Fast-Charging Halide-Based All-Solid-State Batteries by Manipulation of Current Collector Interface

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Poor rate capability is a significant obstacle for the practical application of inorganic all-solid-state lithium-ion batteries (ASSLIBs). The charge transfer kinetics at the interface of current collectors is crucial for high-rate capacity, but is typically neglected. In this paper, the interfacial evolution between Al foil current collectors and composite cathodes is studied in the LiCoO2/Li3InCl6 (LCO/LIC) ASSLIBs at both 25 and −10 °C. The results indicate that the side reactions between Al foil and LIC are the main challenges for the interfacial stability of current collector at 25 °C. The design of a graphene-like carbon (GLC) coating for the modification of Al avoids side reactions at the interface of current collector, resulting in improved cycling stability and high-rate capacity. GLC Al ASSLIB exhibits a high initial capacity of 102.9 mAh g−1 with a capacity retention of 89.1% after 150 cycles at 1 C. A high-rate capacity of 69 mAh g−1 is also achieved at 5 C. At −10 °C, the low Li+/electron transfer kinetics along with side reactions is the key limitation for the rate capability. Thanks to the GLC coating, the improved electrochemical performance is achieved with the enhanced charge transfer kinetics at the interface of current collector.

1. Introduction

Inorganic all-solid-state lithium-ion batteries (ASSLIBs) have advanced rapidly in recent years because of their intrinsic safety and continually improving ionic conductivity and interfacial stability.[3] For example, the high ionic conductivity of sulfide-based solid-state electrolytes (SSEs) has even surpassed those of conventional liquid electrolytes.[2] Halide-based SSEs, such as Li3InCl6 (LIC) and Li2.633Er0.633Zr0.367Cl6, with a wide electrochemical stable window realized along with a stable cathode interface, even without protective coatings.[3] As a result, the cycling stability of inorganic ASSLIBs has been significantly improved in recent literatures.[4] The long-term cycling performance of over 850 cycles has been achieved with a high capacity retention of 91.5%.[5] However, the high-rate capability of inorganic ASSLIBs still falls far below the requirements for the practical application of ASSLIBs in electric vehicles. From a U.S. Advanced Battery Consortium (USABC) report, fast-charging is defined as 40% capacity retention at current density of 4 C.[6] Unfortunately, state-of-the-art inorganic ASSLIBs can only operate at very low current densities, such as 0.1 and 0.2 C.

The main challenge of fast-charging inorganic ASSLIBs is the limited Li+ and electronic conductivities at both the internal and external interfaces of composite cathode. At the internal interface of composite cathode, on the one hand, the volume change of cathode materials led to reduced contact between cathode materials and SSEs, resulting in reduced Li+ transfer at the cathode/SSE interface.[7] To enhance the Li+ transfer kinetics, various in-situ SSE coating strategies for the surface modification of cathode materials were developed by solution-based methods.[8] Furthermore, the fabrication of thin SSE layer is also beneficial toward the shorter Li+ transfer.[9] On the other hand, the application of carbon additives in composite cathode to enhance the charge transfer kinetics faced tremendous obstacles. The high electronic conductivity of carbon additives accelerated the decomposition of SSEs, resulting in the formation of an undesirable interfacial layer in the composite cathode.[10] Although a strategy of applying semi-conductive additive...
obtained the improved rate capacity in our previous study,[11] the charge transfer kinetics still need further improvement at the internal interface of composite cathode. For example, the morphologies of conductive additives are very important to affect the utilization of the cathode and the degree of decomposition of SSEs.[12] At the external interface of the composite cathode, the interface of current collector is of crucial importance but is left neglected. Only a simulation work speculated that both the Li\(^{+}\) and electronic conductivities are restricted at the interface of current collector.[13] Accordingly, understanding of the degradation mechanism and design of rational strategy at the interface of current collector is critical for the high-rate performance of ASSLIBs.

In this study, we comprehensively investigate the interfacial evolution between Al foil and composite cathode during the electrochemical reactions in halide-based LIC ASSLIBs. Detailed electrochemical and X-ray characterizations combined with density functional theory (DFT) calculations and microscopy results indicate that the side reactions between Al foil and LIC SSE lead to the corrosion of Al foil and decomposition of LIC, resulting in the degradation of cycling stability and poor rate capability. Promisingly, a graphene like carbon (GLC) coating modified Al foil avoids the direct contact between Al foil and LIC, therefore circumventing the side reactions at the interface of current collector. As a result, the GLC Al ASSLIB demonstrates obviously improved rate capability and enhanced cycling stability. Impressively, a discharge capacity of 69 mAh g\(^{-1}\) is obtained at the current density of 5 C in the LiCoO\(_2\) (LCO) based ASSLIBs, which shows great potential for the application of fast-charging ASSLIBs. Promisingly, the GLC Al ASSLIB also shows much improved electrochemical performance at low temperature (\(-10\) °C), indicating that GLC modification not only avoids the side reactions but also enhances the Li\(^{+}\) and electron transfer kinetics at the interface of current collector. This study offers an idea of the interfacial modification for the fast-charging ASSLIBs in all-climate environments.

2. Results and Discussion

To investigate the interfacial evolution of the current collector, the bare and GLC Al foils were applied in this study. The morphologies of the as-prepared Al foils are shown in Figure 1a,b. Compared to the bare Al foil, GLC Al foil demonstrates enhanced surface roughness. From the enlarged scanning electron microscope (SEM) image of the GLC Al foil (Figure 1b3), the irregularly layered graphene sheets are uniformly coating on the surface of Al foil. The physical properties of the GLC coating layer are investigated by Raman and X-ray photoelectron spectroscopic (XPS) characterizations, respectively. As shown in Figure 1c, the Raman spectrum of GLC Al foil shows the characteristic peaks of graphene (D’ and 2D bands).[34] Meanwhile, the intensity ratio of 2D/G peaks indicates the multilayered character of GLC on the surface of Al foil.[35] C 1s XPS spectrum shown in Figure 1d indicates that the GLC coating layer has the nature of sp\(^2\) carbon. Moreover, the emerged C–O band suggests the strong bonding between GLC layer and native oxide layer on the Al foil, which is helpful for the effective adhesion and great electron transfer at the interface between the Al foil and GLC coating layer.[36]

In addition to the physical characterizations, electrochemical analyses are also conducted to investigate the interfacial stability between the as-prepared Al foils and LIC SSEs. First of all, the chemical stability is studied and the configuration of the designed model cell is shown in Figure S1a (Supporting Information). Electrochemical impedance spectroscopy (EIS) plots of the bare Al and GLC Al cells measured at various resting times are shown in Figure S2 (Supporting Information). The obviously increased interfacial resistance can be observed in the bare Al cell at the initial 2 h (Figure 1e). Although the interfacial resistance of bare Al cell is finally stable after 15 h, the large resistance of 250 Ω is still higher than that of the GLC Al cell. This result suggests that the interface between the bare Al foil and LIC is not stable even without electrochemical process. To evaluate the electrochemical stability between Al foil and LIC, the configuration of a model cell is designed (Figure S1b, Supporting Information) and the chronoamperogram profiles of the bare and GLC Al cells are shown in Figure 1f. The polarization voltage of the as-prepared cells was set at 4.2 V versus Li+/Li and held for 1 h. Interestingly, the initial current of the bare Al cell increased to 17.57 μA sharply and gradually decreased to 0.5 μA after 167 s. In contrast, the initial current maximum of the GLC Al cell is only 5.24 μA and the current quickly drops to 0.5 μA after 66 s. Furthermore, the cyclic voltammogram (CV) profiles of the bare and GLC Al cells are shown in Figure S3 (Supporting Information). Although the oxidation current of GLC Al cell is higher than that of the bare Al cell at 4.2 V because of the higher contact area in GLC Al cell, the interfacial resistance between Al foil and LIC is suppressed by the modification of GLC coating after the CV cycling (Figure S4, Supporting Information). Moreover, the change in contact resistance after CV testing indicates that the electronic conductivity at the interface between Al foil and LIC is improved by the GLC coating. Both the chronoamperogram and CV results suggest that the side reactions are actively occurring at the interface between bare Al foil and LIC during the electrochemical process. Impressively, GLC coating layer helps to stabilize the interface between Al foil and LIC SSE.

DFT calculations were conducted to obtain fundamental insights regarding the interfaces of LIC/Al and LIC/GLC, including their stability and electronic properties. The relaxed atomic structures of GLC, Al, and LIC are shown in Figure S5 (Supporting Information) with optimized lattice parameters summarized in Table S1 (Supporting Information). The previous DFT simulations have demonstrated that Al(111) and LIC(100) are the most stable surfaces for Al foil and LIC structures, respectively (Figure S6, Supporting Information).[37] Therefore, LIC(100)/Al(111) and LIC(100)/GLC surfaces were energetically optimized to explore their stability and the optimized lattice parameters and binding energies are shown in Figure 1g,h. At the interface between GLC and LIC, the higher binding energy of ~3.21 eV atom\(^{-1}\) indicates that the LIC(100)/GLC is energetically favored to form a more stable interface than the LIC(100)/Al(111). The Bader charge analysis for these two hybrid heterostructures was also performed.[38] As shown in Table S2 (Supporting Information), Li and In atoms lose electrons and the Cl atom gains electrons. Interestingly, Cl atoms...
gain electrons with partial transfer of 15.613 $|e|$ at the LIC(100)/GLC interface, which is higher than that of the LIC(100)/Al(111) interface with partial transfer of 15.613 $|e|$. When Cl atoms gain more electrons, stronger interactions between Cl atoms and other elements could be achieved. This result indicates that there are more significant charge transfer interactions at the LIC/GLC interface than that of the LIC/Al interface, proving that GLC has better contact with composite cathodes. Furthermore, Figure 1i shows the density of state (DOS) of both the LIC(100)/Al(111) and LIC(100)/GLC interfaces. Because of the absence of energy gap at the Fermi level, both LIC(100)/Al(111) and LIC(100)/GLC interfaces show a metallic character and are able to maintain a high electronic conductivity at the interface of current collector.

The electrochemical performance of the bare and GLC Al ASSLIBs at room temperature (25 °C) is comprehensively studied (Figure 2). LCO and LIC are mixed as the composite cathode combined with LIC as the electrolyte layer and In-Li
foils as the anode (Figure S1c, Supporting Information). To exclude the effect of other interfaces on the performance of the as-prepared ASSLIBs, 5 nm LiNbOx coated LCO fabricated by atomic layer deposition (ALD) is adopted as shown in Figure S7 (Supporting Information) and a thin Li6PS5Cl (LPSCl) layer was set between LIC and In-Li anode. Figure 2a compares the initial charge–discharge curves between the bare and GLC Al ASSLIBs at 0.1 C. An initial discharge capacity of 132.8 mAh g⁻¹ and a high initial Coulombic efficiency of 92.6% are achieved by the ASSLIB with GLC Al. In contrast, the bare Al ASSLIB delivers a lower initial discharge capacity of 125.6 mAh g⁻¹ with a larger irreversible capacity loss. Notably, at the beginning of discharge, the more obvious voltage plateaus derived from the phase transition of LCO can be observed in the GLC Al ASSLIB. This phenomenon suggests faster Li⁺ and electron transfer at the interface between GLC Al and composite cathode, resulting in higher average discharge voltage (3.91V vs 3.89 V) than that of the bare Al ASSLIB as shown in Figure 2b. From the CV profiles in Figure 2c, the GLC Al ASSLIB demonstrates smaller voltage intervals between the pairs of anodic–cathodic peaks and higher peak intensities than that of the bare Al ASSLIB as shown in Figure 2b. From the CV profiles in Figure 2c, the GLC Al ASSLIB demonstrates smaller voltage intervals between the pairs of anodic–cathodic peaks and higher peak intensities than that of the bare Al ASSLIB, indicating enhanced electrochemical reaction activity with lower resistance at the interface between GLC Al and composite cathode. Furthermore, the GLC Al ASSLIB also shows the half of the current compared to the bare Al ASSLIB at the cut-off voltage (4.2 V), suggesting the suppressed side reactions at the interface between GLC Al and cathode composites. The lithium-ion diffusion kinetics of the bare and GLC Al ASSLIBs are investigated by the galvanostatic intermittent titration technique (GITT). The corresponding polarization plots and lithium-ion diffusion coefficients (D_Li) during the initial charge–discharge process are demonstrated in Figure S8 (Supporting Information). The GLC Al ASSLIB shows higher D_Li at the end of the charge process and during the entire discharge process than that of the bare Al ASSLIB. This result indicates that Li⁺ and electron transfer at the interface between GLC Al and composite cathode is higher than that of the bare ASSLIB.

Figure 2d compares the rate capability of the bare and GLC Al ASSLIBs at variable charge–discharge current densities ranging from 0.1 to 5 C. The discharge capacities of the bare Al ASSLIB dramatically decay with an increase of current density. The capacities drop to zero when the current density increased to 5 C. In contrast, the GLC Al ASSLIB demonstrates improved rate capacities at each current density. The discharge capacities of over 103 and 69 mAh g⁻¹ are achieved at 1 and 5 C, respectively. Furthermore, the capacity retention of over 99% is achieved after 55 cycles in the GLC Al ASSLIB when the current density switches back to 0.1 C, which is much higher than the capacity retention of 89% in the bare Al ASSLIB. The long cycling stability of the bare and GLC Al ASSLIBs at 1 C is also demonstrated in Figure 2e. The GLC Al ASSLIB delivers an initial discharge capacity of 102.9 mAh g⁻¹ with a capacity retention of 89.1% after 150 cycles. In contrast, the bare Al ASSLIB shows a low initial discharge capacity of 84.4 mAh g⁻¹ with a poor capacity retention of 15.2% after 150 cycles. Moreover, the corresponding Coulombic efficiency and average discharge voltage during the cycling are shown in Figures S9 and S10 (Supporting Information), respectively. The GLC Al ASSLIB shows both improved Coulombic efficiency and average discharge voltage, thus obtaining an energy density greater than that of the bare ASSLIB. Furthermore, as shown in Figure S11 (Supporting Information), the GLC Al ASSLIB shows a smaller interfacial resistance after 150 cycles.
than that of the bare Al ASSLIB, demonstrating that the interface between Al foil and composite cathode could be stabilized by the modification of GLC coating during the cycling. The aforementioned electrochemical performance demonstrated in LIC-based ASSLIBs suggests that the GLC modified Al foil not only suppresses the side reactions but also helps to achieve the enhanced Li$^+$ and electron transfer at the interface between current collector and cathode. The improved performance of GLC Al ASSLIB is undoubtedly competitive when compared to other halide-based ASSLIBs (Figure 2f and Table S3, Supporting Information).

To investigate the interfacial evolution between the as-prepared Al foils and composite cathode during the electrochemical process, XPS measurements were performed. The cycled ASSLIBs were disassembled and both the surface of Al foils and composite cathodes were tested as shown in the schematic diagrams of Figure 3a,e,k, respectively. Compared to the Al 2p spectrum of the bare Al before cycling (Figure 3i), the obvious increased peak intensity of Al oxide is observed in the cycled bare Al. Interestingly, a new peak at 75.1 eV is emerged in the cycled bare Al, suggesting the formation of AlCl$_3$ or Al–O–Cl species after cycling (Figure 3b). This result suggests the severe corrosion of Al foil and/or the decomposition of LIC after cycling. Although the Cl 2p XPS signal is also detected in the cycled GLC Al, no obvious change in the Cl chemistry is observed when compared to the Cl 2p XPS spectrum of the pristine LIC. This result demonstrates that LIC just adhered on the surface of GLC layer rather than reacted with GLC layer during cycling.

In addition to the XPS analysis for the cycled current collectors, the XPS characterizations of the cycled bare and GLC composite cathodes are also performed as shown in Figure 3d,h, respectively. Consistent with the results of the cycled Al foils, the peak of AlCl$_3$ and/or InCl$_3$ is also observed in the Cl 2p XPS spectrum of the cycled bare cathode. In contrast, the well maintained Cl chemistry is shown in the cycled GLC cathode. Although there is no change of the In 3d XPS spectra in both the cycled bare Al and GLC cathodes (Figure S13, Supporting Information), the evolution of Cl 2p XPS spectra is enough to

Figure 3. XPS characterizations of the cycled bare and GLC Al current collectors and cathodes. a) Schematic illustration of X-ray beam on the surface of the cycled bare Al, b) Al 2p and c) Cl 2p XPS spectra of the cycled bare Al, d) Cl 2p XPS spectrum of the cycled bare cathode. e) Schematic illustration of X-ray beam on the surface of the cycled GLC Al, f) Al 2p and g) Cl 2p XPS spectra of the cycled GLC Al, h) Cl 2p XPS spectrum of the cycled GLC cathode. i) Al 2p spectrum of the bare Al. j) Cl 2p spectrum of Li$_3$InCl$_6$. k) Schematic illustration of X-ray beam on the surface of the cycled composite cathode.
demonstrate the side reactions between bare Al and LIC during the cycling. Furthermore, the unchanged Co 2p XPS spectra shown in Figure S14 (Supporting Information) indicate the ALD LiNbOₓ coated LCO is stable with both LIC and Al foil during the cycling.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was further performed to identify the appearance and depth information at the interface between Al foil and composite cathode after the cycling. With the Cs⁺ ion beam etching, the secondary ions of C⁻ and Al₃⁻ are measured in the GLC Al foil, indicating the GLC coating on the surface of Al foil with the thickness of 0.5 µm (Figure S15, Supporting Information). From the chemical ion images (Figure 4a), obvious Cl⁻ species are observed in the cycled bare Al, which is barely detected in the cycled GLC Al. In Figure 4b, the Cl⁻ signal is very strong at the beginning of sputtering in the cycled bare Al. Although decreasing quickly, Cl⁻ signal still can be detected after 300 s, indicating the severe side reactions between bare Al foil and LIC after cycling. In contrast, Cl⁻ signal dropped dramatically and disappeared after 400 s in the cycled GLC Al because of the protection of GLC coating layer (Figure 4c). The distributions of C⁻, Al₃⁻, and Cl⁻ species are also clearly presented in Figure 4d. The obvious Cl⁻ signal is observed on the surface of bare Al, which is suppressed in the cycled GLC Al. The Cl⁻ signal observed on the surface of GLC coating layer in a very small region may come from the LIC particles adhered on the surface of GLC layer. The aforementioned XPS and ToF-SIMS results indicate that the bare Al foil reacted with LIC during the cycling, resulting in the corrosion of Al foil and decomposition of LIC. However, the application of GLC Al avoids the direct contact between Al foil and LIC, therefore circumventing the side reactions at the interface between current collector and cathode.

The surface morphology evolutions of the bare and GLC Al after cycling are evaluated by the SEM characterization. Figure 5a,b shows the SEM images of the top view of the cycled bare Al. The severe cracks can be observed and extend to the deep inside of the Al foil after cycling (Figure 5a). Meanwhile, the by-products deposited on the surface of Al foil also can be observed because of the side reactions between bare Al and LIC during the cycling (Figure 5b). Energy-dispersive X-ray spectroscopy (EDS) mapping of the cycled bare Al confirms that the by-products enriched on the surface of Al, indicating the interfacial deterioration between Al foil and LIC after cycling (Figure 5c,d). In contrast, from the SEM image of the cycled GLC Al as shown in Figure 5e, the morphology of the GLC coating layer maintains well after cycling. Meanwhile, there is no Cl signal on the surface of the cycled GLC Al (Figure 5f), indicating that GLC coating layer is beneficial toward the stability of the interface between current collector and cathode.

The interfacial evolution of current collector is also investigated at low temperature (−10 °C). At the low temperature, the Li⁺ and electron transfer kinetics at the cathode interface are critical toward achieving good electrochemical performance. Figure 6a shows the initial charge–discharge curves of the bare and GLC Al ASSLIBs at −10 °C under the current density of 0.05 C. The reduced capacity in the as-prepared ASSLIBs is achieved as expectation compared to the counterparts at 25 °C. The decreased ionic conductivity of SSEs at low temperature is the main reason that leading to the slow Li⁺ and electron transfer kinetics. The ionic conductivity of SSEs at −10 °C is only one-tenth of that at 25 °C (Figure S16, Supporting Information). In addition to the limited ionic conductivity of SSEs, the interface of current collector is of crucial importance for the kinetics at the external interfaces of composite cathode. The GLC Al ASSLIB shows an initial discharge capacity of
99.9 mAh g⁻¹ with the Coulombic efficiency of 91.3%. However, the bare Al ASSLIB only delivers a discharge capacity of 76.5 mAh g⁻¹ with a lower Coulombic efficiency of 81.0%. Figure 6b shows the GITT curves of the bare and GLC Al ASSLIBs during the charging process. An obvious space-charge-layer effect is observed at the beginning of charging in the bare Al ASSLIB, indicating the inhomogeneous charge distribution at the interface of current collector. During the entire charging process, the bare Al ASSLIB demonstrates severe polarization voltage, which is 2.5 times higher than that of the GLC Al ASSLIB (Figure S17a, Supporting Information). Moreover, the $D_{Li}$ in the bare Al ASSLIB is limited by the reduced Li⁺ transfer kinetics, which can be enhanced by the GLC modification (Figure S17b, Supporting Information). The cycling stability of the bare and GLC Al ASSLIBs are shown in Figure 6c. The capacity retention of GLC Al ASSLIB is 85.9% after 100 cycles, which is much higher than the capacity retention of 421% in the bare Al ASSLIB. Furthermore, the GLC Al ASSLIB also demonstrates the improved Coulombic efficiency with higher average discharge voltage and reduced interfacial resistance (Figures S18 and S19, Supporting Information). In contrast, the Coulombic efficiencies of the bare Al ASSLIB are very low at the initial 10 cycles, further indicating the poor charge transfer kinetics at the interface of bare Al foil. The rate capability at −10 °C is shown in Figure S20 (Supporting Information). Compared to the bare Al ASSLIB, GLC Al ASSLIB exhibits much improved capacities at each current density, demonstrating a better charge transfer kinetics at low temperature.

The XPS characterization was conducted to study the interfacial stability between Al foil and LIC SSE at low temperature. Figure 6d shows the Al 2p XPS spectrum of the cycled bare Al. There is no AlCl₃ signal indicating that the corrosion of Al...
foil is suppressed at low temperature. Interestingly, the signal of InCl$_3$ is observed in the Cl 2p XPS spectrum of the cycled bare Al as shown in Figure 6e, suggesting the decomposition of LIC still occurs at low temperature. In contrast, both the Al 2p and Cl 2p XPS spectra of the cycled GLC Al indicate that the interface between Al foil and LIC SSE is stabilized by GLC coating (Figure 6f and Figures S21 and S22, Supporting Information). Furthermore, the composition of GLC coating layer was also not changed after cycling at low temperature, which is confirmed by the C 1s XPS spectrum (Figure S23, Supporting Information). SEM images of the cycled bare and GLC Al foils are shown in Figure S24 (Supporting Information). The defects on the surface of the bare Al are obviously suppressed at low temperature compared to the situation at room temperature. The aforementioned results indicate that the performance of ASSLIBs at low temperature is limited by the Li$^{+}$ and electron transfer kinetics along with the side reactions at the interface between current collector and composite cathode.

3. Conclusion

In conclusion, the interfacial stability between the current collector and composite cathode in inorganic ASSLIBs is investigated at both 25 and −10 °C by the comprehensive electrochemical, DFT, XPS, ToF-SIMS, and SEM characterizations. At room temperature, the side reactions at the interface between Al foil and LIC SSE are the main challenges that deteriorates the electrochemical performance. The modification of Al by GLC coating avoids the direct contact between Al foil and LIC SSE, therefore circumventing both the corrosion of Al foil and decomposition of LIC SSE. As a result, the notably improved electrochemical performance is achieved, including higher capacity, reduced voltage polarization, and better cycling stability. More importantly, the high-rate capability is significantly improved by the GLC modification. The discharge capacity of 69 mAh g$^{-1}$ is achieved in the GLC ASSLIB at 5 C, which surpasses the USABC target for fast-charging batteries. At low temperature, in addition to side reactions, the low Li$^{+}$ and electron transfer kinetics limit the electrochemical performance of inorganic ASSLIBs. GLC coating layer is beneficial toward the Li$^{+}$ and electron transfer at the interface between current collector and composite cathode, resulting in the improved capacity with the enhanced cycling stability. The results collected in this research indicate that current collector as the external interface in cathode is of critical importance for the performance of inorganic ASSLIBs. Both the interfacial reactions and kinetics should be considered when designing fast-charging ASSLIBs under the all-climate environments.

4. Experimental Section

Preparation of Current Collectors, Cathodes, and Solid-State Electrolytes: The synthesis process of bare and graphene like carbon (GLC) coated Al foils was reported in the previous studies and US patents [15a,21]. The commercial LiCoO$_2$ (LCO) was obtained from Sigma-Aldrich (99.8%). The ALD LiNbO$_x$ coated LCO was fabricated in a Savannah 100 ALD system (Ultratech/Cambridge Nanotech., USA) by using (CH$_3$)$_3$COLi, Nb(OCH$_2$CH$_3$)$_5$, and water as precursors. The deposition temperature was 235 °C. For the preparation of solid-state electrolytes (SSEs), Li$_3$InCl$_6$ (LIC) was synthesized by a water removal route. LiCl and InCl$_3$
were dissolved in deionized water with the stoichiometric molar ratio. The solution was dried under vacuum at both 100 and 200 °C. Li2PS5Cl (LPSCl) was synthesized following the mechanical milling and annealing process. Li2S, P2S5, and LiCl were mixed with the stoichiometric molar ratio and milled at 550 rpm. After that, the mixture was sealed in a quartz tube and annealed at 550 °C for 5 h.

**Assembly of the Model Cells and Electrochemical Testing:** In order to investigate the electrochemical performance, different types of model cells were fabricated. In the Al/LIC model cells, 60 mg LIC was pressed at 3 tons with 10 mm diameter to form a pellet, and then a piece of as-prepared Al foil with the same 10 mm diameter was put onto one side of LIC pellet and pressed at 0.5 tons of pressure. In the Al/LIC/LPSCl/In-Li cells, 60 mg LIC was first pressed at 1 ton, and then 30 mg LPSCl was spread onto one side of LIC and pressed at 3 tons. After that, the as-prepared Al foils were put onto the other side of LIC pellet and pressed at 0.5 tons. Finally, In and Li foils were put onto the surface of LPSCl and pressed at 0.5 tons. In the Al/LICO-LIC/LPSCl/In-Li cells, the difference was 3.5 mg and LCO power was mixed well with 1.5 mg LPSCl, and then uniformly spread onto the surface of LIC layer and pressed under 3 tons of pressure. Other parts were same as the process of Al/LIC/LPSCl/In-Li cells. All the processes were performed in an argon-filled glove box.

The galvanostatic charge–discharge characteristics were tested in the range of 2.1–3.6 V versus Li+/Li and Li/Li+, corresponding to 2.7–4.2 V versus Li+/Li. By using a multichannel battery tester (LAND CT-2001A, Wuhan Rambo Testing Equipment Co., Ltd., China). Cyclic voltamograms (CV) were collected on a versatile multichannel potentiostat 3/Z (VMP3) by applying an AC voltage of 10 mV amplitude in the 7000 kHz frequency range. For galvanostatic intermittent titration technique (GITT) measurements, the cells were charged and discharged with 0.1 C for 10 min and rest for 1 h. According to the GITT theoretical analysis, Li+ diffusion coefficient can be calculated by following equation:

$$D_{Li^+} = \frac{4}{\pi^2} \left( \frac{m_{Li^+} \Delta E_s}{M_{LCO} \Delta E_s} \right)^2 \left( \tau \ll L^2 / D \right)$$

where $D$ is chemical diffusion coefficient; $S$ is interfacial contact area between LCO and LIC SSEs in this case, the specific area of LCO is 0.5 $m^2$ g$^{-1}$; $\tau$ is pulse duration (600 s in this case), $\Delta E_s$ is the steady-state voltage change; $\Delta E_p$ is the transient voltage change; $m_{Li^+}$ is the mass of the LCO in the cathode composite (3.5 mg); $M_{LCO}$ is the molecular weight of LCO (97.87 g mol$^{-1}$); $V_{LCO}$ is the molar volume of LCO (19.56 $cm^3$ mol$^{-1}$).

**Characterizations:** The morphology and microstructure of the pristine and treated NMC811 were characterized using field emission scanning electron microscopy (FESEM, Hitachi S4800). The LiNbO3, coating layer on the surface of LCO was observed by a high-resolution transmission electron microscopy (HRTEM, JEOL 2010F). Raman scattering spectra were carried out by a HORIBA Scientific LabRAM HR Raman spectrometer system. X-ray photoelectron spectroscopy (XPS) testing was measured with a monochromatic Al Kα source (1486.6 eV) in a Kratos AXIS Nova Spectrometer. The Al filled glovebox was connected with the XPS machine to avoid the exposure of air. In the time-of-flight (ToF-SIMS) measurements, the action of the primary ion beam bombardment on the sample surface induced the emission of negative secondary ions. Sputtering with a Cs+ ion beam (3 keV) was used for depth profiling analysis.

**DFT Calculation:** All calculations were carried out within the DFT framework as implemented in Vienna Ab Initio Simulation Package (VASP). The projector augmented-wave pseudopotentials were used to describe the interaction between ions and electrons, and the exchange-correlation effects were treated using the Perdew–Burke–Ernzerhof (PBE) functional under the generalized gradient approximation (GGA). The electronic configurations were $1s^22s^2$ for Li, $2s^22p^2$ for C, $3s^33p^3$ for Cl and $5s^25p^3$ for In. The lattice parameters of Al and LIC were optimized using a Monkhorst-Pack grid k-point of $4 \times 4 \times 4$, and the kinetic energy cutoffs 520 eV were used. The VESTA package was used to visualize the various bulk, surface, and interface structures.[2] For surface calculations, the van der Waals (vdW) correction function proposed by Grimme was adopted, which can well describe the long-range vdW interaction.[24] The vacuum space in the z direction was about 15 Å to avoid the interaction between neighboring. The k-point mesh was set to be $4 \times 2 \times 1$ for hybrid heterostructures. All the atoms were optimized until the total energies converged to below $10^{-4}$ eV and the forces acting on atoms were less than $10^{-2}$ eV Å$^{-1}$. Furthermore, the binding energy was determined using the expression: $E_{Binding} = E_{A/LIC} - (E_A + E_{LIC})$, where $E_A$/LIC, $E_A$, and $E_{LIC}$ represent the total energy of the graphene/LIC(100)/[Al(111)/LIC(100)] interface, graphene (Al(111) surface), and LIC(100) surfaces slab. To keep the consistency of experiment and consider the time consumption, the multi-layered graphene was selected for DFT calculation.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

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