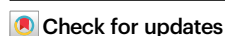


Li_2ZrF_6 protective layer enabled high-voltage LiCoO_2 positive electrode in sulfide all-solid-state batteries

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The application of high-voltage positive electrode materials in sulfide all-solid-state lithium batteries is hindered by the limited oxidation potential of sulfide-based solid-state electrolytes (SSEs). Consequently, surface coating on positive electrode materials is widely applied to alleviate detrimental interfacial reactions. However, most coating layers also react with sulfide-based SSEs, generating electronic conductors and causing gradual interface degradation and capacity fading. To address this, we propose a Li_2ZrF_6 coating layer on LiCoO_2 , which exhibits minimal reaction with SSEs, and its decomposition products are electron-conductive-free. Furthermore, this coating layer also efficiently mitigates the layered-to-spinel/rock-salt surface structural transformation in LiCoO_2 . As a result, the $\text{In-Li}|\text{Li}_6\text{PS}_5\text{Cl}|\text{Li}_2\text{ZrF}_6\text{-LiCoO}_2$ all-solid-state cell demonstrates an initial areal capacity of 5.2 mAh cm^{-2} and a capacity retention of 80.5% after 1500 cycles at 70 mA/g with high LiCoO_2 areal mass loading (30.19 mg cm^{-2}) and a cut-off voltage of 3.9 V (corresponding to potential of 4.5 V versus Li^+/Li), at 25°C .

Rechargeable batteries constitute pivotal technologies in the realm of clean energy storage and electric vehicle deployment¹. While conventional lithium-ion batteries have long powered a multitude of contemporary tools, they have increasingly raised safety apprehensions due to their utilization of flammable organic liquid electrolytes. In response, there has been a growing shift towards enhancing safety by replacing these organic liquid electrolytes with solid-state electrolytes (SSEs) to produce all-solid-state lithium batteries (ASSLBs). This transition is regarded as a promising strategy, given the substantially improved safety and the potential for achieving high energy densities in ASSLBs^{2,3}.

Among various types of SSEs, sulfide SSEs are the most attractive candidate for the next generation of energy storage technology due to their high ionic conductivity up to $10^{-2} \text{ S cm}^{-1}$ at room temperature, and favorable mechanical ductile nature^{4–8}. In pursuit of high energy densities in ASSLBs, the integration of high-voltage positive electrode active materials is generally implemented, such as LiCoO_2 (LCO), $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, and lithium-rich layered oxides^{9–16}. Unfortunately, multiple challenges have been encountered at the interface between positive electrode materials and sulfide SSEs. These challenges encompass the electrochemical oxidation of sulfide SSEs stemming from their inherent narrow electrochemical windows, undesired

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chemical reactions between positive electrode materials and sulfide SSEs due to the thermodynamic instability, and structural degradation of positive electrode materials resulting from O loss and the formation of spinel/rock-salt phase^{17–22}. All these issues adversely affect the electrochemical performance of ASSLBs and require urgent solutions.

The replacement of sulfide SSEs with halide SSEs may be a promising solution, given the latter possesses high stability against electrochemical oxidation and good chemical compatibility with high-voltage positive electrode materials^{23,24}. However, their metal cations can be easily reduced, leading to the formation of a mixed Li-ion and electronically conductive interlayer at the negative electrode interface, therefore necessitating the incorporation of an additional layer of sulfide SSEs²⁵. This will not only increase the difficulties of the fabrication process, but also lower the cell energy density. In addition, surface modification of sulfide SSEs is a possible method, but at the expense of lower ionic conductivity¹⁰. In addition to modifying SSEs, constructing a protective layer on the surface of positive electrode materials is a widely adopted and promising approach in common practice. For example, Liang et al.¹¹ showed gradient coating of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ with $\text{Li}_3\text{P}_{1-x}\text{O}_4\text{S}_{4x}$ can hinder the structural degradation during cycling and enable the stable electrochemical performance over 250 cycles. Additionally, Wang et al.¹⁵ presented a LiNiO_2 -based ASSLB with high areal capacity and stable cycling performance for over 200 cycles, achieved through the enhancement of structural stability and interfacial dynamics of positive electrode materials by a $\text{Li}_x\text{Al}_y\text{Zn}_z\text{O}_6$ protective layer. Furthermore, it has been demonstrated that prominent electrochemical performance can also be attained through the application of various other protective layers, such as $\text{Li}_{0.35}\text{La}_{0.5}\text{Sr}_{0.05}\text{TiO}_3$ ²⁶, TiNb_2O_7 ¹³, $\text{Li}_2\text{CoTi}_3\text{O}_8$ ²⁷, and the most representative LiNbO_3 (LNO)^{28–33}.

However, despite the use of these protective layers, sulfide-based ASSLBs still face challenges with capacity decay during cell operation. As shown in Supplementary Table 1, the majority of sulfide-based ASSLBs demonstrate restricted cycle life, often not exceeding 250 cycles, even under conditions of low positive electrode materials mass fraction and loading. Since the underlying factors are still obscure, it is essential to carefully evaluate the additional characteristic of coating materials other than ionic/electronic conductivity and electrochemical stability window. Two crucial factors are frequently underestimated when choosing coating materials: the reaction energy between the coating material and the electrolyte, and the electronic conductivity of the resultant reaction products between them. The reaction energy between previously reported coating materials and sulfide SSEs exhibits a notable decrease compared to that between positive electrode materials and sulfide SSEs, yet it cannot be disregarded, especially when the reaction products contain electronically conductive species. Since the reaction products are most probably ion conductive, the presence of electronically conductive species will eliminate kinetic barriers of the reaction. As a result, the differences in chemical potential of various elements between coating materials and sulfide SSEs propels the continuous progression of the reaction until the coating material is entirely consumed to form mixed Li-ion and electronically conductive cathode-electrolyte interlayer (CEI) and fails in its protection role. This is particularly significant, considering the protective layer is only a few nanometers thick. Once the protective layer transforms into a mixed conductive interlayer, the disparity of elemental chemical potential between positive electrode materials and sulfide SSEs (such as Li, Co, O) drives persistent structural degradation of positive electrode materials and decomposition of sulfide SSEs, ultimately leading to failure of ASSLBs. Hence, the meticulous selection of coating materials plays a crucial role in enabling ASSLBs to achieve the electrochemical performance necessary for commercial applications.

Herein, we introduce Li_2ZrF_6 (LZF) as a protective layer on the surface of LCO, and investigate its electrochemical performance in

comparison with the representative protective layer of LiNbO_3 (LNO). The LZF material is characterized by its wide electrochemical stability window and minimal reaction energy when in contact with $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI). Most importantly, the reaction products resulting from the interaction between LZF and LPSCI do not include any electronically conductive species, which provides assurance regarding the kinetic stability of their interface and the sustained function of LZF. Benefiting from these merits, LZF can protect efficient ion transport across the LCO/LPSCI interface from the chemical decomposition of LPSCI and structural degradation of LCO. In contrast, the representative LNO protective layer loses its function prematurely due to the non-negligible reaction energy with LPSCI and the high volume fraction of electronic conductor in their decomposition products. As a result, the ASSLBs with a composite positive electrode containing 80 wt.% LZF-coated LCO exhibit remarkable rate capability (96.2 mAh g^{-1} at 700 mA g^{-1}) and cycling retention (88.5% after 2492 cycles) with an LCO loading of 11.58 mg cm^{-2} at a cutoff potential of 4.5 V versus Li^+/Li . In particular, available areal capacity exceeding 3.8 mAh cm^{-2} can be achieved at 70 mA g^{-1} with LCO loading of 30.19 mg cm^{-2} and retain 80.5% after 1500 cycles.

Results

The LCO particles were coated with 1 wt.% LZF via a simple wet-chemistry method followed by annealing. For comparison, the conventionally employed 1 wt.% LNO-coated LCO (LNO-LCO) was also prepared following the procedures reported in existing literature³⁴. X-ray diffraction (XRD) was employed to examine the crystal structure of the materials. The XRD patterns (Supplementary Fig. 1) demonstrate that both LNO-LCO and LZF-coated LCO (LZF-LCO) samples correspond well to the hexagonal $R\bar{3}m$ structure, indicating no structural damage occurred during the coating process. Scanning electron microscopy (SEM) images (Supplementary Fig. 2) depict that the LCO consists of particles ranging from 2–10 μm in size. After being modified with LNO or LZF, the surface of particles appears hazy due to the covering of a protective layer. The homogeneous distribution of Nb on the surface of LNO-LCO was also detected by energy dispersive spectroscopy (EDS) mapping (Supplementary Fig. 3).

To investigate the composition and structure of the protective layer on LZF-LCO unequivocally, high-resolution transmission electron microscopy (HRTEM) was employed (Fig. 1a). A thin layer with a thickness of 6–13 nm is observed to uniformly cover the LCO particle. Enlarged images of the region of interest clearly exhibit nanocrystalline with lattice fringes, which match well with (002), (111), and (201) planes of LZF with trigonal $P\bar{3}1m$ structure. The corresponding fast Fourier transform (FFT) further confirms the presence of LZF. Scanning transmission electron microscopy (STEM) also verifies the structure of the protective layer consisting of LZF nanocrystalline embedded in an amorphous matrix (Supplementary Fig. 4). While other regions are mainly composed of amorphous phases. In order to identify the composition of the large amounts of amorphous matter in the coating, we carefully examined the coating layer with STEM and EDS mapping. We found that Zr and F element cover the entire surface of LCO uniformly, rather than being sporadically distributed (Fig. 1b). This indicates that our target product (i.e., LZF) includes not only nanocrystalline structures but also a significant amount of amorphous matter in the coating layer. Density of states (DOS) result indicated the nanocrystalline embedded in amorphous matrix can help reduce electronic conductivity of coating layer (Supplementary Fig. 5 and Supplementary Data 1). Meanwhile, an about 3 nm reconstruction from layered to disordered layered to rock salt structure had occurred on the surface after the coating process (Fig. 1b). In addition, the EDS mapping results from different scales (Supplementary Figs. 6–8) reveal a uniform distribution of Zr and F elements on the surface of LCO particles after coating process as well.

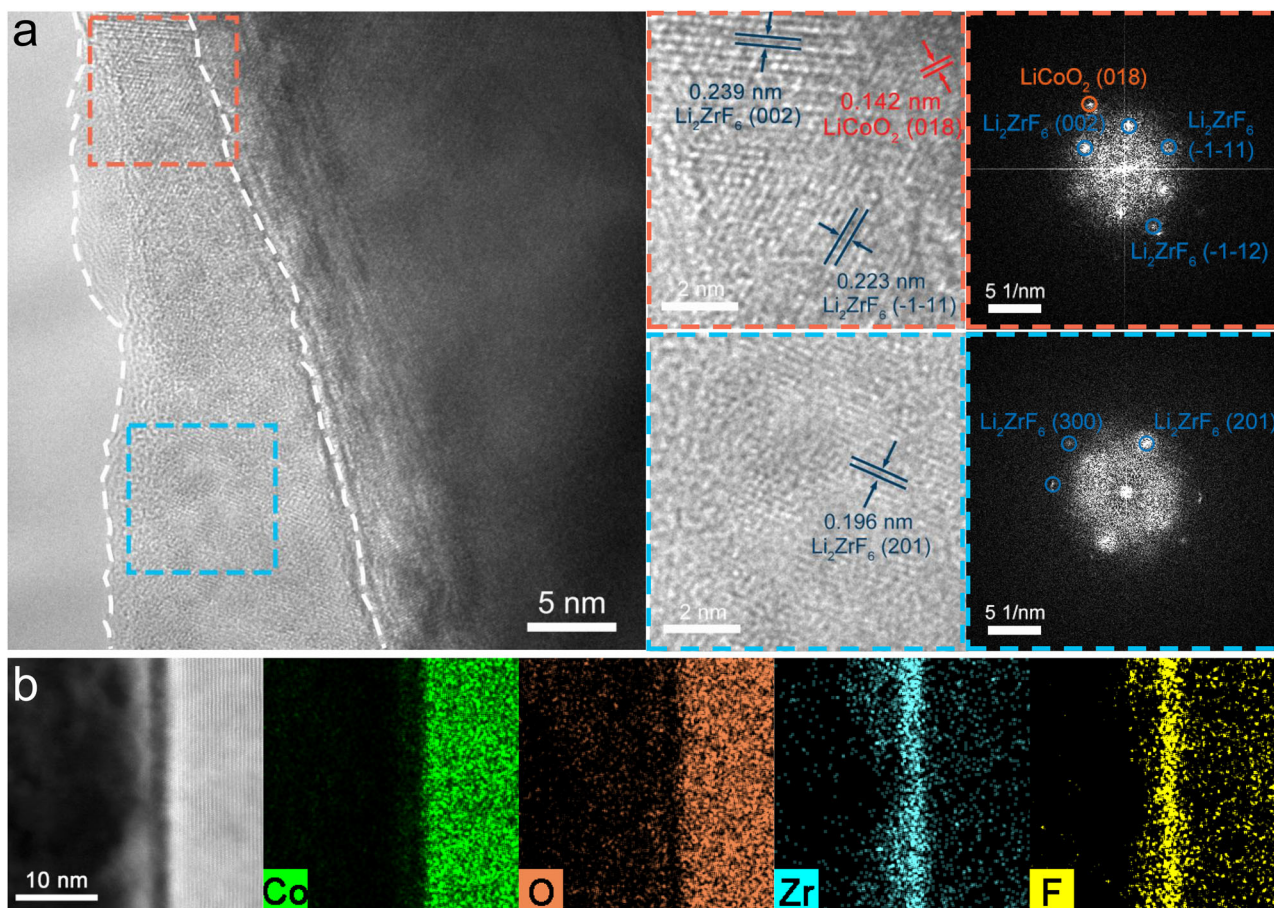


Fig. 1 | Structural and chemical characterization of LZF-LCO. a HRTEM images and corresponding FFT images of LZF protective layer. **b** Typical HAADF-STEM image of LZF-LCO particle surface and corresponding EDS mappings of Co, O, Zr and F elements.

The X-ray photoelectron spectroscopy (XPS) spectra of LZF-LCO powders also show signals of Zr^{4+} and F^- , further corroborating the presence of LZF (Supplementary Fig. 9). Furthermore, the morphology of LNO coating layer was also characterized. The STEM and EDS results clearly show that the LNO coating layer with a thickness of 10–18 nm homogeneously covers the LCO particles (Supplementary Fig. 10). We noticed that the thickness of our LNO coating layer falls within the optimal range for LNO (9–18 nm) in terms of electrochemical performance³⁵.

The electrochemical performance of In-Li|LPSCl|LZF-LCO and In-Li|LPSCl|LNO-LCO all-solid-state cells with an LCO loading of 11.07–11.58 mg cm^{-2} was investigated to validate the efficacy of the LZF protective layer. It is worth noting that the mass fraction of LCO in composite positive electrode is as high as 80 wt.%. As shown in Fig. 2a–d, the In-Li|LPSCl|LZF-LCO exhibits an initial discharge capacity of 154.1 mAh g^{-1} between 2.6 and 4.5 V at 70 mA g^{-1} . Surprisingly, a capacity of 96.2 mAh g^{-1} can still be delivered even at a high rate of 700 mA g^{-1} . In stark contrast, the In-Li|LPSCl|LNO-LCO displays a significantly larger overpotential than In-Li|LPSCl|LZF-LCO (Fig. 2c). Consequently, it exhibits a much lower initial discharge capacity of 127.1 mAh g^{-1} at 70 mA g^{-1} , and only a capacity of 35.2 mAh g^{-1} can be maintained at 700 mA g^{-1} . It is noted that the electrochemical performance displayed by In-Li|LPSCl|LNO-LCO is comparable to that reported in previous studies^{28–33}, proving the successful coating of LNO. The high-voltage cycling stability was also evaluated at 70 mA g^{-1} (Fig. 2e). The In-Li|LPSCl|LNO-LCO displays substantial capacity decay and only retains 69% of its initial capacity after 100 cycles. While this severe performance deterioration can be considerably alleviated by replacing LNO with the

LZF protective layer, achieving 90% capacity retention after 100 cycles.

In order to elucidate the basis for the significant performance gap between LZF-LCO and LNO-LCO, we have synthesized pure LNO and LZF powders and compared their ionic and electronic conductivity more comprehensive insights (Supplementary Figs. 11–13, Supplementary Tables 2–3). The ionic conductivity of LNO, as determined from electrochemical impedance spectroscopy (EIS) tests, is $3.4 \times 10^{-8} \text{ S cm}^{-1}$, while LZF exhibits a lower ionic conductivity of $7.6 \times 10^{-9} \text{ S cm}^{-1}$. Both coating materials exhibit similar electronic conductivity, with LNO having a value of $2.8 \times 10^{-10} \text{ S cm}^{-1}$ and LZF having $1.8 \times 10^{-10} \text{ S cm}^{-1}$. According to the ionic and electronic conductivity test results, the LNO-LCO should have delivered similar or even better electrochemical performance compared to the LZF-LCO. However, this was not observed in our experiments.

In addition to ionic and electronic transport properties, Young's modulus (E) is also considered a critical parameter, as it affects the ability of coating materials to inhibit volume strain and intragranular cracking in positive electrode materials. It can be calculated from Eq. (1).

$$E = 2G(1 + \nu) \quad (1)$$

where the G is shear modulus and the ν is Poisson's ratio. Using corresponding data from the Materials Project database, we determine the Young's modulus of LNO to be 126 GPa and that of LZF to be 88 GPa. This result implies that the LNO coating can better resist the volume strain of LCO. The particle integrity of LNO-LCO after 100 cycles has also been verified by STEM images, with no intragranular

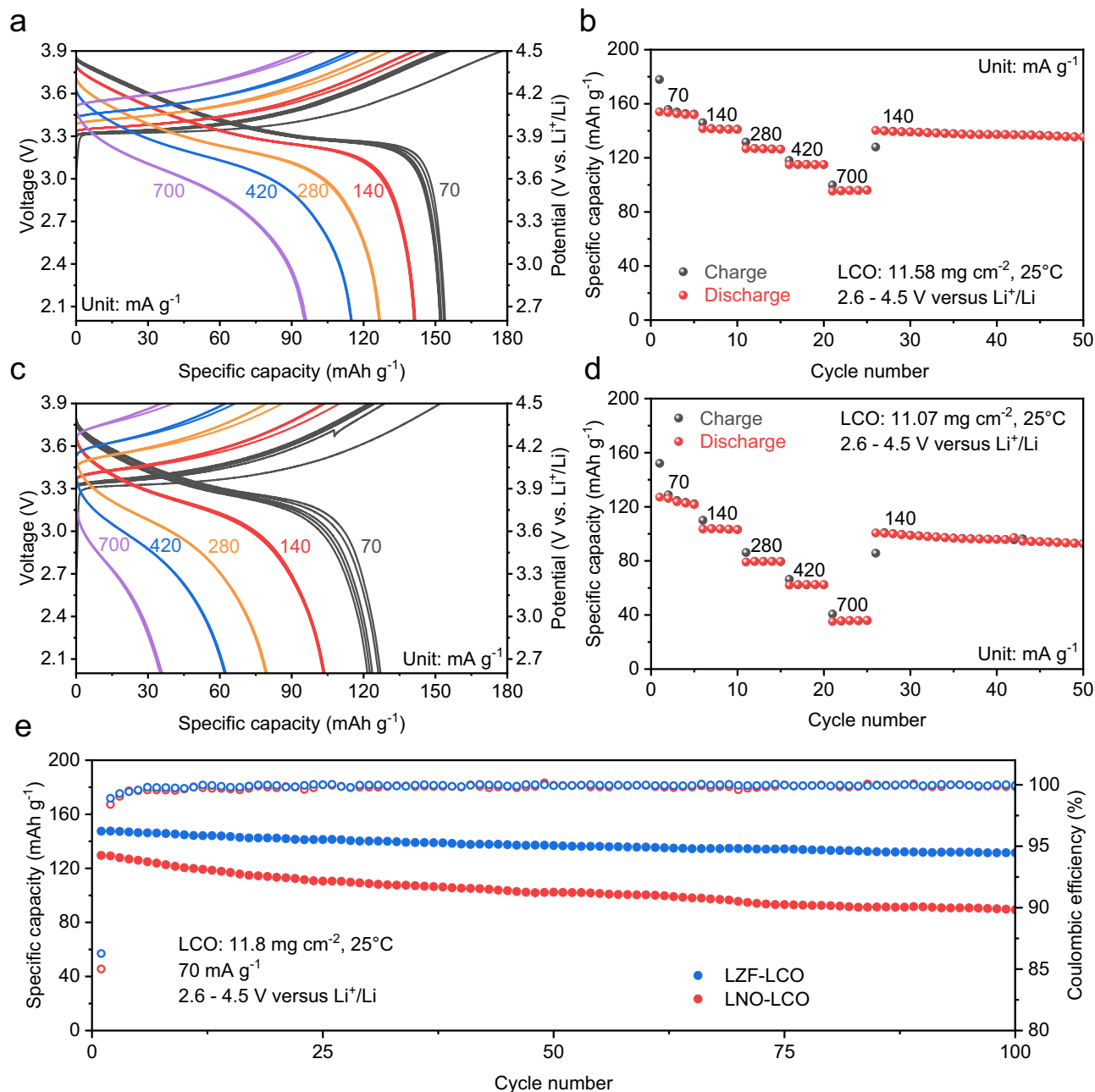


Fig. 2 | Electrochemical performance of In-Li|LPSCI|LZF-LCO and In-Li|LPSCI|LNO-LCO at 25°C. a Galvanostatic charge-discharge voltage profiles of In-Li|LPSCI|LZF-LCO at different rates. **b** Rate capability of In-Li|LPSCI|LZF-LCO.

c Galvanostatic charge-discharge voltage profiles of In-Li|LPSCI|LNO-LCO at different rates. **d** Rate capability of In-Li|LPSCI|LNO-LCO. **e** Cycling stability and Coulombic efficiency of In-Li|LPSCI|LZF-LCO and In-Li|LPSCI|LNO-LCO.

cracks observed (Supplementary Fig. 14). These results further validate that the mechanical stability of the coatings is not responsible for the distinct electrochemical performance between LNO-LCO and LZF-LCO. Additionally, the LZF-LCO particles also maintain their intact structure after 100 cycles, suggesting the LZF coating is sufficient to inhibit the volume strain of LCO (Supplementary Fig. 15).

Therefore, in order to reveal underlying factors, we conducted potentiostatic electrochemical impedance spectroscopy (PEIS) after each cycle within the initial 50 cycles at 70 mA g⁻¹ (Fig. 3a–b, Supplementary Fig. 16). The In-Li|LPSCI|LNO-LCO cell initially exhibits an acceptable cell impedance of 125.7 Ω cm² after the first cycle. However, this value continues to increase in each of the subsequent cycles, eventually reaching 346.4 Ω cm² after 50 cycles. In contrast, the In-Li|LPSCI|LZF-LCO cell exhibits a lower cell impedance of 89.2 Ω cm² after

the first cycle. This value shows a modest increase to 132.8 Ω cm² after 10 cycles and remains stable for the subsequent cycles. Given that the same negative electrode was utilized in both cells, the substantial difference between them arises entirely from the positive electrode side.

For a more profound understanding, distribution of relaxation time (DRT) analysis was employed to comprehend the evolution of the PEIS spectrum and decouple the contributions of different electrochemical processes (Fig. 3c–d). Five kinetic processes can be distinguished depending on their specific relaxation time. The peaks at 10⁻⁵ and 10⁻⁴ s are respectively attributed to ionic transport through the grain boundary of the SSE and solid electrolyte interphase (SEI) at the negative electrode side. The multiple peaks at 10⁻⁴ to 1 s are assigned to the CEI with complex composition. Charge

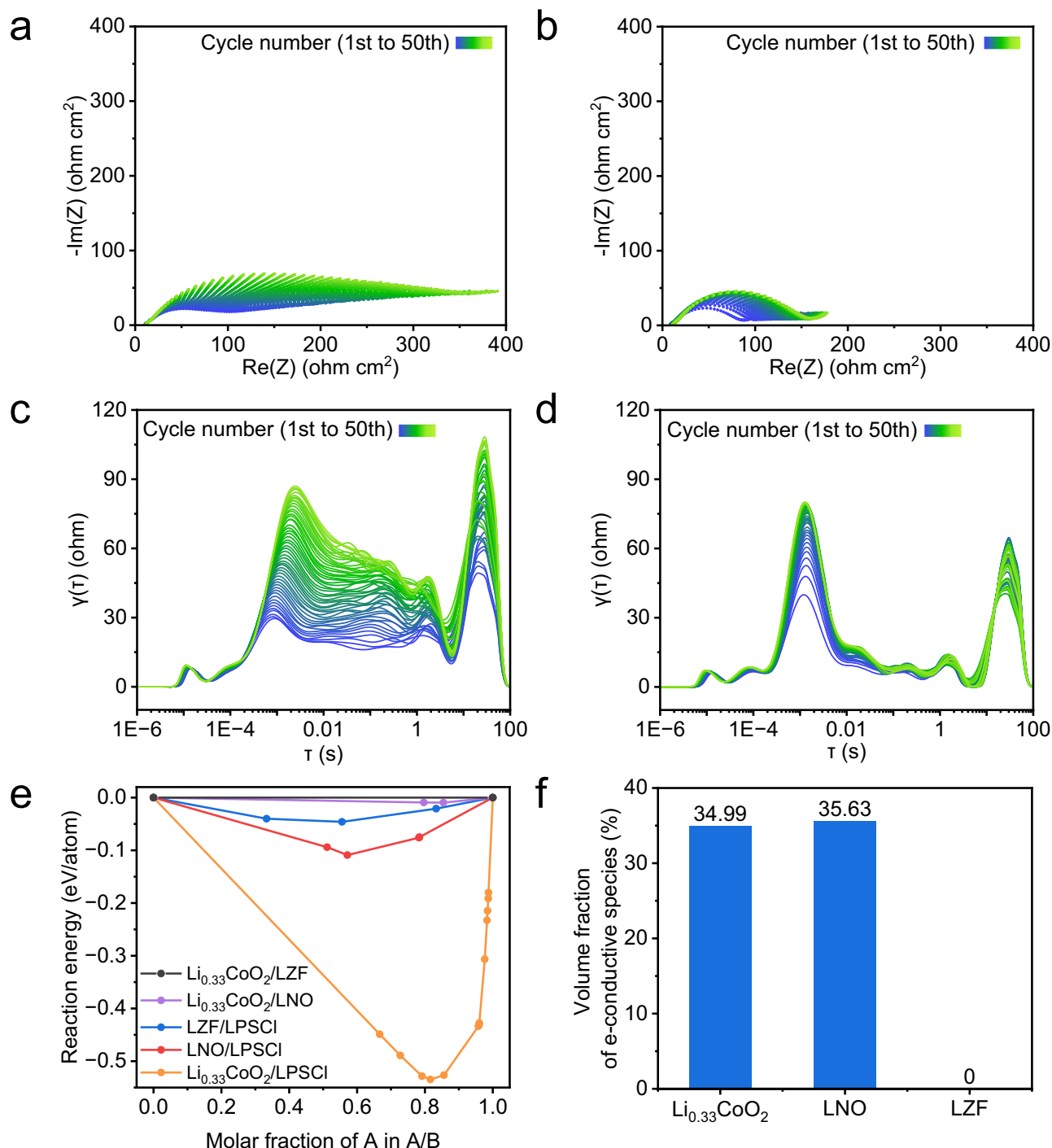


Fig. 3 | PEIS and DRT analysis showing the different impedance evolution process and underlying thermodynamic and kinetic mechanisms. a, b Nyquist plots of In-Li|LPSCI||LNO-LCO (a) and In-Li|LPSCI||LZF-LCO (b) at each discharged state in the first 50 cycles at 70 mA g^{-1} and 25 °C. **c, d** Corresponding DRT results of

In-Li|LPSCI||LNO-LCO (c) and In-Li|LPSCI||LZF-LCO (d). **e** Calculated mutual reaction energies of different interface. **f** The volume fraction of electron conductive species (0 eV band gap) in the decomposition products of LZF/LPSCI, LNO/LPSCI and LCO/LPSCI.

transfer impedance (R_{ct}) between LCO and SSEs is also identified as a peak located at 1 to 10 s. While the charge transfer process between negative electrode and SSEs is too small to be individually recognized. In addition, the peak at 10 to 100 s is attributed to the diffusional impedance (R_d) of Li^+ in LCO³⁶. For In-Li|LPSCI||LNO-LCO cell, it is evident that the impedance related to the electrochemical processes of the positive electrode increases with each successive cycle and does not saturate, including R_{CEI} , R_{ct} , and R_d . The results indicate that the continuous growth of CEI between LCO and SSEs

albeit with LNO protective layer, combined with the persistent structural degradation of LCO to impede Li^+ diffusion, collectively increase the challenges associated with interfacial charge transfer (Fig. 3c). Conversely, the In-Li|LPSCI||LZF-LCO cell exhibits an increase in R_{CEI} only during the first 10 cycles, with the other impedance contributions remaining stable throughout the entire 50 cycles (Fig. 3d). This highlights the remarkable protective role played by LZF to control CEI growth and preserve layer structure of LCO.

To gain deeper insights into the factors that dictate the divergent electrochemical behaviors, possible interfacial decomposition before and after the incorporation of the LNO/LZF protective layer were investigated (Supplementary Tables 4–8), and corresponding thermodynamic mutual reaction energies were calculated (Fig. 3e). The results disclose that the $\text{Li}_{0.33}\text{CoO}_2/\text{LPSCI}$ interface is not thermodynamically stable but undergoes spontaneous decomposition reactions with a maximum decomposition energy of $-0.5346 \text{ eV}\cdot\text{atom}^{-1}$ (Supplementary Table 4), aligning well with previous literature³⁷. The introduction of an LNO protective layer significantly enhances the interfacial stability of $\text{Li}_{0.33}\text{CoO}_2/\text{LNO}$, as evidenced by a notable decrease in the maximum decomposition energy to $-0.0095 \text{ eV}\cdot\text{atom}^{-1}$ (Supplementary Table 5). However, it is noteworthy that, despite this improvement, the LNO/LPSCI interface still exhibits a non-negligible maximum decomposition energy of $-0.109 \text{ eV}\cdot\text{atom}^{-1}$ (Supplementary Table 6). Moreover, from the interfacial decomposition products between LNO and LPSCI, it can be found that NbS_3 and $\text{Li}_5(\text{NbS}_2)_7$, which possess a band gap of 0 eV (Supplementary Table 7), constitute a significant portion of the resultant products (35.63 vol%). This value is comparable with that of reaction products between $\text{Li}_{0.33}\text{CoO}_2$ and LPSCI (34.99 vol%). More importantly, we noticed that the S and Nb elements are largely overlapped in the surface particles on LNO-LCO after 100 cycles, which is an evidence to support above calculations (Supplementary Fig. 14). This characteristic expedites the exhaustion of LNO, converting it into a mixed conductive interlayer. This transformation enhances electron mobility and eradicates the kinetic barrier for the chemical interaction between LCO and SSEs, instigated by differences in the chemical potential of various elements. As Co diffuses into LPSCI, it generates electronic conductors such as CoS_2 , Co_3S_4 , and Co_9S_8 with a band gap of 0 eV, ensuring a continuous supply of electrons for the persistent reaction (Supplementary Table 8).

Consequently, this process results in forming a thick CEI and disintegrating the layered LCO structure. When the LZF protective layer was employed, not only the $\text{Li}_{0.33}\text{CoO}_2/\text{LZF}$ interface is thermodynamically stable (maximum decomposition energy is $0 \text{ eV}\cdot\text{atom}^{-1}$), but better interfacial stability can also be achieved between LZF and LPSCI, with a negligible maximum decomposition energy of $-0.046 \text{ eV}\cdot\text{atom}^{-1}$ (Supplementary Table 7). Of greater significance, none of the reaction products are electronic conductors, amongst which the ZrS_2 possesses the smallest band gap of 1.04 eV (Supplementary Table 8), thus effectively preventing electron leakage even if the LZF protective layer was decomposed. This property avoids the interfacial reaction between LCO and LPSCI and assures the structural integrity of LCO over an extended period. The interfacial stability was also validated through long-term high-temperature testing (Supplementary Fig. 17 and Supplementary Note 1). In addition, the distinct electrochemical stability windows of LNO and LZF also contribute to the different stability during cycling (Supplementary Fig. 18).

X-ray photoelectron spectroscopy (XPS) was first employed to study the detailed chemical insights into the composite positive electrode of $\text{In-Li}|\text{LPSCI}|\text{LZF-LCO}$ and $\text{In-Li}|\text{LPSCI}|\text{LNO-LCO}$ after cycles (Fig. 4a, b). The samples' surfaces were cleaned by Ar^+ sputtering before the test to remove the possible surface contamination. For comparison, XPS was also conducted on LPSCI powder (Supplementary Fig. 19). The S 2p spectrum and the P 2p spectrum of LPSCI both display doublets, with the S $2p_{3/2}$ peak at 161.4 eV and the P $2p_{3/2}$ peak at 131.8 eV. These features align well with the PS_4^{3-} tetrahedra of the argyrodite structure. After 20 cycles, the S 2p spectrum of LNO-LCO composite positive electrode exhibits three new doublets with the $2p_{3/2}$ peaks at 162.9 eV, 163.8 eV, and 169 eV, suggesting the formation of bridging sulfur in P_2S_x , elemental sulfur (S) and sulfate (SO_4^{2-}), respectively. Extending the cycling process to 100 cycles leads to the appearance of a new doublet with the $2p_{3/2}$ peak at 167.1 eV, which corresponds to sulfite (SO_3^{2-}), while also intensifying the signal

associated with SO_4^{2-} . These high oxidation state species severely hinder Li^+ transport within the composite positive electrode. After substituting LNO with LZF, the chemical/electrochemical formation of these products can be effectively mitigated, with no SO_4^{2-} detected after 20 cycles. Moreover, even after 100 cycles, the decomposition products still show intensities comparable to those of LNO-LCO composite positive electrode after 20 cycles. It should be noted that the signal of Co_9S_8 may not be discernible, probably due to its merging with the S signal owing to their close binding energies (-163.9 eV)³⁸. The P 2p core-level XPS data of LNO-LCO composite positive electrode after 20 cycles displays two new doublets at higher binding energy, corresponding to P_2S_x and P-O, which show an increase after 100 cycles. Similar to evolution in S 2p spectra, the LZF protective layer efficiently alleviates the generation of these resistive decomposition species. These results demonstrate the capability of LZF to stabilize the interface, thereby achieving better electrochemical performance.

X-ray absorption spectra (XAS) were characterized on the composite positive electrode after cycles to further investigate the interfacial stability (Fig. 4c–d). The S K-edge and P K-edge XAS of pristine LZF-LCO composite positive electrode displayed identical characteristics as those of LPSCI, indicating the preserved integrity of the argyrodite structure^{15,32}. However, for LNO-LCO composite positive electrode after 100 cycles, there are notable alterations in the peak shape of S K-edge XAS. These changes include a pronounced increase in the intensity of the peaks at -2472 eV (typically Li_2S) and -2477 eV (typically SO_3^{2-}), indicative of severe oxidation reactions and a rearrangement of the local structure of LPSCI. Similarly, the features in P K-edge XAS also display substantial changes, encompassing a decreased intensity of the main peak and the emergence of a new peak at -2152 eV , ascribed to P_4O_{10} ³⁹. Additionally, the broad peak around 2170 eV can be attributed to the multiple scattering of P-O⁴⁰. These results underscore that the LNO protective layer loses its protective function against chemical interactions between LCO and LPSCI prematurely. In the case of the LZF-LCO composite positive electrode after 100 cycles, despite a slight decrease in peak intensity and minor alterations in peak shape, its S K-edge and P K-edge XAS exhibit a significantly improved retention compared to the LNO-LCO composite positive electrode.

Additionally, interphase growth between LCO and LPSCI after 100 cycles was probed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements with LNO or LZF protective layer (Fig. 4e–f). Ar^+ sputtering was also applied before the test to avoid misunderstanding. Chemical ion images of Co^+ and S^- are utilized to locate LCO and LPSCI, respectively. Various other species are also observable, including CoS^+ , SO_3^- , and PO_3^- . CoS^- can be recognized as a distinctive component of Co_9S_8 or Co_3S_4 , SO_3^- can be attributed to SO_3^{2-} or SO_4^{2-} , and PO_3^- can be associated with P_4O_{10} or PO_4^{3-} . It is clear that all ions related to decomposition products exhibit higher intensities in the LNO-LCO composite positive electrode when compared to the LZF-LCO composite positive electrode. Normalized intensity of these ionic fragments was also provided (Supplementary Fig. 20). These results provide strong evidence that LNO is not stable enough to inhibit chemical interaction between LCO and LPSCI, leading to thick CEI formation, especially at high voltage. On the other hand, LZF can remarkably reduce chemical degradation and ensure fast Li^+ transport within the composite positive electrode.

The gas generation from the composite positive electrode during charge was also detected by differential electrochemical mass spectrometry (DEMS) experiments (Fig. 4g–i). As depicted in Fig. 4g, SO_2 release from the LNO-LCO composite positive electrode was detectable even when LCO was slightly oxidized to $\text{Li}_{0.95}\text{CoO}_2$ (Fig. 4g). The presence of an LZF protective layer significantly delayed the onset of SO_2 generation occurring when LCO underwent oxidation to $\text{Li}_{0.7}\text{CoO}_2$ (Fig. 4h). Furthermore, the accumulation of SO_2 from the LZF-LCO composite positive electrode was notably lower, accounting for only

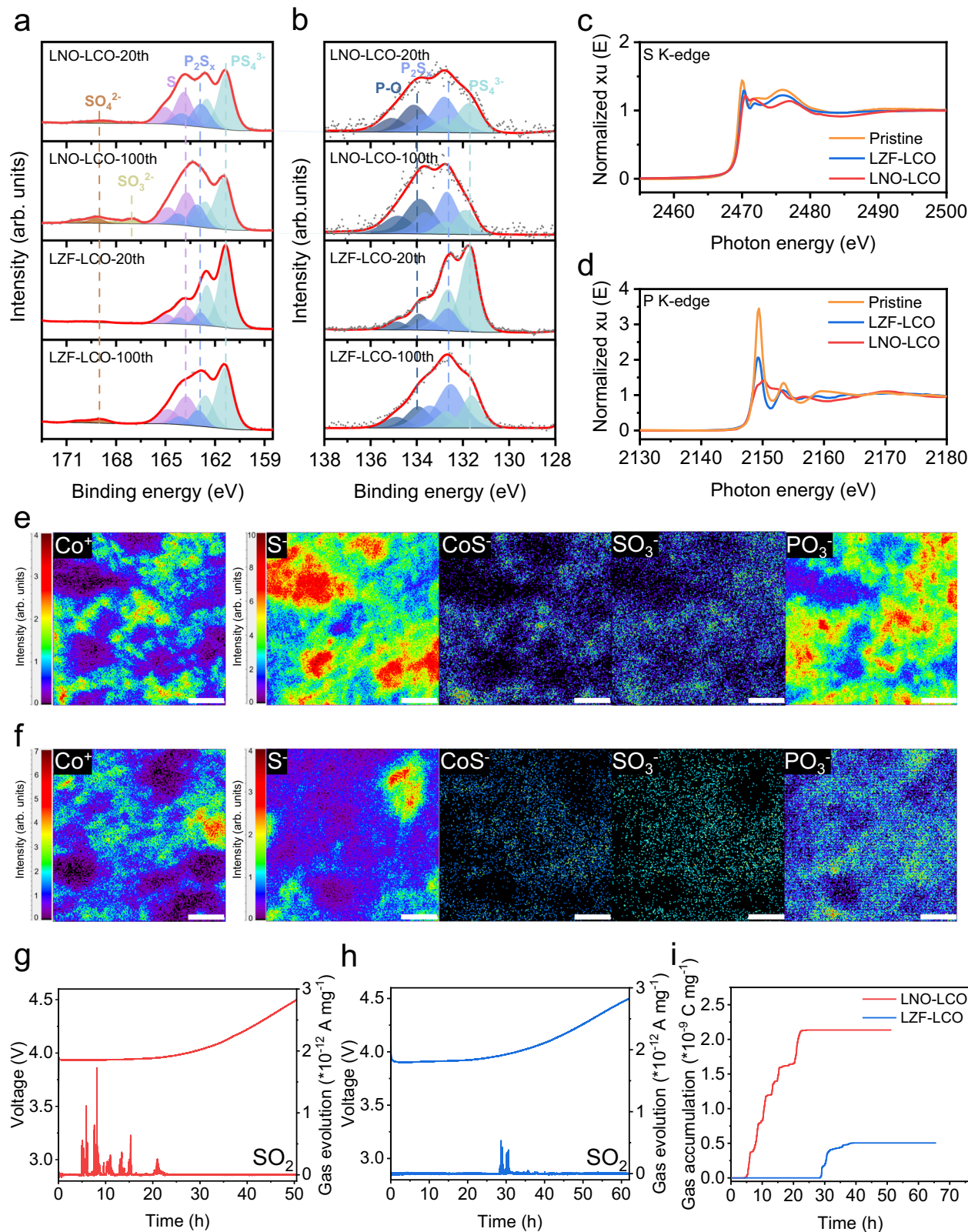


Fig. 4 | Characterizations on chemical interaction between LCO and LPSCI with LNO or LZF protective layer. a, b S 2p (a) and P 2p (b) XPS spectra of LNO-LCO and LZF-LCO at discharged state after 20 or 100 cycles. The cells cycled at 70 mA g^{-1} and 25 $^\circ\text{C}$ before disassembly and sampling for the ex situ XPS measurements. **c, d** S K-edge (c) and P K-edge (d) XANES spectra of pristine composite positive electrode, LNO-LCO composite positive electrode and LZF-LCO composite positive electrode at discharged state after 100 cycles. The cells cycled at 70 mA g^{-1} and 25 $^\circ\text{C}$ before disassembly and sampling for the ex situ XANES measurements. **e, f** ToF-SIMS

secondary ion images of Co^+ , S^- , CoS^- , SO_3^- , PO_3^- for LNO-LCO (e) and LZF-LCO (f) composite positive electrode at discharged state after 100 cycles. The color bars have been provided in the form of cation mode and anion mode. The scale bar is 10 μm . The cells cycled at 70 mA g^{-1} and 25 $^\circ\text{C}$ before disassembly and sampling for the ex situ ToF-SIMS measurements. **g, h** DEMS test of SO_2 generation in first charge process of In-Li|LPSCI|LNO-LCO (g) and In-Li|LPSCI|LZF-LCO (h) at 7 mA g^{-1} and 25 $^\circ\text{C}$. **i** The accumulation of SO_2 in the first charge process of In-Li|LPSCI|LNO-LCO and In-Li|LPSCI|LZF-LCO.

23.6% of that from the LNO-LCO composite positive electrode (Fig. 4i). It is important to note that the detection of SO_2 below 4 V serves as evidence that SO_2 originates from a chemical reaction between LCO and LPSCI, rather than being formed by O_2 released from LCO interacting with LPSCI. DFT calculations were employed to elucidate the mechanism by which LCO reacts with the electrolytes LPSCI during charging to produce SO_2 . When a potential of 4 V (versus Li^+/Li) is applied, the reaction energy for the formation of SO_2 from LCO and LPSCI is -0.592 eV/atom (Supplementary Fig. 21). This suggests that the oxygen from LCO is thermodynamically favored to combine with sulfur to produce SO_2 at this potential. Given the spontaneous reaction between LNO and LPSCI, sulfur from the electrolytes can diffuse into LNO coating layer, leading to the formation of electron-conductive niobium sulfide compounds and the fast decomposition of LNO. This process can facilitate the combination of oxygen and sulfur, resulting in the formation of SO_2 . In stark contrast, the enhanced thermodynamic and kinetical stability between LZF and LPSCI effectively impedes the combination of oxygen and sulfur, preventing the production of SO_2 . DEMS data for Ar and N_2 were also displayed to verify the airtightness of the setup during cell cycling (Supplementary Fig. 22).

Besides the characterization on chemical decomposition and CEI growth, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was utilized to distinguish the structural transformation of LNO-LCO and LZF-LCO particles after 100 cycles (Fig. 5a–f). These samples were prepared by focused ion beam (FIB). As depicted in Fig. 5a, the layered structure of LCO was reconstructed in the near-surface region despite the presence of the LNO coating. The amplified lattice fringes and the corresponding fast Fourier transform (FFT) further elucidate that this reconstruction phase is dominated by $Fd\bar{3}m$ spinel Co_3O_4 (Fig. 5b–c). Additionally, the HRTEM results validate the presence of not only the spinel phase but also a more undesired $Fm\bar{3}m$ rock-salt phase (Supplementary Figs. 23–24). The formation of these reconstruction phases is associated with O oxidation (O^{2-} to $\text{O}^{\alpha-}$, $0 < \alpha < 2$) at voltages exceeding 4.3 V and subsequent $\text{O}^{\alpha-}$ diffuse and release from the surface due to LNO layer has decomposed and failed in its role^{41,42}. In this case, the chemical reaction between LCO and SSEs also contributes to the formation of the reconstruction layer due to their disparity in O chemical potential. This reconstruction layer not only impedes Li^+ diffusion in LCO particles but also leads to the loss of active materials. Moreover, these O species diffuse to SSEs to form resistive products, increasing Li^+ transport impedance within the composite positive electrode as discussed above. Excitingly, these layered-to-spinel/rock-salt transformation behaviors were significantly mitigated in LZF-LCO (Fig. 5d–f). The enlarged lattice fringes and corresponding FFT results confirm the well-preserved layered structure of LCO, owing to the LZF protective layer, which effectively prevents the release of $\text{O}^{\alpha-}$ and possesses long-term stability at the interface between LCO and LPSCI.

The electron energy loss spectroscopy (EELS) measurement was further performed to distinguish the states of Co and the loss of O in different depths (Figs. 5g–j, Supplementary Fig. 25). O K-pre-edge features in LCO have been identified as the result of a transition of electrons from the 1s state to the hybridized O 2p-Co 3d orbitals^{43,44}. Concerning LNO-LCO particle after 100 cycles, the decreased O pre-edge peak and slight peak shift to higher energy loss within 15 nm from the surface indicate a decrease in the number of unoccupied states in the hybridized O 2p-Co 3d orbitals, which is assigned to the reduction of transition metal and the sharing of d-orbitals holes with the oxygen ligands, including the associated decrease in covalency¹⁵. Moreover, the shift of Co L-edge to the lower energy loss and higher Co $\text{L}_{3/2}$ area ratio in the near-surface region also manifests the occurrence of undesired spinel/rock-salt phase (Figs. 5i–j, Supplementary Fig. 26). Impressively, only about 7 nm reconstruction layer exists in the surface of LZF-LCO after 100 cycles. Furthermore, the EDS mapping of the

interface between LNO-LCO particle and LPSCI reveals the diffusion of Co into LPSCI (Supplementary Fig. 27a). This indicates that the LNO coating layer has already lost its functionality, and Co can readily diffuse into LPSCI, triggering its decomposition due to their differences in Co chemical potential. In contrast, the signals of Co in LZF-LCO remain confined to the LCO region (Supplementary Fig. 27b), once again highlighting the remarkably different protective effects of the two coatings. These results presented here demonstrate that LZF not only more effectively helps mitigate the SSEs decomposition but also plays a more substantial role in alleviating the structural transformation of LCO, jointly facilitating the interfacial charge transfer between LCO and SSEs, in accordance with the finding from the PEIS and DRT results.

Since the veiled factors that made a significant difference between LNO and LZF protective layers have been clarified, further testing was conducted on the $\text{In-Li}|\text{LPSCI}||\text{LZF-LCO}$ to fully exploit its potential. Its cycling durability at a high rate was demonstrated after evaluation of its rate capability (Fig. 6a, c). The voltage profile displays a high degree of overlap, particularly in the initial 1000 cycles. Impressively, highly stable cycling performance can be maintained for 2492 cycles at 420 mA g^{-1} with a capacity retention of 88.5%. To further verify the capability of LZF at an areal capacity of commercial interest (typically $> 3 \text{ mAh cm}^{-2}$), high-loading $\text{In-Li}|\text{LPSCI}||\text{LZF-LCO}$ with an LCO areal loading of 30.19 mg cm^{-2} was evaluated (Fig. 6b, d). An areal capacity of 5.2 mAh cm^{-2} can be delivered at 7 mA g^{-1} in the first five cycles. When the current density is increased to 70 mA g^{-1} , an areal capacity of up to 3.8 mAh cm^{-2} can be achieved. Excitingly, a capacity retention of 80.5% can be obtained after 1500 cycles. Another high-loading $\text{In-Li}|\text{LPSCI}||\text{LZF-LCO}$ with an LCO areal loading of 30.82 mg cm^{-2} can display a high areal capacity of 2.95 mAh cm^{-2} at a high rate of 140 mA g^{-1} , and achieve good capacity retention of 80% after 320 cycles (Supplementary Fig. 28). Such encouraging results again highlight the interfacial design principle for high-voltage all-solid-state batteries.

Following the established design criteria for coating materials, we have also investigated 69 types of $\text{Li}_x\text{M}_y\text{F}_z$ compounds using data from the Materials Project. According to the basic evaluation criteria, which include electrochemical windows, band gap, and reaction energies of $\text{Li}_x\text{M}_y\text{F}_z/\text{Li}_{0.33}\text{CoO}_2$ and $\text{Li}_x\text{M}_y\text{F}_z/\text{LPSCI}$, an initial computational screening identified 18 types of $\text{Li}_x\text{M}_y\text{F}_z$ (Supplementary Table 9). Subsequently, we calculated the reaction products between 18 types of $\text{Li}_x\text{M}_y\text{F}_z$ and LPSCI and analyzed their band gaps (Supplementary Table 10). Our analysis revealed that Li_2TiF_6 and Li_3CrF_6 should be excluded due to the formation of electron-conductive reaction products. Ultimately, we identified $\text{Li}_x\text{M}_y\text{F}_z$ compounds with $\text{M} = \text{Lu}, \text{Y}, \text{Zr}, \text{Be}, \text{Al}, \text{Th}, \text{Cs}, \text{Sc}$, and Ba as suitable coating materials. We observed that the electron transport properties of the metal sulfide in reaction products (e.g., $\text{Li}_x\text{M}_y\text{S}_z$, M_xS_y) is a key factor in choosing $\text{Li}_x\text{M}_y\text{F}_z$ coating materials, highlighting the critical role of elements M (e.g., Zr in this work).

Discussion

In summary, an LZF protective layer was proposed to coat on the surface of LCO to tackle the long-standing challenge at the interface of positive electrode materials and SSEs for sulfide ASSLBs. The LZF coating layer is 6–13 nm in thickness, with some nanocrystalline clusters embedded in the amorphous matrix. The minimal thermodynamic mutual reaction energy between LZF and LPSCI and their electron insulative decomposition products make the LZF protective layer exist stably during long-term cycling. In contrast, the conventionally employed LNO materials lose their functionality prematurely due to their transformation into a mixed conductive interlayer, which removes the kinetic barrier for progressing interaction between LCO and SSEs. Consequently, compared to LNO, the LZF protective layer is more crucial in reducing the accumulation of unfavored side products with high electronic conductivity and high oxidation state species with low ionic conductivity. Simultaneously, it provides more effective

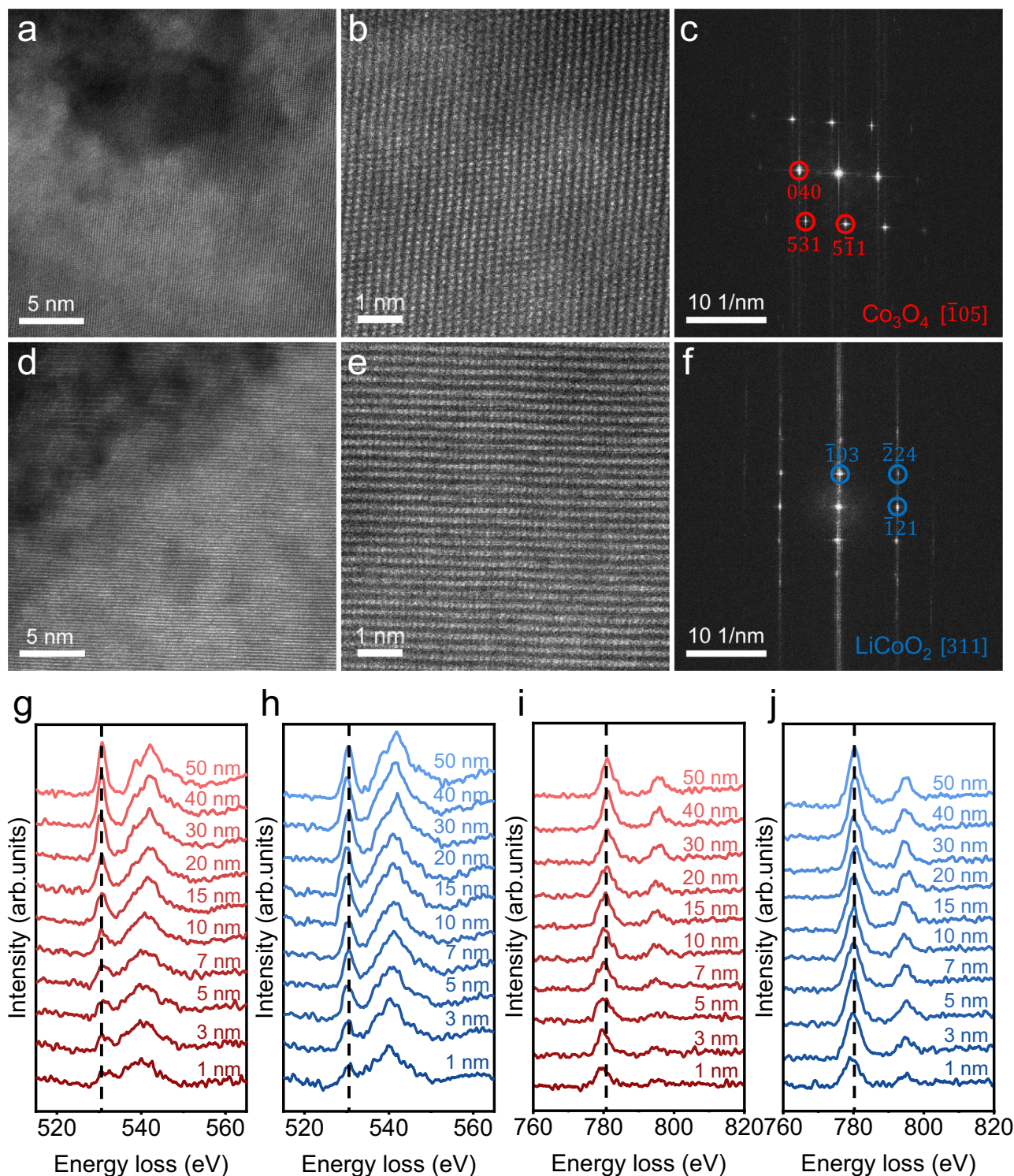


Fig. 5 | Characterizations on chemical interaction between LCO and LPSCI with LNO or LZF protective layer. **a–c** Cross-sectional STEM images of LNO-LCO showing the reconstructed spinel Co_3O_4 phase and the corresponding FFT image. **d–f** Cross-sectional STEM images of LZF-LCO showing the well preserved layered LCO phase and the corresponding FFT image. **g, h** EELS line scan of O K-edge at the

near-surface region of LNO-LCO particle (**g**) and LZF-LCO particle (**h**). **i, j** EELS line scan of Co $\text{L}_{2,3}$ -edge at the near-surface region of LNO-LCO particle (**i**) and LZF-LCO particle (**j**). All the cells cycled at 70 mA g^{-1} and 25°C before disassembly and sampling for the ex situ measurements. And all the samples were characterized at discharged state after 100 cycles.

mitigation of the surface reconstruction of LCO. As a result, the In-Li|LPSCI||LZF-LCO all-solid-state cell with high LCO mass fraction (80 wt.%), substantial LCO areal loading (30.19 mg cm^{-2}), and cutoff potential of 4.5V versus Li^+/Li , shows a notable areal capacity (5.2 mAh cm^{-2} at 7 mA g^{-1} , 3.8 mAh cm^{-2} at 70 mA g^{-1}) and a good capacity retention (80.5% after 1500 cycles at 70 mA g^{-1}) at 25°C at the

same time. Meanwhile, all-solid-state cell with an LCO loading of 11.58 mg cm^{-2} can deliver a specific capacity of 96.2 mAh g^{-1} at 700 mA g^{-1} and retain 88.5% after 2492 cycles. This work highlights a critical factor that should be taken into account during the meticulous selection of coating materials and demonstrates a high-quality protective layer with long-term stability for the challenging 4.5V-class

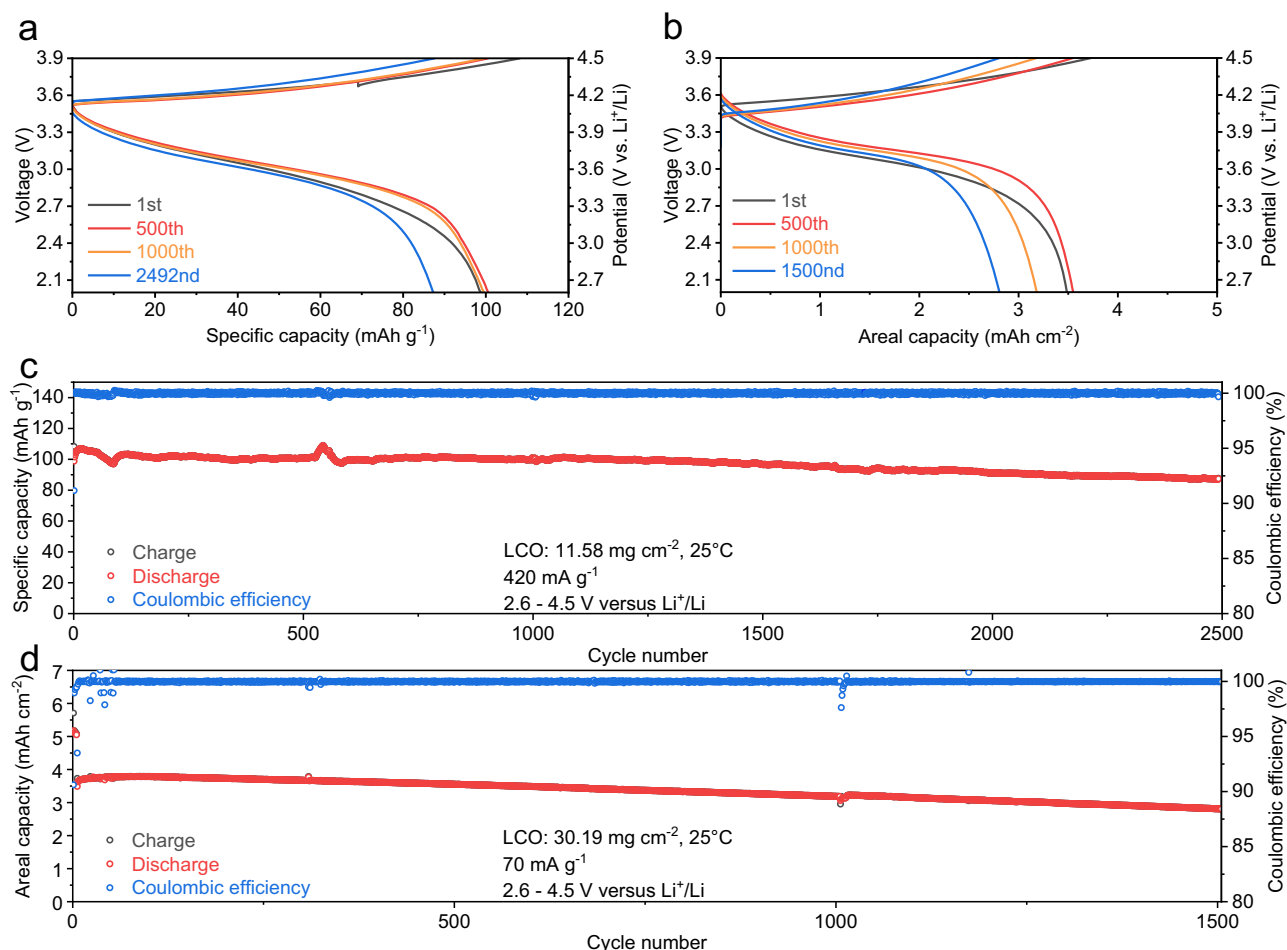


Fig. 6 | Electrochemical performance of In-Li|LPSCI|LZF-LCO at high rate or high LCO loading. **a, b** Galvanostatic charge-discharge voltage profiles of In-Li|LPSCI|LZF-LCO at 420 mA g⁻¹ and LCO loading of 11.32 mg cm⁻² (**a**) and at 70 mA g⁻¹ and LCO loading of 30.19 mg cm⁻² (**b**). **c, d** Electrochemical cycling stability of In-Li|

LPSCI|LZF-LCO at 420 mA g⁻¹ and LCO loading of 11.32 mg cm⁻² (**c**) and at 70 mA g⁻¹ and LCO loading of 30.19 mg cm⁻² (**d**). The LCO mass fraction in composite positive electrode is 80 wt.%. The experiments were performed between 2.0–3.9 V versus Li⁺/LiIn, corresponding to -2.6–4.5 V versus Li⁺/Li. All cells were operated at 25 °C.

ASSLBs, which presents promising opportunities for their widespread utilization.

Methods

Material synthesis

The LZF protective layers were coated on the LCO particles via a facile liquid phase method followed by annealing. Before coating process, LCO powders were annealed at 700 °C for 5 hours in ambient air. The heating rate for all sintering steps was 3 °C per minute, and the samples were naturally cooled after sintering. For preparing LZF solution, 3 mg of Li₂CO₃ (99.9%, Aladdin) and 21 mg of H₂ZrF₆ solution (45 wt.%, Macklin) were mixed in 30 mL of deionized water. The pH of the solution is tested to be 3.45 at 25 °C. After that, 1 g of LCO powders (99.5%, Aladdin) was slowly added into the aforementioned solution and subjected to ultrasonication for ten minutes. Then, the mixture was vacuum-heated using a rotary evaporator at 60 °C for 1 hour with all the water had evaporated entirely. Last, the powders were collected and annealed at 700 °C for 2 hours in ambient air. The LNO protective layers were coated on the LCO particles as reported in previous literature³⁴. Typically, 0.5 mg of Li metal (99.9%, China Energy Lithium Co., Ltd) was dissolved in 30 mL of anhydrous ethanol (Titan) and mixed with 21.5 mg of niobium pentaethoxide (99.5%, Aladdin). Next, 1 g of LCO powder was gradually introduced into the solution and subjected to ultrasonication for ten minutes. Subsequently, the mixture was vacuum-heated using a rotary evaporator at 30 °C for 1 hour

until all the ethanol had evaporated entirely. Last, the powders were collected and annealed at 400 °C for 2 hours in ambient air. The mass fraction of LZF/LNO in the resulting positive electrode powder was about 1%.

Material characterization

X-ray powder diffraction (XRD) patterns were obtained by means of a Bruker D8 advance diffractometer equipped with Cu K α radiation ($\lambda = 1.54178$). Kapton films were used to isolate air during XRD test. Scanning electron microscopy (SEM, Hitachi S4800) in conjunction with energy-dispersive X-ray spectroscopy (EDS) was used to study the morphology and element distribution. X-ray photoelectron spectroscopy (XPS) measurements were carried out by means of a Thermo Scientific K-Alpha+ with monochromatic Al K α radiation (1486.6 eV). The collection of all test electrodes was carried out by slowly applying pressure on the negative electrode side using a mold in Ar-filled glovebox, thereby extracting the entire solid-state battery. Time-of-flight secondary-ion mass spectrometry (ToF-SIMS) was performed by means of a PHI nanoTOF II. For the XPS and ToF-SIMS tests, the chamber was directly connected to the argon glovebox to prevent the sample surface from contacting air and moisture. Ar⁺ ion sputtering was also applied before the test to remove possible contamination. The XAS at the P K-edge and the S K-edge were measured using fluorescence yield mode at 16 A beamline (1800–7500 eV) at the Taiwan Synchrotron Radiation Research Center. An inert atmosphere

sample holder was used to transfer the samples. For atomic structural analysis, the particles were first sliced by a focused ion beam (FIB/SEM, FEI Scios 2 HiVac), and then high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and electron energy loss spectroscopy (EELS) spectra were obtained using a JEM-ARM300F microscope. For FIB and TEM/STEM characterization, the samples were briefly exposed to air for less than one minute. For DEMS test, the all-solid-state cell (10 mm diameter, 25 mg cm⁻² LCO loading) was assembled as it was for the electrochemical test and then carefully demolded. The demolded cell was subsequently placed inside the DEMS setup. Electrochemical cycling was performed at a rate of 7 mA g⁻¹ and 25 °C in the voltage range of 2.0–3.9 V (versus Li⁺/LiIn) and 2.6–4.5 V (versus Li⁺/Li) using a Land battery test system. A 10 h open-circuit voltage period was included in the beginning. The flow of carrier gas was controlled to be 1.0 mL min⁻¹. Due to the distance between the cell and the mass spectrum, the lag of the mass spectrum data was about 280 s compared with the battery data.

Electrochemical measurements

All battery assembly procedures were carried out in an argon glovebox with H₂O < 0.1 ppm and O₂ < 0.1 ppm. The In-Li|LPSCI|LCO all-solid-state cells were tested in a polyether ether ketone cylinder with an inner-wall diameter of 10 mm at 25 °C. To prepare a composite positive electrode, coated LCO, LPSCI, and PTFE (Aladdin, 5–10 μm) with a weight ratio of 80:19:1 were mixed to form a single flake. Subsequently, the flake was hot rolled repeatedly by hand using a stainless-steel cylindrical rod at 80 °C. An 80 mg of LPSCI powder (Hefei Kejing Material Technology Co., Ltd) was first added into the cylinder, followed by uniaxial pressing with 300 MPa for 2 minutes. Then, the composite positive electrode flake with 10 mm diameter was punched out and pressed on one side of the LPSCI pellet at 360 MPa for 2 minutes. The mass loading of LCO was 11.07–11.8 mg cm⁻² (~30 μm thickness) and 30.19–30.82 mg cm⁻² (~100 μm thickness) for the high-loading tests. After the second pressing step, a 0.1-mm-thick indium foil disc of 10 mm diameter and a 0.1-mm-thick lithium foil disc of 5 mm diameter (Kairui New Material Technology Co., Ltd.) were carefully removed with a punching pin, and then successively added to the other side of the LPSCI pellet. The metal foil was used as received without surface cleaning. The assembly was then pressed at a pressure of 150 MPa for 2 minutes. A constant pressure of ~50 MPa was applied to the cell using the screw of the stainless-steel framework during electrochemical test. Galvanostatic charge/discharge tests of cells were conducted in an Ar atmosphere using a Land battery test system (Wuhan, China) at 25 °C inside a static-heated environmental chamber, between 2.0–3.9 V versus Li⁺/LiIn, corresponding to ~2.6–4.5 V versus Li⁺/Li. PEIS was carried out after one complete cycle (discharged state) and 0.5 h of rest to achieve equilibrium in the first 50 cycles with Autolab electrochemical workstation. The applied cycling current density was 70 mA g⁻¹ and the testing temperature was 25 °C. An amplitude of 10 mV was chosen for measurements in the frequency range of 1 MHz to 20 mHz with 10 points per decade. For the DRT analysis, a MATLAB code contributed by Prof. Francesco Giucci was employed⁴⁵.

Theoretical studies

The DFT calculations were performed using Vienna Ab initio Simulation Package. The initial crystal structure was obtained from the Materials Project⁴⁶ (Li₂ZrF₆ (mp-4002)). The chemical reactions (Li_xM_yF_z and Li_{0.33}CoO₂, Li_xM_yF_z and Li₆PS₅Cl) were analyzed by Pymatgen⁴⁷. Precomputed data used in the phase diagram construction can be obtained from the Material Project database. The band gap of different Li_xM_yF_z are obtained from Material Project.

Data availability

The data generated in this study are provided in the Supplementary Information/Source Data file. Source data are provided with this paper.

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Author contributions

X.Z. and Y.W. conceived and designed the research project. X.Z., K.Z., and Z.L. carried out the material characterization. C.Y.C. and S.K.J. carried out the XANES experiments. X.Z. performed the battery measurements. D.Y. and Y.Z. carried out the calculations. X.Z. wrote the manuscript. Y.Z., Y.X., B.J.H., and Y.W. directed the entire study.

Competing interests

The authors declare no conflicts of interest.

Additional information

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