Nanoscale Interface Modification of LiCoO₂ for Solid-State Li Batteries

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Abstract

Cycle stability of solid state lithium batteries (SSLBs) using a LiCoO$_2$ cathode is improved by atomic layer deposition (ALD) on active material powder with Al$_2$O$_3$. SSLBs with LiCoO$_2$/Li$_{3.15}$Ge$_{0.13}$P$_{0.85}$S$_4$/77.5Li$_2$S-22.5P$_2$S$_5$/Li structure were constructed and tested by charge-discharge cycling at a current density of 45 $\mu$A cm$^{-2}$ with a voltage window of 3.3 ~ 4.3 V (vs. Li/Li$^+$). Capacity degradation during cycling is suppressed dramatically by employing Al$_2$O$_3$ ALD-coated LiCoO$_2$ in the composite cathode. Whereas only 70% of capacity retention is achieved for uncoated LiCoO$_2$ after 25 cycles, 90% of capacity retention is observed for LiCoO$_2$ with ALD Al$_2$O$_3$ layers. Electrochemical impedance spectroscopy (EIS) and transmission electron microscopy (TEM) studies show that the presence of ALD Al$_2$O$_3$ layers on the surface of LiCoO$_2$ reduces interfacial resistance development between LiCoO$_2$ and solid state electrolyte (SSE) during cycling.
Lithium-ion batteries (LIBs) are widely utilized in portable electronics and are one of the major contestants for the hybrid electric-vehicle (HEV) and electric-vehicle (EV) market because of their high energy density.\textsuperscript{1} Despite of their broad exploitation in the energy storage field, certain issues such as flammability and vulnerability in high temperature environments related to the use of organic liquid electrolytes in commercialized LIBs are primary concerns which prevent a large scale-up of LIBs for HEVs and EVs today.\textsuperscript{2,3} As a result, there is a growing interest in solid state lithium batteries (SSLBs) employing a solid state electrolyte (SSE) which is safer and more durable than LIBs with a liquid electrolyte.\textsuperscript{4} However, inferior cycle performance resulting from the continous development of interfacial resistance layer between cathode and electrolyte materials in SSLBs is one of the major drawbacks which needs to be overcome for the successful commercialization of secondary SSLBs.\textsuperscript{3,5}

LiCoO$_2$ is the most widespread cathode material for commercial LIBs.\textsuperscript{5} It is typically utilized at voltages up to 4.2 V (vs. Li/Li$^+$) to prevent a significant capacity fade.\textsuperscript{6} Enabling stable cycling in a higher voltage region above 4.2 V (vs. Li/Li$^+$) would result in an increase of an available capacity. However, it is well known that the interfacial resistance between LiCoO$_2$ and SSE increases significantly and leads to the rapid capacity fade when the battery is cycled at a high voltage over 4.2 V (vs. Li/Li$^+$).\textsuperscript{6} Surface modification of LiCoO$_2$ by oxide coating has been proven to be effective for (i) lowering interfacial resistance between LiCoO$_2$ and SSE, (ii) reducing cobalt dissolution of LiCoO$_2$ into an electrolyte, and (iii) repression of side reactions between LiCoO$_2$ and electrolyte.\textsuperscript{5-7} Therefore, a good capacity retention is achieved by oxide coatings on LiCoO$_2$ even with a high upper limit voltage over 4.2 V (vs. Li/Li$^+$).\textsuperscript{6,7} In most cases, however, heat treatments of oxide-coated LiCoO$_2$ at high temperatures were needed.\textsuperscript{6-11} It was shown that an enhancement in the electrical conductivity for oxide-coated LiCoO$_2$ occurred by ionic diffusion between oxide coating layer and LiCoO$_2$ after such heat treatments.\textsuperscript{8,9} Also, an improvement of Li ion diffusion in Al$_2$O$_3$-coated
LiCoO$_2$ after the heat treatments was achieved by forming the layer with a high Li ion conductivity near LiCoO$_2$.$^{10,11}$

Typically, wet chemical methods such as spray coating and the sol-gel method are used for surface modification.$^{3,5-9}$ However considerable quantities of solvent and precursor are consumed in these methods. On the other hand, our group’s previous works have successfully demonstrated the application of Al$_2$O$_3$ ALD on LiCoO$_2$ powder for LIBs employing liquid electrolytes, showing large improvements in cycle performances.$^{12,13}$ ALD is a conformal coating method which needs minimal amounts of precursors.$^{12}$ Also, ALD can provide uniform coatings on nanosized LiCoO$_2$ particles because of its atomic thickness control.$^{13}$ The thickness of 1.1 ~ 1.2 Å is achieved for each ALD Al$_2$O$_3$ layer from one ALD sequence.$^{14,15}$

In this work, we prepared SSLBs using a double layer SSE configuration which has previously shown to provide stable interfaces between electrodes and SSE layers.$^{16}$ LiCoO$_2$ powders with/without ALD Al$_2$O$_3$ layers have been investigated. Galvanostatic charge-discharge behaviors and electrochemical impedance during cycling were monitored to investigate the effect of ALD Al$_2$O$_3$ layer on the cycle stability of the battery using LiCoO$_2$. The interfaces between uncoated and Al$_2$O$_3$ ALD-coated LiCoO$_2$ and Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE were investigated using TEM and energy dispersive spectroscopy (EDS). Results show that the employment of ALD Al$_2$O$_3$ layers on LiCoO$_2$ powders drastically improves cycle stability of SSLBs.

**Experimental**

Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE and 77.5Li$_2$S–22.5P$_2$S$_5$ (mol %) SSE were synthesized by planetary ball milling (PBM) of reagent-grade powders of Li$_2$S (Alfa Aesar, 99.9%), P$_2$S$_5$ (Sigma Aldrich, 99%), and GeS$_2$ (City Chemical LLC., 99.99%) in appropriate weight ratios in a stainless steel jar with stainless steel balls for grinding. PBM (SFM-1, MTI Corporation)
proceeded at 500 rpm for 20 continuous hours to generate well mixed SSE powders. Heat treatment (HT) for as-ball-milled (ABM) \( \text{Li}_{3.15}\text{Ge}_{0.15}\text{P}_{0.85}\text{S}_4 \) SSE powder was performed inside the glove box on a hot plate and heated up to 360°C at approximately +10 °C min\(^{-1}\) in a sealed glass container. SSE remained at 360°C on the hot plate for 2 hours before being removed and placed on a cooling rack. All sample preparations and HTs were done in a dry Ar-filled glove box.

ALD \( \text{Al}_2\text{O}_3 \) layers were deposited directly on \( \text{LiCoO}_2 \) powders (LICO Technology Corp.) using a rotary reactor as described in our previous work.\(^{12}\) \( \text{LiCoO}_2 \) powders with ALD \( \text{Al}_2\text{O}_3 \) layers were put in a Petri dish and placed on a hot plate for HT (+10°C min\(^{-1}\), 400°C, 14 hours) inside a dry Ar-filled glove box before battery construction. \( \text{LiCoO}_2 \) (uncoated/\( \text{Al}_2\text{O}_3 \) ALD-coated), heat-treated \( \text{Li}_{3.15}\text{Ge}_{0.15}\text{P}_{0.85}\text{S}_4 \) SSE, and acetylene black (AB, Alfa-Aesar, 50% compressed) were mixed in a weight ratio of 20:30:3 and ground with a mortar and a pestle to prepare the composite cathode material. The double layer SSE was constructed by hand-pressing 100 mg of heat-treated \( \text{Li}_{3.15}\text{Ge}_{0.15}\text{P}_{0.85}\text{S}_4 \) SSE on the top of 100 mg of hand pressed ABM 77.5Li\(_2\)S-22.5P\(_2\)S\(_5\) (mol %) SSE followed by cold-pressing at 1 metric ton for 3 minutes. 10 mg of the composite cathode material was evenly spread on the top of \( \text{Li}_{3.15}\text{Ge}_{0.15}\text{P}_{0.85}\text{S}_4 \) SSE layer and pelletized by cold-pressing at 5 metric tons for 3 minutes. Lithium foil (Alfa-Aesar, 0.75 mm thick) was then attached to the 77.5Li\(_2\)S-22.5P\(_2\)S\(_5\) (mol %) SSE side at 2 metric tons. All pressing and experimental operations were done in a polyaryletheretherketone (PEEK) mold (\( \varphi = 1.3 \text{ cm} \)) with Ti metal cylinders as current collectors for both working and counter electrodes. Figure 1 shows the schematic of our \( \text{LiCoO}_2/\text{Li}_{3.15}\text{Ge}_{0.15}\text{P}_{0.85}\text{S}_4/77.5\text{Li}_2\text{S}-22.5\text{P}_2\text{S}_5/\text{Li} \) battery. Galvanostatic charge-discharge cycling was carried out between 3.3 ~ 4.3 V (vs. \( \text{Li/\text{Li}^+} \)) at a current of 45 \( \mu \text{A cm}^{-2} \) at 30°C using an Arbin BT2000. All battery fabrication processes and charge-discharge cycling were conducted in a dry Ar filled glove box.
Electrochemical impedance spectroscopy (EIS) measurements of SSLBs utilizing uncoated and Al$_2$O$_3$ ALD-coated LiCoO$_2$ were collected using a Solartron 1280C. AC impedance profiles were obtained using amplitude of 10 mV and a frequency range from 20 kHz to 1 mHz. Batteries were charged to 4.3 V (vs. Li/Li$^+$) with a current of 45 $\mu$A cm$^{-2}$ and held at 4.3 V (vs. Li/Li$^+$) for 1 hour before AC impedance profiles were recorded at the open-circuit voltage.

Pellets of our double layer SSLBs were collected from PEEK molds inside the glove box after the 33rd charge process for TEM analysis. A mobile air-lock chamber which keeps the pellets in a vacuum state was used during the loading of a pellet from the glove box to focused ion beam (FIB) machine (FEI NOVA200 dual beam system) to avoid air contact. TEM samples were prepared from cathode layers using FIB to investigate the interface of LiCoO$_2$/Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE. FIB sectioning was performed with Ga ion source. Figure 2 describes the process of TEM sample preparation using the FIB. A Pt deposition process shown in Fig. 2a mechanically protects the surface of cathode composites which contain LiCoO$_2$, SSE, and AB. Cross-sectioning of the sample is shown in Fig. 2b. Fig. 2c depicts the lift-out technique to obtain the cross-sectional sample which is followed by the attachment of the sample to a Cu TEM grid performed with a manipulating probe (100.7$^{\text{TM}}$, Omniprobe). The sample was milled with the beam condition of 10 kV and 30 ~ 50 pA to obtain a thickness of 50 ~ 90 nm. The resultant TEM sample is shown in Fig. 2d. LiCoO$_2$/Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE interfaces were investigated using the TEM (FEI Tecnai F20) operated at 200 kV to observe interfacial layers. Energy dispersive spectroscopy (EDS, EDAX Tecnai 136-5) analyses were performed to verify the thickness of interfacial layers formed at LiCoO$_2$/Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE interfaces.

**Results and Discussion**

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Figure 3 shows the 1st discharge voltage profiles of SSLBs using uncoated and Al$_2$O$_3$ ALD-coated LiCoO$_2$ powders. The initial discharge capacity decreases as the number of ALD Al$_2$O$_3$ layers increases. The same phenomena were reported in our group’s previous work of liquid LIB using Al$_2$O$_3$ ALD-coated LiCoO$_2$ powders. The decrease in discharge capacity is attributed to the insulating property of ALD Al$_2$O$_3$ layer which compromises electronic conductivity between active LiCoO$_2$ cathode particles.

In order to investigate the effect of ALD Al$_2$O$_3$ layer on cycle stability of our SSLBs, galvanostatic charge-discharge cycling was carried out between 3.3 ~ 4.3 V (vs. Li/Li$^+$). Figure 4a displays cycle performances of the SSLBs with uncoated LiCoO$_2$ powders and LiCoO$_2$ powders with ALD Al$_2$O$_3$ layers. As shown in Fig. 3, the initial discharge capacities of batteries using LiCoO$_2$ powders with 2 & 4 ALD Al$_2$O$_3$ layers are smaller than that of the battery using uncoated LiCoO$_2$ powders. However, capacity fade is reduced for LiCoO$_2$ powders with 2 & 4 ALD Al$_2$O$_3$ layers. As a result, SSLBs using LiCoO$_2$ powders with 2 & 4 ALD layers maintain 90% of their initial discharge capacities after the 25th cycle whereas the battery with uncoated LiCoO$_2$ retains only 70% of the initial discharge capacity. It is clear that ALD Al$_2$O$_3$ layers on LiCoO$_2$ powders improve cycle stability significantly.

Charge-discharge voltage profiles of SSLBs using uncoated and Al$_2$O$_3$ ALD-coated LiCoO$_2$ powders at the 3rd and the 21st cycle are compared in Fig. 4b, 4c, and 4d. All of them exhibit the decrease in both charge and discharge capacities between the 3rd and the 21st cycle. As cycle number progresses, however, smaller overpotentials during both charge and discharge processes develop for batteries using LiCoO$_2$ powders with 2 & 4 ALD Al$_2$O$_3$ layers. This result indicates that there is smaller increase in interfacial resistance in batteries using Al$_2$O$_3$ ALD-coated LiCoO$_2$ powders than that in the battery using uncoated LiCoO$_2$ powders. This improved interfacial stability is corroborated by EIS and TEM analyses in Fig. 5 and 6.
The comparison of the AC impedance profiles of SSLBs at various cycles using uncoated LiCoO$_2$ powders and LiCoO$_2$ powders with 4 ALD Al$_2$O$_3$ layers is presented in Fig. 5. Similar to previous works by Sakuda et al., the bulk resistance of the SSE is shown in the high frequency region while the charge transfer resistance at the LiCoO$_2$/Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ interface corresponds to the size of the large semicircle.\textsuperscript{6,18} Significant growth in the size of the semicircle during cycling is observed in the SSLB with uncoated LiCoO$_2$ powders as shown in Fig. 5a. This increase in the resistance is attributed to the increased charge transfer resistance at the interface between uncoated LiCoO$_2$ and the Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE in the cathode composite during cycling. Sakuda et al. showed that the formation of an interfacial layer between LiCoO$_2$ and SSE is one of the mechanisms for increased interfacial resistance during charge-discharge cycling.\textsuperscript{5} On the other hand, the charge transfer resistance at the interface between LiCoO$_2$ with 4 ALD Al$_2$O$_3$ layers and SSE increases in early cycles but exhibits little change after the 12th cycle. This result indicates that the increase of the charge transfer resistance resulting from undesirable side reactions at the interface between LiCoO$_2$ and SSE can be suppressed by ALD Al$_2$O$_3$ layers.

TEM Analyses of the interface between LiCoO$_2$ and Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE in composite cathodes were performed to elucidate the mechanism for the increase in the interfacial resistance during cycling. Two SSLBs using uncoated LiCoO$_2$ powders and LiCoO$_2$ powders with 4 ALD Al$_2$O$_3$ layers were charged up to 4.3 V (vs. Li/Li$^+$) and held at 4.3 V (vs. Li/Li$^+$) for 1 hour in the 33rd cycle and then pellets of SSLBs were collected from PEEK molds for TEM analyses. Figure 6a shows the high-angle annular dark field (HAADF) TEM image of the boundary between uncoated LiCoO$_2$ and Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE. It clearly shows an interfacial layer at the interface between the uncoated LiCoO$_2$ and Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE. Figure 6b shows elemental concentration profiles by EDS line scan across the interface which was conducted to obtain the compositional information of the interfacial layer. Co is chosen for the element representing LiCoO$_2$ region while S and P are selected for the
elements defining the SSE region. EDS line profiles show the region where Co, S, and P coexist indicating mutual diffusion of these 3 elements which we attribute to the formation of an interfacial layer between LiCoO$_2$ and the SSE during cycling. We chose the Co profile as a criterion to determine the thickness of the interfacial layer since Co is the heaviest elements among three elements and thus least affected by Ga ion milling during FIB process. The diffusion of Co is estimated to be approximately 30 nm as shown in Fig. 6b. The development of this interfacial layer is believed to contribute to increased interfacial resistance during cycling.$^5$ Observation of the HAADF TEM image of the boundary between LiCoO$_2$ with 4 ALD Al$_2$O$_3$ layers and Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE is shown in Fig. 6c. EDS analysis in Fig. 6d show that the slope of the Co concentration profile in the interfacial layer region is steeper than that in Fig. 6b. The diffusion distance of Co which corresponds to the thickness of interfacial layer is estimated to be approximately 17 nm as shown in Fig. 6d. This reduced thickness of the interfacial layer is consistent with smaller increase in the charge transfer resistance of the battery using LiCoO$_2$ with 4 ALD Al$_2$O$_3$ layers discussed in Fig. 5. This result also indicates that the diffusion of Co out of LiCoO$_2$ with 4 ALD Al$_2$O$_3$ layers is greatly suppressed compared to the diffusion of Co out of uncoated LiCoO$_2$.

Conclusions

ALD coating of Al$_2$O$_3$ onto LiCoO$_2$ powders was adopted to enhance the cycle performance of SSLBs. The initial discharge capacity decreases with increasing number of ALD Al$_2$O$_3$ layers due to the insulating property of ALD Al$_2$O$_3$ layer. The batteries using LiCoO$_2$ powders with 2 and 4 ALD layers exhibit improved capacity retention during cycling compared to those using uncoated LiCoO$_2$ powders. Smaller overpotentials during charge/discharge process are observed from the batteries using LiCoO$_2$ powders with 2 and 4 ALD Al$_2$O$_3$ layers compared to that from the battery using uncoated LiCoO$_2$ powders. EIS studies reveal that ALD Al$_2$O$_3$ layers on LiCoO$_2$ powders suppress the development of
interfacial resistance at LiCoO$_2$/Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE interface. Microstructural and elemental analyses of LiCoO$_2$/Li$_{3.15}$Ge$_{0.15}$P$_{0.85}$S$_4$ SSE interfaces in composite cathodes were performed by using high resolution TEM and EDS. The interfacial layer thickness of the SSLB using LiCoO$_2$ with 4 ALD Al$_2$O$_3$ layers was thinner than that of the SSLB using uncoated LiCoO$_2$. We demonstrate that ALD Al$_2$O$_3$ layers on active materials effectively reduce the formation of interfacial layer which causes capacity fade during cycling. Therefore, Al$_2$O$_3$ ALD is proven to be an effective method for the modification of an interface between LiCoO$_2$ and SSE to improve the cycle performance of SSLBs.

Acknowledgments

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References


Figure captions

Figure 1. The schematic diagram of our double layer SSLB.

Figure 2. The process of TEM sample preparation by FIB. (a) Pt deposition. (b) Cross sectioning of the desired sample. (c) Sample lift out using a manipulating probe. (d) Obtained TEM sample on Cu grid.

Figure 3. The 1st discharge voltage profiles of SSLBs using uncoated and Al_2O_3 ALD-coated LiCoO_2 powders.

Figure 4. (a) Cycle performances of SSLBs using uncoated and Al_2O_3 ALD-coated LiCoO_2 powders. Charge-discharge voltage profiles of SSLBs at the 3rd & the 21st cycle using (b) uncoated LiCoO_2, (c) LiCoO_2 with 2 ALD Al_2O_3 layers, and (d) LiCoO_2 with 4 ALD Al_2O_3 layers.

Figure 5. AC impedances profiles of SSLBs using (a) uncoated LiCoO_2 and (b) LiCoO_2 with 4 ALD Al_2O_3 layers at various cycles.

Figure 6. (a) HAADF TEM image of uncoated LiCoO_2/Li_{3.15}Ge_{0.15}P_{0.85}S_4 SSE interface after the 33rd charging. (b) Elemental concentration profiles of Co, S, and P elements by EDS line scan at uncoated LiCoO_2/Li_{3.15}Ge_{0.15}P_{0.85}S_4 SSE interface after the 33rd charging. (c) HAADF TEM image of LiCoO_2 with 4 ALD Al_2O_3 layers/Li_{3.15}Ge_{0.15}P_{0.85}S_4 SSE interface after the 33rd charging. (d) Elemental concentration profiles of Co, S, and P elements by EDS line scan at LiCoO_2 with 4 ALD Al_2O_3 layers/Li_{3.15}Ge_{0.15}P_{0.85}S_4 SSE interface after the 33rd charging. Red arrows in (a) and (c) represent the positions and the directions of EDS line scans.
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 6.

(a) LiCoO$_2$ region
Interfacial layer
SSE region

(b) LiCoO$_2$ region
Interfacial layer
SSE region

(c) LiCoO$_2$ region
Interfacial layer
SSE region

(d) LiCoO$_2$ region
Interfacial layer
SSE region