical capacity of LiCoO₂ is positively related to the charging cut-off voltage, a high cut-off charge voltage is required for high energy density applications. However, charging cut-off voltage over 4.5 V remains a challenge for PEO-based SPEs due to the decomposition of PEO-based SPEs at high voltage. 

One solution to enable PEO-based SPEs coupling with high voltage LiCoO₂ is interfacial engineering SPEs and LiCoO₂ active materials interface with coating player. Coatings on LiCoO₂ particles with Al₂O₃, Li₂PO₄, poly(ethylcyanoacrylate) (PECA), and Li₄AlₓTi₄₋ₓ(PO₄)₃ (LATP) have been reported to improve the solid-state batteries performances. However, most of these previous studies only studied the coating effect on active materials/SPE interface while conductive carbon/SPE interface is ignored. Unfortunately, conductive carbon has been proved to be able to accelerate the decomposition of SSEs including PEO-based SPE, oxide-based SSEs and sulfide-based SSEs. Thus, the detrimental effect of conductive carbon for the PEO-based SPE cannot be neglected in high voltage ASSLBs. Therefore, systematic studies on the effects of coatings on active material particles versus on the whole electrodes (i.e. covering both active materials and conductive carbon) are important to disclose the interfacial engineering mechanism and can provide us helpful insights for future high energy density ASSLBs’ designs.

Herein, atomic layer deposition (ALD), as an emerging technique, which is capable of depositing uniform and conformal thin films with precise thickness control by self-limited chemical reactions, is chose for realizing active material coating and whole electrode coating because ALD process can be carried out at a low temperature compared to other chemical/physical deposition techniques such as chemical vapor deposition (CVD), physical vapor deposition (PVD), sol-gel method, etc. Thus, ALD can be non-destructive to electrode components (cathode particles and conductive carbon). In this study, ALD derived lithium tantale protective coatings are demonstrated to stabilize the interface between PEO-based SPEs and LiCoO₂ electrodes at high voltage (4.5 V vs. Li/Li’). Effects of coatings on either the LiCoO₂ particles, the whole electrode, and conductive carbon particles are compared. The results show that coating on LiCoO₂ particles cannot improve the performance of ASSLBs, while the coating on whole electrode sheets (coating on both LiCoO₂ particles and carbon particles) show significant enhancement in cycling performance so the same as the coating on conductive carbon particles. The working mechanism of ALD coating is illustrated at Figure 1. These results highlight that a suitable coating approach is critical in preventing the electrochemical oxidation of PEO-based SPE at high voltage for the stabilization of high voltage performance of ASSLBs.

### Preparation of PEO-based SPE

PEO (M.W. 1000,000), LiClO₄ (purity, 99.9 %) and garnet-type SSE (Li₆.₄La₂Zr₁.₄Ta₀.₄O₁₉, LLZTO) were dried in a vacuum oven before use. 0.24 g of LLZTO was added into 50 mL of acetonitrile (AN) and mixed by ultrasonication for 5 h. Then, 1.2 g of PEO and 0.19 g of LiClO₄ were added into the mixture and stirred overnight at room temperature. This homogeneous mixture was cast onto a Teflon substrate and dried at room temperature overnight to slowly evaporate the AN, followed by vacuum drying at 60 °C for 2 days. The obtained PEO-LiClO₄-LLZTO SPE membrane was immediately transferred to an Ar-filled glovebox and rest over 3 days before use.

### LiCoO₂ electrode preparation

Bare LiCoO₂ electrodes were prepared by mixing 90 wt. % of LiCoO₂ particles, 6 wt. % carbon-black (Acetylene Black) and 4 wt.% poly(vinylidene) fluoride binder in the N-methylpyrrolidinone (NMP) solvent. The slurry was coated on an Al foil by doctor blade method. The electrode was obtained after drying in a vacuum oven at 120 °C overnight. The loading of LiCoO₂ was around 1.5 - 2 mg/cm². The obtained bare LiCoO₂ electrode was used directly for electrode coating. ALD LTO coatings on LiCoO₂ particles or electrodes followed a previously reported ALD procedure from our group, Briefly, the LTO coatings were deposited using an ALD reactor (Savannah 100, Cambridge Nanotechnology Inc., USA) by alternatively pulsing lithium tert-butoxide, tantalum(V) ethoxide and H₂O at 235 °C.

### Electrochemical performance testing

All solid-state LiCoO₂ batteries were assembled in the 2032 type coin cells in an argon-filled glove box (Vacuum Atmosphere Company, moisture and oxygen level less than 1 ppm). The LiCoO₂ electrodes and lithium foils were used as the working electrodes and the counter electrodes, respectively. PEO-LiClO₄-LLZTO SPE was used as both separator and lithium ion conductor. No additional solvent or liquid electrolyte was applied into the LiCoO₂ ASSLBs. Galvanostatic charge/discharge were tested between 2.7 and 4.5 V in a 60 °C oven using a LAND Battery Tester. The ASSLBs were rested at 60 °C over 30 h before testing. For LiCoO₂ battery with liquid electrolyte, 2032 type coin cells were assembled with a liquid electrolyte containing 1 M LiPF₆ in ethylene carbonate (EC): ethylmethyl carbonate (EMC): diethyl carbonate (DEC) solvents with 1:1:1 of volume ratio, using a Celgard separator. Cyclic Voltammogram of the LiCoO₂ batteries were tested between 2.7 and 4.5 V (vs. Li/Li’) at 60 °C. Linear sweep voltamogram of Li/SPE/PEO-carbon cell was conducted from open-circuit voltage to 4.5 V on the versatile multichannel potentiotstat 3/Z (VMP3). PEO-carbon composite electrodes consisted of 70 wt.% PEO and 26 wt.% carbon-black (with/without LTO coating) and 4 wt.% LiClO₄ was used as the working electrode. Electrochemical impedance spectroscopy (EIS) were performed on the versatile multichannel potentiotstat 3/Z (VMP3) by applying an AC voltage...
with 10-mV amplitude in the frequency range from 500 kHz to 0.01 Hz.

Material characterizations

The morphology of the samples was characterized using a Hitachi S-4800 field emission scanning electronic microscopy (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDX). FIB was conducted in LED (Zeiss) 1540XB FIB/SEM machine. Mass Spectrometry was conducted in a Shimadzu GCMS-QP2010 gas chromatograph/Mass Spectrometer. X-ray absorption spectroscopy (XAS) measurements using total electron yield (TEY) and fluorescence yield (FLY) modes at Co K-edge were collected at Canadian light source (CLS) at the Soft X-ray Micro-characterization Beamline (SXRMB) with a photon energy range of 1.7 - 10 keV utilizing a Si (111) crystal monochromator.

Results and discussion

Cathodes were prepared with LiCoO$_2$ particles, carbon black (Acetylene Black), and poly(vinylidene) fluoride binder at a weight ratio of 90:6:4. Using the advanced ALD technique, the lithium tantalate (LTO) coating was deposited on either the LiCoO$_2$ particles before electrode preparation (coating on LiCoO$_2$ active materials, referred to as LCO-coating) or on the electrode surface after casting and drying (coating on electrode, referred to as LCO+CB-coating) or on the carbon black particles before electrode preparation (coating on CB particles, referred to as CB-coating). Fig. S1a-c show the scanning electron microscope (SEM) images of a pristine LiCoO$_2$ electrode, an electrode with ALD LTO coated LiCoO$_2$ particles (LCO-coating), and an ALD LTO coated electrode (LCO+CB-coating). The three electrodes with or without these two types of coatings show very similar morphology, indicating that the ALD LTO coatings were conformal and non-destructive. The LCO-coating did not alter the distribution of the conductive carbon on the electrode surface, nor did LCO+CB-coating. In addition, from the SEM images, one can easily find that the electrode/SPE interface actually has a large proportion of conductive carbon/SPE interface since carbon black is uniformly distributed/covered on the LiCoO$_2$ particles surface.

![Fig. 1 Schematic diagram shows the working mechanism of ALD coating for enabling stable, high voltage solid polymer electrolyte-based lithium ion batteries. The decomposition of SPE on (a) unprotected LiCoO$_2$ electrode and (b) electrode with protected LiCoO$_2$ particles (LCO-coating), and the working mechanism of (c) protected electrode (LCO+CB-coating) in ASSLBs after extensive charge/discharge cycles. Conductive carbon can accelerate the decomposition of SPE at high voltage, thus, the protection of carbon/SPE interface is very important for stabilizing high voltage solid-state lithium ion batteries.](image_url)

Transmission electron microscopy (TEM), SEM and Energy-dispersive X-ray spectroscopy (EDX) analysis were used to confirm the deposition of the ALD coatings on active materials and electrode (Fig. 2 and Fig. S2-5). Fig. 2a shows the TEM image of ALD coating on LiCoO$_2$ particle and the schematic illustration of LCO-coating electrode is presented in Fig. 2b. Differently, ALD LTO coated electrode (LCO+CB-coating) shows a coating on both carbon black and LiCoO$_2$ particles (Fig. 2c). EDX mapping in Fig. S3 confirms that ALD LTO is deposited on both CB and LCO particles surface for LCO+CB-coating electrode. This type of electrode structure is schematically illustrated in Fig. 2d. Hereby, two types of protective coverages are established: (I) partial protection between the LiCoO$_2$/SPE interface only and (II) full protection on the entire electrode covering both LiCoO$_2$ and conductive carbon. The electrochemical performance will be compared systematically.

Cyclic voltammetry (CV) was performed to study the electrochemical process of LiCoO$_2$ ASSLBs with different coatings. For comparison, CV of a regular LiCoO$_2$ battery with commercial carbonate-based liquid electrolyte was collected for a comprehensive understanding. As shown in Fig. S6a, the anodic peaks corresponded to the Li$^+$/oxide process, and the cathodic peaks were related to the Li$^+$ insertion process. There are three pairs of peaks which are correspondent to three oxidation/reduction couples. The redox pair at 4.07/3.74 V is the result of the conversion between Co$^{3+}$ and Co$^{4+}$ for the first-order phase transformation between two hexagonal phases. The other two pairs of anodic/cathodic peaks were related to the order-disorder phase transformation between hexagonal...
and monoclinic phases.\textsuperscript{26-28} In contrast, in ASSLBs, the three pairs of redox peaks are combined into a pair of broad peaks for all three cells with bare LiCoO\textsubscript{2} electrode, electrodes with LCO-coating protection and LCO+CB-coating protection (Fig. S6b-d). This is probably because of the sluggish Li\textsuperscript{+} transport in SPE and electrodes that broadens the peaks related to the first-order phase transformation reaction, overlapping the other weak peaks. Nevertheless, the ASSLBs with different cathodes still exhibit obvious difference in electrochemical behaviours. For the ASSLB with bare LiCoO\textsubscript{2} electrode, an anodic peak and a cathodic are observed with decreasing peak current intensities and increase in overpotentials over the three scans (Fig. S6b). This is a typical indication of decay in electrochemical redox reversibility. The decrease in peak current intensities and increase in overpotentials also occurs in the ASSLB with LCO-coating protection (Fig. S6c). As a conclusion, LCO-coating protection was insufficient in preventing the reversibility decay. In great contrast, instead of a decrease in peak current intensities and increase in overpotentials, the slightly increase in peak current intensities and the decrease in overpotentials indicates a more reversible electrochemical process of the LCO+CB-coating protected electrode (Fig. S6d).

![Image](https://example.com/image1.png)

**Fig. 2.** (a) Transmission electron microscopy (TEM) shows the ALD 10 cycles LTO (thickness is ~5 nm) coating on LiCoO\textsubscript{2} particle and its (b) schematic diagram of LiCoO\textsubscript{2} electrode with LCO-coating where conductive carbon is not protected. (c) SEM under backscattered electrons mode shows the ALD 20 cycles LTO (thickness is ~10 nm) coating on both conductive carbon and LiCoO\textsubscript{2} particles from the LCO+CB-coating sample after focused ion beam (FIB) cutting, and its (d) schematic diagram shows LiCoO\textsubscript{2} electrode where both LiCoO\textsubscript{2} and conductive carbon are protected. Binder is omitted in the schematic diagrams.

The electrochemical performances of ASSLBs with different protection coverages were characterized at 60 °C. Firstly, the coating thickness is optimized. Different ALD cycles of LTO were deposited on LCO-coating and LCO+CB-coating electrodes and their results are presented in Fig. S7. Clearly, the ALD LTO coating thicknesses were optimized to 10 ALD cycles for LCO-coating protection and 20 ALD cycles for LCO+CB-coating protection.

The ASSLBs performances with optimised ALD coating thickness for bare, LCO-coating, LCO+CB coating are compared in Fig. 3. In consistence with the CV results, observable voltage polarization along with serious capacity fading are already observed during the first 20 cycles of galvanostatic testing at 0.2 C for both ASSLBs with bare LiCoO\textsubscript{2} electrode (Fig. 3a) or LCO-coating protected electrode (Fig. 3b). This is possibly due to the severe decomposition of PEO-based SPE at high voltage that increases the interfacial resistance. Even though the LCO-coating protection can protect LiCoO\textsubscript{2}/SPE interface, the conductive carbon was still in direct contact with the SPE.

In contrast, much smaller polarization is observed for the ASSLB with LCO+CB-coating protected electrode (Fig. 3c). The discharge capacities are also relatively stable compared to the other two cells without protection or only with LCO-coating protection. Thus, the protection on carbon/SPE interface is evidently very important.

The dramatically different effects between LCO-coating and LCO+CB-coating protections on the electrochemical performance can be further verified by cycling performance and rate performance. Using the optimized conditions, ASSLBs with LCO+CB-coating protection demonstrates substantially enhanced performance over the ASSLBs without protection or with LCO-coating protection (Fig. 3d-f). While all three ASSLBs deliver a similar initial discharge capacity around 170-177 mAh/g, the retaining capacity of 110.4 mAh/g at 100th cycles for the ASSLB with LCO+CB-coating protected electrode is significantly higher than the remaining capacity of ~71 mAh/g for the other two ASSLBs (Fig. 3d). As disclosed in Fig. 3e, LCO+CB-coating protection also markedly enhanced the rate performance at lower current densities up to 0.6 C. However, at higher current densities, a higher capacity is achieved for LCO-coating electrode. The reason can be possibly attributed to the higher lithium ion diffusion in LCO-coating electrode compared to
to those of the bare and LCO+CB coating electrodes. In LCO-coating electrode, LCO particles are totally coated with LTO, which is a good lithium ion conductor. While in LCO+CB-coating protected electrode, only partial of LCO particles are exposed for ALD LTO deposition. Therefore, the lithium ion diffusion of LCO-coating protected electrode is better than those of LCO+CB-coating protected electrode (Fig. S8) and bare electrode. At high current density, lithium ion diffusion becomes a determining step for redox reaction. Thus, electrode with higher lithium ion diffusion can deliver a higher capacity.

LCO+CB-coating protection also can improve the initial Coulombic efficiency and subsequent average Coulombic efficiency. The initial Coulombic efficiencies for the ASSLBs with bare LiCoO$_2$ electrode, LCO-coating protection, and LCO+CB-coating protection electrodes are 93.8 %, 93.2 %, and 94.9 %, respectively; the subsequent average Coulombic efficiencies are 99.0 %, 98.6 %, and 99.3 % in orders. LCO-coating protection electrode actually shows barely any improvement over the bare LiCoO$_2$ electrode, indicating the protection of only LiCoO$_2$ particles is not enough in PEO-based ASSLB. The higher Coulombic efficiency by LCO+CB-coating protection indicates reduced decomposition of PEO-based SPE during high voltage charge/discharge cycles in ASSLBs.

![Graph](https://example.com/graph.png)

**Fig. 3** Charge/discharge profiles of ASSLBs with (a) bare LiCoO$_2$ electrode, (b) LCO-coating protected electrode, and (c) LCO+CB-coating protected electrode at 0.2 C and 60 °C. Corresponding (d) cycling performance, (e) rate performance, and (f) long-term cycling after rate performance for ASSLBs with different LiCoO$_2$ electrodes at 60 °C.

Electrochemical impedance spectroscopy (EIS) was conducted to study the evolution of interfacial resistance in the LiCoO$_2$ ASSLBs upon cycling (Fig. 4). The three ASSLBs without coating or with LCO-coating or with LCO+CB-coating present EIS spectra with similar shape but different evolution trends. There are two semicircles with one at high frequency and one at low frequency. Fig. 4d shows the equivalent circuit for fitting these EIS spectra. $R_e$ is the impedance from solid polymer electrolyte, $R_a$ is the interfacial impedance between lithium anode and SPE, and $CPE_1$ is its corresponding constant phase element. $R_c$ is the interfacial impedance between cathode and SPE, and $CPE_2$ is its corresponding constant phase element. All ASSLBs show relatively stable anode/SPE interfacial resistance with similar values, while dramatic difference present at the cathode/SPE interfaces. For the bare LiCoO$_2$ ASSLB (Fig. 4a), a significant increase in the cathode/SPE interfacial resistance is observed over 30 cycles, enlarging from 1338 Ω at the 10th cycle to 1843 Ω at the 20th cycle to 2891 Ω at the 30th cycle. Similarly, and
consistently with the electrochemical performance, a significant increase in the cathode/SPE interfacial resistance is also observed in the ASSLB with LCO-coating protection (Fig. 4b). The increase in cathode/SPE interfacial resistance can be attributed to the accumulation of insulating SPE decomposition products, which can block the Li\(^+\) ion transportation at the interface. In contrast, the cathode/SPE interfacial impedance of the ASSLB with LCO+CB-coating protection is stabilized to ~920 \(\Omega\) after 30 cycles, confirming the stable SPE/cathode interface enabled by the ALD LTO coating on the electrode. The EIS results strongly support the superior effects of ALD LTO protection for high-voltage ASSLBs.

To confirm that conductive carbon/SPE interface is important for the ASSLBs’ performances enhancement, a ASSLB with CB-coated electrode (a electrode with bare LiCoO\(_2\) and LTO coated CB). The results are presented in Fig. S10. It shows that LTO coating on carbon particles can also enhance the cycling performance of ASSLB, and its cycling performance is very similar to that of LCO+CB coated ASSLBs.

Why conductive carbon/SPE interface is so critical? It is well known electrochemical oxidation potential of PEO-based SPEs is around 3.8 V vs.Li/Li\(^+\) according to the linear sweep voltammogram method using a PEO-carbon composite electrode.\(^{10}\) Conventionally, it has been reported that electronic conductive additives (usually carbon black) play an important role in realizing completely utilization of electrode active materials for batteries, because the occurrence of electrochemical reactions requires both electrons and Li\(^+\) ions. However, in ASSLBs with Li\(^+\) ions conductive SSEs, the presence of conductive carbons could also trigger irreversible decomposition of the SSEs,\(^{23}\) leading to low Coulombic efficiency and performance decay.

![EIS spectra of ASSLBs](image)

**Fig. 4.** EIS spectra of ASSLBs with (a) bare LiCoO\(_2\) electrode, (b) LCO-coating protected LiCoO\(_2\) electrode, (c) LCO+CB-coating protected LiCoO\(_2\) electrode after 10, 20, and 30 cycles of charge/discharge. The insert tables show the critical frequency values on top of the high frequency semi-circle (Fa) and low frequency semi-circle (Fc) at different cycles of charge/discharge, respectively. (d) The equivalent circuit for fitting the EIS spectra.
Even conductive carbon black particles occupy low weight content in the electrodes, the large proportion of carbon/SPE interface among the cathode/SPE interface cannot be neglected (Fig. S1a-c). This could explain the similar performance of ASSLBs with bare LiCoO$_2$ electrode and LCO-coating electrode, whereas the carbon black particles are in direct contact with the SPE in either case. The linear sweep voltammetry results of carbon-SPE composite electrodes with or without ALD LTO coating also confirmed the importance of carbon/SPE interface. As shown in Fig. 5a, the overshooting current approaching 4.5 V is observed for bare carbon-PEO electrode, which indicates the serious decomposition of PEO at 4.5 V. In contract, this overshooting current is significantly reduced by the ALD LTO coated conductive carbon. As supported by the mass spectrometry results in Fig. S11b, the significant signals from decomposed SPE products is presented in bare carbon-PEO electrode. However, with ALD LTO coating on carbon, the signals from decomposed SPE is reduced (Fig. S11c), which demonstrates the excellent capability of LTO in stabilizing the carbon/SPE interface at high voltage. This may be the reason why the protection of conductive carbon/SPE interface can achieve such a significant enhancement in electrochemical performance.

However, why LCO-coating electrode shows almost no enhancement. It is possible that LiCoO$_2$ active particles are stable and further ALD protection cannot enhance its stability in our study. This conclusion is supported by the X-ray absorption spectroscopy (XAS) on the unprotected LiCoO$_2$ electrodes before and after cycling with the PEO-based SPE. The Co K-edge XAS for LiCoO$_2$ electrodes before and after 5 charge/discharge cycles at discharge state in ASSLBs showed almost no difference under both total electron yield (TEY) mode (Fig. 5b) and fluorescence yield (FLY) mode (Fig. 5c). TEY mode provides surface chemical information up to several nanometers, FLY mode reveals bulk chemical information. The XAS results indicated that the LiCoO$_2$ active materials are relatively stable from surface to bulk upon cycling in PEO-based ASSLBs. This is also supported by the stable cycling performance of LiCoO$_2$ battery with carbonate-based liquid electrolyte (Fig. S12).

Conclusions

The effects of ALD lithium tantalate coatings on cathode active material particles, coating on carbon black particles or coating on electrode surface were studied systematically for enhancing the high-voltage performance of PEO-based ASSLBs. Using stable LiCoO$_2$ particles as an example for high voltage cathode up to 4.5 V, we demonstrated the importance of the protection on the conductive carbon/SPE interface. It is found that interfacial protection covering the carbon/SPE interface was very important to stabilize the PEO-based SPE at high voltage and enhance the cycling performance of ASSLBs. Significantly improved cycling performance and rate performance were demonstrated in ASSLBs with simply 20 ALD cycles of lithium tantalate coating on the electrodes surface. This study shed lights on the important guidance for rational design of protective coating for polymer electrolyte-electrode interface to enhance the high voltage performance of ASSLBs.

Conflicts of interest

There are no conflicts to declare.

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Statement of Contributions

J. Liang, Q. Sun and X. Sun conceived the idea and experiments; J. Liang conducted the electrode/SPEs preparations, electrochemical performance testing, SEM. Y. Zhao, F. Zhao and Y. Sun helped to conduct ALD coating experiment. Y. Sun assisted in the Synchrotron XAS measurement; J. Luo, X. Li, R. Li, X. Lin, L. Zhang, S. Lu and H. Huang participated data analysis and discussion; J. Luo polished the manuscript; X. Sun supervised the overall project. All authors discussed the results and commented on the manuscript.

Notes and references


