

Harnessing database-supported high-throughput screening for the design of stable interlayers in halide-based all-solid-state batteries

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All-solid-state Li metal batteries (ASSLMBs) promise superior safety and energy density compared to conventional Li-ion batteries. However, their widespread adoption is hindered by detrimental interfacial reactions between solid-state electrolytes (SSEs) and the Li negative electrode, compromising long-term cycling stability. The challenges in directly observing these interfaces impede a comprehensive understanding of reaction mechanisms, necessitating first-principle simulations for designing novel interlayer materials. To overcome these limitations, we develop a database-supported high-throughput screening (DSHTS) framework for identifying stable interlayer materials compatible with both Li and SSEs. Using Li_3InCl_6 as a model SSE, we identify Li_3OCl as a potential interlayer material. Experimental validation demonstrates significantly improved electrochemical performance in both symmetric- and full-cell configurations. A $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{LiCoO}_2$ cell exhibits an initial discharge capacity of 154.4 mAh/g (1.09 mA/cm², 2.5–4.2 V *vs.* Li/Li⁺, 303 K) with 76.36% capacity retention after 1000 cycles. Notably, a cell with a conventional $\text{In-Li}_6\text{PS}_5\text{Cl}$ interlayer delivers only 132.4 mAh/g and fails after 760 cycles. An additional interlayer-containing battery with $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ as the positive electrode achieves an initial discharge capacity of 151.3 mAh/g (3.84 mA/cm², 2.5–4.2 V *vs.* Li/Li⁺, 303 K), maintaining stable operation over 1650 cycles. The results demonstrate the promise of the DSHTS framework for identifying interlayer materials.

Li-ion batteries power the modern world, from smartphones to electric vehicles¹. However, the increasing demand for higher energy densities, enhanced safety, and extended lifespans necessitate the development of next-generation energy storage solutions. While Li metal negative electrode offer high energy storage capacity, their propensity for

instability when combined with conventional liquid electrolytes raises significant safety concerns. All-solid-state Li-metal batteries (ASSLMBs) have emerged as a potential solution to this challenge². ASSLMBs face significant hurdles to commercialization, including the low ionic conductivity of solid-state electrolytes (SSEs), suboptimal interfacial

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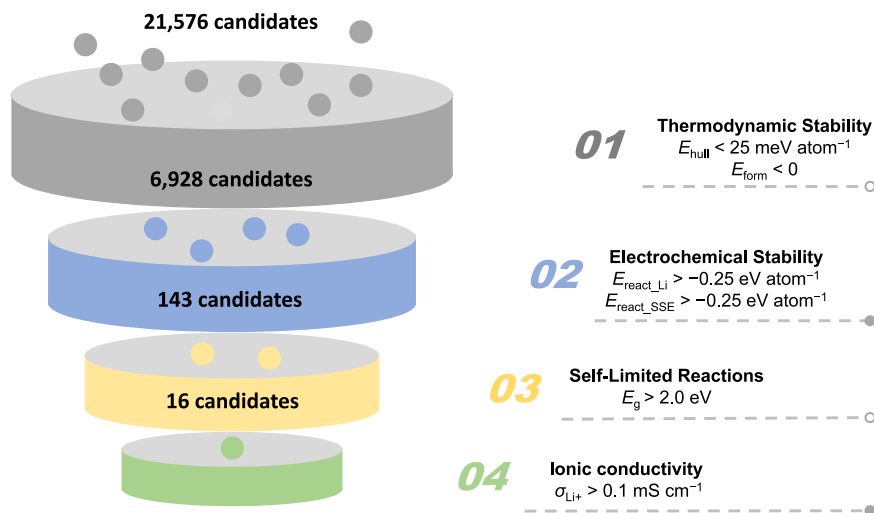


Fig. 1 | Database-supported high-throughput screening framework for interlayer materials at the Li|SSE interface. The framework consists of four sequential screening steps to identify promising interlayer material candidates. The gray, blue,

yellow, and green sections represent the screening for thermodynamic stability, electrochemical stability, self-limiting reaction behavior, and ionic conductivity, respectively.

contact, and poor electrochemical compatibility. Despite extensive research, a battery architecture with sustained, long-term stability remains elusive. These challenges underscore the critical importance of developing systematic approaches to identify and optimize viable battery configurations. Conventional approaches, such as trial-and-error experimentation and resource-intensive density functional theory (DFT) calculations³, are inadequate. Rapid and accurate screening methodologies are crucial to accelerate the discovery of suitable interlayer materials and advance the development of ASSLMBs.

Halide SSEs are promising candidates for ASSLMBs due to their high ionic conductivity at room temperature (exceeding 1.5 mS cm⁻¹ for compounds such as Li₃InCl₆⁴, Li₃YBr_{5.7}F_{0.3}⁵, and 1.6Li₂O-TaCl₅⁶), low Young's modulus (indicating good interface contact⁷), electrochemical stability up to 4.3 V *vs.* Li⁺/Li⁰⁸, and compatibility with commercial positive electrode materials, such as LiCoO₂ and Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O₂⁹. Despite these advantages, halide SSEs exhibit inherent reactivity with Li metal^{5,10–16}, leading to uncontrolled interfacial reactions that degrade electrochemical performance and long-term stability¹⁵. Interfacial engineering, particularly introducing an interlayer between Li and the halide SSE, offers a promising avenue to circumvent the inherent instability arising from their direct contact. Previous studies have explored the use of interlayer materials, including polymer electrolyte poly(butylene oxide)¹⁷, sulfides like Li₆PS₅Cl¹⁸, and composite materials incorporating In and Li₆PS₅Cl^{4,6,7,9,11,19–23}. However, these interlayer materials undergo continuous reactions with both the Li and the halide SSE, resulting in progressive interfacial resistance growth²⁴ and shortened battery lifespan^{5,17}. Although high-throughput screening studies have explored electrolyte-electrode stability and methods to mitigate interfacial reactions^{25–29}, systematic investigations that simultaneously evaluate interlayer material compatibility with both the SSE and electrodes have yet to be conducted.

Utilizing Li₃InCl₆ as a model SSE, we sought an interlayer material demonstrating thermodynamic and electrochemical stability with Li and Li₃InCl₆, while possessing high Li⁺ conductivity and negligible electronic conductivity. Rapid database-supported high-throughput screening (DSHTS) of over 20,000 Li-containing compounds³⁰ identified Li₃OCl as a promising interlayer candidate due to its thermodynamic and electrochemical stability, Li⁺ conductivity of 0.48 mS cm⁻¹ at 298 K and negligible electronic conductivity³¹. Scanning electron microscopy (SEM) confirmed that Li₃OCl forms a denser layer than Li₃InCl₆ on Li, supporting its suitability. Relative to conventional interlayers (*i.e.*, Li₆PS₅Cl and In-Li₆PS₅Cl), Li₃OCl significantly improved

the critical current density (CCD) from 2.4 mA cm⁻² to 4.2 mA cm⁻². The corresponding symmetric cell cycled more than 2400 h at 1 mA cm⁻² and 1 mAh cm⁻², exceeding the 50 h achieved with the Li₆PS₅Cl interlayer and the 800 h of the In-Li₆PS₅Cl interlayer at 0.016 mA cm⁻² and 0.016 mAh cm⁻². Full cells utilizing the Li₃OCl interlayer demonstrated significantly enhanced performance. Li|Li₃OCl|Li₃InCl₆|LiCoO₂ cells with high positive electrode material mass loading (6.2 mg cm⁻²) maintained 76.4% capacity retention (117.9 mAh g⁻¹) after 1000 cycles at 1 C (1.1 mA cm⁻²), while Li|Li₃OCl|Li₃InCl₆|Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O₂ cells sustained stable cycling for 1500 cycles at 3 C (3.84 mA cm⁻²) with ~50% capacity retention. These results represent a significant advancement over previously reported performance metrics for both Li₃InCl₆-based and other ASSLMB systems^{11,32–38}.

In summary, the DSHTS framework rapidly identified Li₃OCl as a promising interlayer material for Li₃InCl₆, establishing a streamlined screening approach for efficient material discovery. Experimental validation of Li₃OCl's efficacy demonstrated that this is a strategy that accelerates the development of high-performance ASSLMBs. Moreover, the versatility of the DSHTS framework is further demonstrated by recommending interlayers for other SSE-based ASSLMB systems, including those with Li₃ScCl₆, Li₃YBr₆, Li₆PS₅Cl, and Li₁₀Ge(PS₆)₂ electrolytes.

Results and discussion

Database-supported high-throughput screening

We employed a DSHTS methodology, leveraging DFT calculations to rapidly and systematically identify stable interlayer materials for the Li|Li₃InCl₆ interface (Fig. 1). This DSHTS framework retrieved 21,576 Li-containing materials from the Materials Project database³⁰. The selection of the interlayer candidates hinged on these four key criteria (further details can be found in Supplementary Note 1):

- (1) **Thermodynamic Stability.** To ensure against self-decomposition, materials with an energy above the convex hull (E_{hull}) below 25 meV atom⁻¹ were considered³⁹, and only those with a negative formation energy (E_{form}) from the constituent precursors were included.
- (2) **Chemical Compatibility.** To guarantee compatibility with both the Li and the SSE, materials exhibiting reaction energies ($E_{\text{react, Li}}$ with Li and $E_{\text{react, SSE}}$ with Li₃InCl₆ as calculated from the grand potential phase diagram⁴⁰) above -0.25 eV atom⁻¹ were selected.
- (3) **Self-Limiting Reaction Behavior and Conductivity.** Controlling electronic conductivity is crucial for limiting undesirable

$\text{Li}_6\text{PS}_5\text{Cl}$, generating In , Li_2S , Li_3P , and LiCl . The calculated reaction energy between Li_xIn_y alloys (x and y represent different ratios) and $\text{Li}_6\text{PS}_5\text{Cl}$ are below $-0.58 \text{ eV atom}^{-1}$ (Supplementary Table 7), indicating higher reactivity relative to the reaction energy between Li and Li_3OCl ($-0.14 \text{ eV atom}^{-1}$, Supplementary Table 1). At the Li_3InCl_6 side, there is a two-step degradation reaction, as combining $\text{Li}_6\text{PS}_5\text{Cl}$ with Li_3InCl_6 results in the formation of LiCl , LiInS_2 , and Li_3PS_4 . Subsequently, Li_3InCl_6 and Li_3PS_4 further react to form In , LiCl , LiInS_2 , and P_2S_7 (Supplementary Table 7). The presence of electron-conducting compounds (In and Li_3P ; Supplementary Table 6) at the interface drives continuous reactions that only stop when reactants are depleted. This progressive degradation results in an increased cell resistance (Supplementary Fig. 5c).

Electrochemical characterization of the interlayer

Li_3OCl was synthesized as described in the “Methods” section. The corresponding X-ray diffraction (XRD) pattern aligned well with both literature³¹ and first-principle simulations (Supplementary Fig. 8a). Due to the hygroscopic nature of Li_3OCl , Fourier-transform infrared spectroscopy (FTIR) analysis was conducted to evaluate sample purity. The absence of characteristic O-H stretching vibrations in the $1800\text{--}2500$ and $3500\text{--}3800 \text{ cm}^{-1}$ regions (Supplementary Fig. 8b)^{52,58} confirms the successful synthesis of phase-pure Li_3OCl without detectable hydrated impurities such as Li_2OHCl ³⁹ or $\text{Li}_4(\text{OH})_3\text{Cl}$ ⁵⁹. The room-temperature ionic conductivity of Li_3OCl was measured to be 0.48 mS cm^{-1} (Supplementary Fig. 9), consistent with the literature³¹.

To evaluate the compatibility of Li_3OCl with both the Li and Li_3InCl_6 , $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}_3\text{OCl}|\text{Li}$ symmetric cells were assembled. Figure. 3a shows the impedance evolution of this cell. Initially, the interfacial resistance was measured to be 690Ω , followed by a slight increase to 720Ω , and then, the resistance then significantly decreased to $\sim 200 \Omega$ within 24 h, stabilizing at 191Ω (details can be found in Supplementary Fig. 10). The rapid decrease in interfacial resistance suggests interface stabilization through two processes: 1) the formation of a stable interfacial passivation layer and 2) the enhanced interfacial contact achieved under externally applied pressure (~ 1.5 tons). SEM analysis reveals the morphology of the interface changed from an initial two-phase structure containing voids to a homogeneously densified $7\text{-}\mu\text{m}$ -thick layer (Fig. 3b, Supplementary Fig. 10). In comparison, the impedance increase is more substantial for symmetric cells with $\text{Li}_6\text{PS}_5\text{Cl}$ interlayer and $\text{In-Li}_6\text{PS}_5\text{Cl}$ interlayer, such that even at low current densities (0.016 mA cm^{-2}), the polarization voltage is up to 2 V , as shown in Supplementary Fig. 5c. Further electrochemical characterization revealed that the cell's CCD (4.2 mA cm^{-2} , Fig. 3c) was considerably higher than the $\text{In-Li}_6\text{PS}_5\text{Cl}$ interlayer (2.4 mA cm^{-2} , Supplementary Fig. 5b). Furthermore, the symmetric cell could cycle stably for over 2400 h at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} (Fig. 3d).

After 500 h of operation, the composition of the interface was analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The resulting ion map (Fig. 3e) acquired over a $250 \mu\text{m} \times 250 \mu\text{m}$ area, reveals a distinct boundary between O^{2-} and In^{3+} . InO^+ was detected within the overlapping region, in agreement with the predicted reaction products of LiInO_2 , In_2O_3 , and InClO as determined by DFT calculations (Supplementary Table 1). Notably, the intensities of O^{2-} and In^{3+} were 2 orders of magnitude higher than those of InO^+ and LiInO^{2+} (Supplementary Fig. 11). This observation suggests the occurrence of self-limiting reactions at the $\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6$ interface. X-ray photoelectron spectroscopy (XPS) analysis of the $\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6$ interface (Fig. 3f) revealed prominent $\text{Li } 1s$, $\text{O } 1s$, and $\text{Cl } 2p$ peaks from the primary phases while showing markedly reduced $\text{In } 3d$ signals, indicating minimal In-O bonds formed at that interface (peak intensity ratios shown in scale bars, lower left of each spectrum). This result aligns with the low intensity of the In-O bond observed in the RDF analysis (Fig. 2c) at the $\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6$ interface, which implies a

limited formation of In-O species at the interface. These findings collectively support the self-limiting nature of the electrochemical reactions at the interface, a critical factor contributing to the stable cycling performance of the cell.

The distinct interfacial stability behaviors of Li_3OCl and $\text{In-Li}_6\text{PS}_5\text{Cl}$ interlayers can be traced to the electronic properties of the corresponding reaction products. When Li_3OCl reacts with $\text{Li/Li}_3\text{InCl}_6$, it forms an electrically insulating layer passivating at the interface. In contrast, $\text{In-Li}_6\text{PS}_5\text{Cl}$ produces electronically conductive reaction products, which trigger continuous interfacial degradation until reactants are depleted.

To evaluate the effectiveness of the Li_3OCl interlayer in enhancing the long-term cycling performance of halide-based ASSLMs, three cell configurations were assembled: i) $\text{Li}|\text{In-Li}_6\text{PS}_5\text{Cl}|\text{Li}_3\text{InCl}_6|\text{LiCoO}_2$ (control cell with LiCoO_2 as the positive electrode material), ii) $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{LiCoO}_2$ (with the Li_3OCl interlayer and LiCoO_2 as the positive electrode material), and iii) $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ (with the Li_3OCl interlayer and $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ as the positive electrode material). All cells had a positive electrode material mass loading of 6.24 mg cm^{-2} . As shown in Fig. 4a, the Li_3OCl -based cell exhibited a significantly higher initial discharge capacity (154.4 mAh g^{-1}) compared to the $\text{In-Li}_6\text{PS}_5\text{Cl}$ control cell (132.4 mAh g^{-1}), which is attributed to the lower electrochemical potential of Li metal relative to the Li-In alloy. Notably, after 1000 cycles, the cell incorporating the Li_3OCl interlayer ($\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{LiCoO}_2$) retained 76.36% of its initial capacity, a substantial improvement over the control cell ($\text{Li}|\text{In-Li}_6\text{PS}_5\text{Cl}|\text{Li}_3\text{InCl}_6|\text{LiCoO}_2$), which exhibited only 5.21% capacity retention and presented a rapid capacity decline after 760 cycles (Fig. 4b).

To assess its performance at high current densities, the $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ cell was subjected to cycling at a rate of 3 C (3.84 mA cm^{-2}), nearing the CCD of 4.2 mA cm^{-2} measured in the symmetric configuration. This full cell delivered a high initial discharge capacity of 151.3 mAh g^{-1} and retained 64.73% of its initial capacity after 1000 cycles, cycling stably more than 1600 times (Fig. 4d). Supplementary Fig. 12 benchmarks our results against previous studies (further details are provided in Supplementary Tables 8 and 9). The Li_3OCl interlayer enhances the electrochemical performance, as evidenced by the high CCD, surpassing previously reported results (Supplementary Fig. 12a). Moreover, its long-term cycling capacity retention (with the dots representing the maximum cycle number and corresponding capacity retention reported in the literature, Supplementary Fig. 12b) is superior to that of ASSLMs based on other interlayer materials.

The DSHTS framework was further validated by extending its application to identify compatible interlayer materials for four additional Li-unstable SSEs , namely Li_3ScCl_6 , Li_3YBr_6 , $\text{Li}_6\text{PS}_5\text{Cl}$, and $\text{Li}_{10}\text{Ge}(\text{PS}_6)_2$. For each SSE, the screening process identified over 40 candidate materials fulfilling the first three criteria outlined in Fig. 1 (detailed in Supplementary Fig. 13 and Supplementary Tables 10–17). Among these candidates, Li_3OCl emerged as the optimal interlayer material for both $\text{Li}|\text{Li}_3\text{ScCl}_6$ and $\text{Li}|\text{Li}_3\text{YBr}_6$ interfaces, satisfying all four screening criteria. Additionally, Li_2Se and Li_2S showed promise as potential interlayers for $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}|\text{Li}_{10}\text{Ge}(\text{PS}_6)_2$ systems, meeting the first three criteria and approaching the fourth criterion with appreciable ionic conductivity (0.01 mS cm^{-1} , Supplementary Table 6). These results demonstrate the DSHTS framework's efficacy in rapidly identifying multiple viable solutions for enhancing the negative electrode stability in ASSLMs across diverse SSE systems.

This study introduces a database-supported high-throughput screening framework to address interfacial instability in halide SSEs-based ASSLMs by considering interlayer material's compatibility with both Li and the SSE. Guided by first-principles calculations and validated experimentally, we identified Li_3OCl as a promising interlayer material for Li_3InCl_6 . The Li_3OCl interlayer with a high ionic conductivity but a low electronic conductivity increased the critical

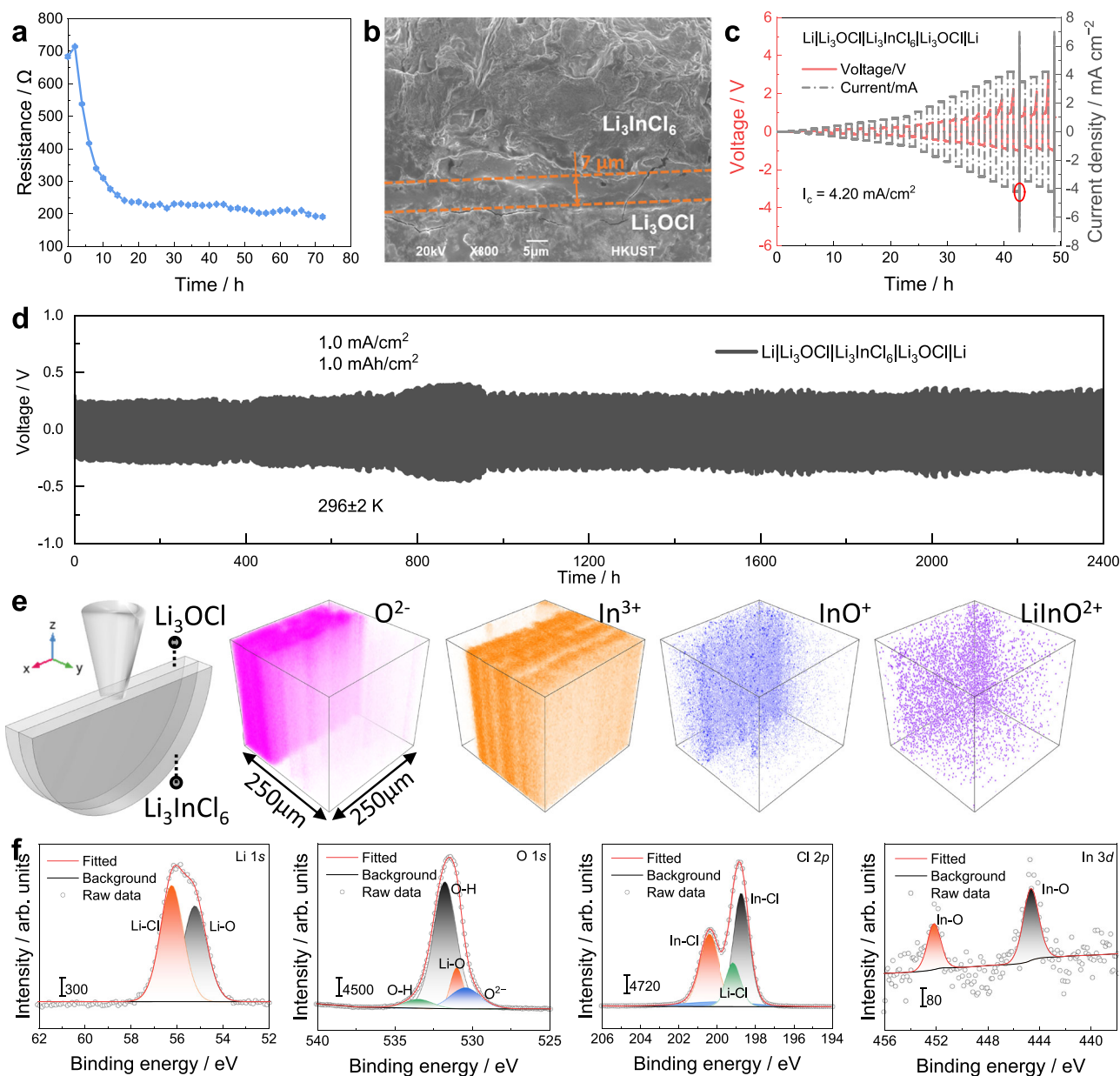


Fig. 3 | Electrochemical and interfacial characterization of Li_3OCl compatibility with Li and Li_3InCl_6 . **a** Time-dependent evolution of interfacial resistance in a $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}_3\text{OCl}|\text{Li}$ symmetric cell. **b** Cross-sectional SEM micrograph of the $\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6$ interface after 72-hour operation. **c** CCD determination via stepwise current polarization. **d** Extended galvanostatic cycling performance of the symmetric cell at 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} . **e** ToF-SIMS analysis showing

sputtering geometry (left) and three-dimensional ion distribution maps (O^{2-} , In^{3+} , InO^+ , and LiInO^{2+}) at the $\text{Li}_3\text{InCl}_6|\text{Li}_3\text{OCl}|\text{Li}$ interface after 500-hour cycling (sputtering parameters: 1000 s duration, $250 \times 250 \mu\text{m}^2$ area). **f** High-resolution XPS core-level spectra (Li 1s, O 1s, Cl 2p, and In 3d) of the cycled $\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6$ interface, with relative peak intensities indicated by scale bars.

current density of a $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}_3\text{OCl}|\text{Li}$ symmetric cell from 2.4 mA cm^{-2} to 4.2 mA cm^{-2} and enabled corresponding symmetric cells to cycle stably for more than 2400 h. Furthermore, full cells with LiCoO_2 and $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ as positive electrode materials demonstrated enhanced cycling stability under varying rates, retaining high capacity retention rates of 76.36% and 64.73%, respectively, after 1000 cycles. These results outperformed those from control cells without the interlayer, which retained only 5.21% of their capacity after 1000 cycles. The screening framework presented here can be readily adapted to identify stable interface materials for a variety of SSEs that react with Li metal. This work contributes meaningfully to the ongoing efforts to commercialize this promising technology, with the potential to usher in a new generation of safer, more powerful, and higher energy density energy storage solutions.

Methods

DFT calculations

DFT simulations were conducted using the Vienna ab initio Simulation Package (VASP)⁶⁰. The projected augmented wave method⁶¹ with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation⁶² was used for all the calculations. For structural relaxation, energy and residual force convergence thresholds were set to 10^{-6} eV and $0.02 \text{ meV atom}^{-1}$, respectively. The plane wave cutoff energy was set to 520 eV, and a proper Monkhorst-Pack k -mesh was employed (Supplementary Data and Legends for Supplementary Data). While the primitive cell of Li_3InCl_6 was obtained from experiments⁴, the primitive cells of Li_3OCl and $\text{Li}_6\text{PS}_5\text{Cl}$ were obtained from the Materials Project database (Material IDs: mp-985585 and mp-985592, respectively). The methods used to compute the interface formation energy are detailed

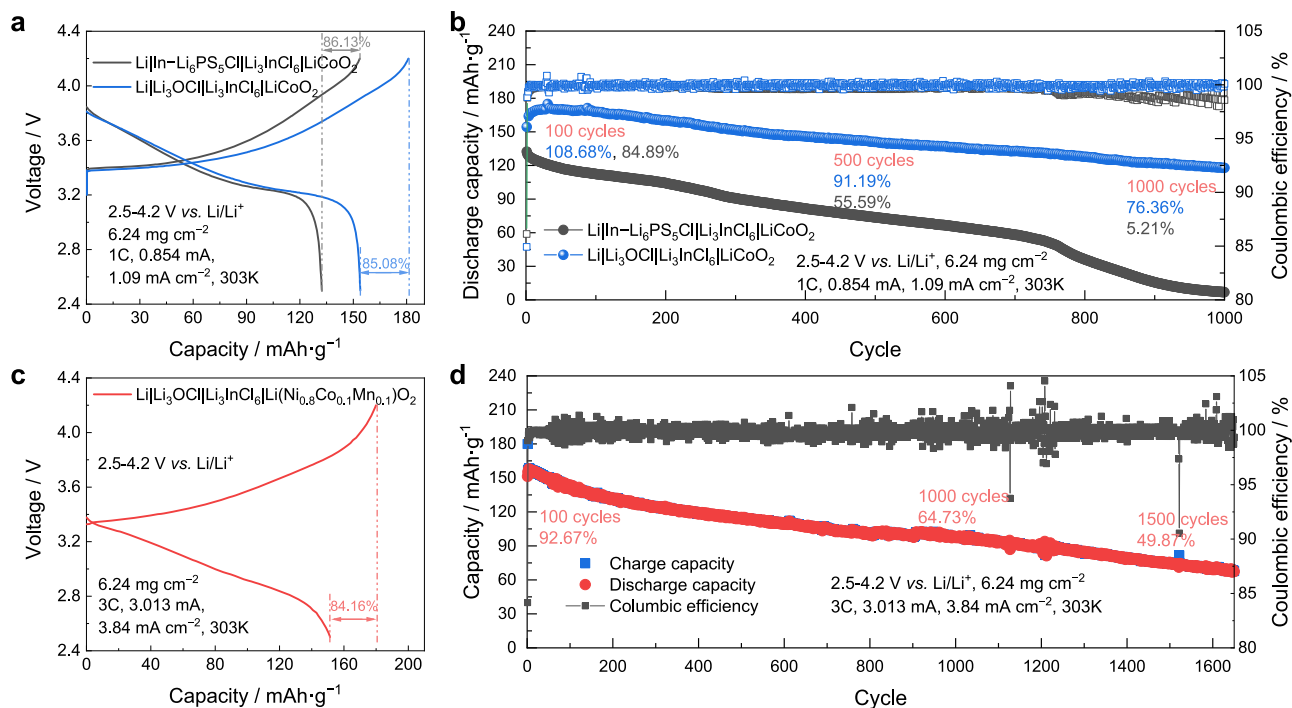


Fig. 4 | Electrochemical performance evaluation of ASSLMBs at 303 K. **a** Initial galvanostatic charge-discharge profiles comparing $\text{Li|In-Li}_6\text{PS}_5\text{Cl|Li}_3\text{InCl}_6\text{|LiCoO}_2$ and $\text{Li|Li}_3\text{OCl|Li}_3\text{InCl}_6\text{|LiCoO}_2$ cells at 1 C rate (1.1 mA cm^{-2}). **b** Cycling stability and Coulombic efficiency of both cell configurations at 1 C rate over 1000 cycles. **c** First-

cycle voltage profile of $\text{Li|Li}_3\text{OCl|Li}_3\text{InCl}_6\text{|Li(Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ cell at 3 C rate (3.8 mA cm^{-2}). **d** Long-term cycling performance and Coulombic efficiency of the $\text{Li|Li}_3\text{OCl|Li}_3\text{InCl}_6\text{|Li(Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ -based cell at 3 C rate through 1500 cycles.

in Supplementary Note 2. The Python Materials Genomics (pymatgen) package⁶³ and the Materials Project API³⁰ were used to analyze the convex hull, formation, and reaction energies with Li and the SSEs.

The atomic coordinates of structurally optimized models for density of states calculations, along with initial/final configurations of the Li_3OCl (1 0 0)| Li_3InCl_6 (1 0 0) and $\text{Li}_6\text{PS}_5\text{Cl}$ (1 0 0)| Li_3InCl_6 (1 0 0) interfacial models, are archived in Supplementary Data 8 and 9.

Materials preparation

Solid-state electrolytes. Li_3InCl_6 was synthesized using a stoichiometric ratio of 3:1 LiCl (Aladdin, $\geq 99\%$) and InCl_3 (Aladdin, 99.99%). The precursors were thoroughly mixed by ball milling using a Retsch MM400 mixer mill at 25 Hz for 10 min in an Ar-filled ZrO_2 grinding jar. The resulting mixture was loaded into a quartz crucible and heated to 533 K in a vacuum tube furnace following a temperature ramp of 5 K min^{-1} . After holding at this temperature for 5 h⁴, the sample was cooled back to room temperature at a controlled rate of 3 K min^{-1} . The synthesized Li_3InCl_6 was characterized using X-ray diffraction (XRD) and its conductivity is presented in an Arrhenius plot (Supplementary Fig. 14).

Li_3OCl was prepared using a similar approach. Stoichiometric quantities of LiOH (99.9%, Aladdin) and LiCl ($\geq 99\%$, Aladdin) were mixed and milled following the same procedure. The mixture was then transferred to a quartz crucible and sintered in a vacuum tube furnace at 623 K for 72 h³¹. Maintaining a high vacuum (barometric pressure less than 0.03 bar) throughout the process was crucial for removing any water vapor produced, as its presence could introduce impurities.

All the synthesis processes were conducted in an Ar-filled ($\geq 99.999\%$, Air Products) glovebox (Mikrouna, Super 1220/750) with O_2 and H_2O concentrations maintained below 0.01 ppm.

$\text{Li}_6\text{PS}_5\text{Cl}$ was purchased from Zhejiang Fengli New Energy Technology Co., Ltd.

Electrodes. The 20 μm thick Li foil and In foil were purchased from China Energy Lithium Co., Ltd and Fuxiang Metal Materials Co., Ltd, respectively. LiCoO_2 , $\text{Li(Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$, and super P were purchased from Canrd Co., Ltd. The composite positive electrode was prepared by mixing Li_3InCl_6 , $\text{LiCoO}_2/\text{Li(Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$, and super P with a mass ratio of 3:7:0.05 with a Retsch MM400 mixer mill at 25 Hz for 10 min. All processes were conducted in an Ar-filled ($\geq 99.999\%$, Air Products) glovebox (Mikrouna, Super 1220/750) with O_2 and H_2O concentrations maintained below 0.01 ppm.

Materials characterization

XRD was detected via a PANalytical Empyrean Pro-diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 10 to 90°. Surface composition of cycled electrodes and interfaces were analyzed using X-ray photoelectron spectroscopy (XPS, PHI5600). Fourier-transform infrared (FTIR) spectra were recorded on a Bruker ALPHA spectrometer. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a JEM 6700 F microscope. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was conducted on an IonToF M6 analyzer employing thermal ionization Cs^+ as the primary ion source.

To prevent atmospheric exposure, samples for XRD and FTIR measurements were sealed within an Ar-filled holder. Samples from cycled batteries, which were initially disassembled in an Ar-filled glovebox, were transferred to the XPS, SEM/EDX, and ToF-SIMS instruments via a transfer vessel.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was conducted on a BioLogic VSP-300 electrochemical workstation using stainless steel rods as blocking electrodes. Measurements spanned a frequency range of 1 Hz to 7 MHz with an AC amplitude of 10 mV and 6 points per decade. 150 mg of either Li_3InCl_6 or Li_3OCl powder was compressed

into 10 mm diameter pellets in a polyether ether ketone (PEEK) mold at a pressure of 2 tons and secured with bolts to obtain a dense pellet. Then, the mold was sealed with rubber rings and brought out of the glovebox for EIS characterization.

To assess the electrochemical compatibility of various interlayers with Li and Li_3InCl_6 , symmetric cells were assembled in the following configurations: $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}|\text{Li}_3\text{InCl}_6|\text{Li}_6\text{PS}_5\text{Cl}|\text{Li}$, $\text{Li}|\text{In-Li}_6\text{PS}_5\text{Cl}|\text{Li}_3\text{InCl}_6|\text{Li}_6\text{PS}_5\text{Cl}|\text{In}|\text{Li}$, and $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}_3\text{OCl}|\text{Li}$. For cell preparation, 90 mg of Li_3InCl_6 powder was initially compressed within a 10 mm diameter PEEK mold at 1.5 tons of pressure for 1 min. Subsequently, 30 mg of either $\text{Li}_6\text{PS}_5\text{Cl}$ or Li_3OCl powder was uniformly distributed on both sides of the Li_3InCl_6 pellet and subjected to the same pressure for 1 min. For the $\text{Li}_6\text{PS}_5\text{Cl}$ and Li_3OCl interlayers, a 9 mm diameter, 20 μm thick Li foil disk was directly attached. For the $\text{In-Li}_6\text{PS}_5\text{Cl}$ interlayer, a 10 mm diameter, 20 μm thick In foil disk was positioned on the $\text{Li}_6\text{PS}_5\text{Cl}$ interlayer, followed by a 9 mm diameter, 20 μm thick Li foil disk. The assembly was then compressed at 1.5 tons for 1 min and secured with bolts. The resulting cells were cycled using a CT2001A battery cycling system (LANHE) within a temperature chamber (ESPEC, SU-242-5) maintained at $303 \pm 1\text{ K}$. CCD measurements were performed on symmetric cells using stepwise increasing current densities, with a fixed plating/stripping duration of 1 h per step. Long-term cycling tests of symmetric cells were conducted at 1.0 mA cm^{-2} for $\text{Li}|\text{Li}_3\text{OCl}|\text{Li}_3\text{InCl}_6|\text{Li}_3\text{OCl}|\text{Li}$ cell, and at $1.6 \times 10^{-2}\text{ mA cm}^{-2}$ for both the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}|\text{Li}_3\text{InCl}_6|\text{Li}_6\text{PS}_5\text{Cl}|\text{Li}$ and $\text{Li}|\text{In-Li}_6\text{PS}_5\text{Cl}|\text{Li}_3\text{InCl}_6|\text{Li}_6\text{PS}_5\text{Cl}|\text{In}|\text{Li}$ cells. The assembly of solid-state batteries followed a procedure analogous to that of the symmetric cells. Initially, 90 mg of Li_3InCl_6 powder was compressed uniaxially in a PEEK mold for 1 min at a pressure of 1.5 tons. Subsequently, 30 mg of either $\text{Li}_6\text{PS}_5\text{Cl}$ or Li_3OCl powder underwent identical compression on one side of the Li_3InCl_6 pellet. For cells incorporating the $\text{In-Li}_6\text{PS}_5\text{Cl}$ interlayer, In foil was sandwiched between the $\text{Li}_6\text{PS}_5\text{Cl}$ and the Li foil. For cells with the Li_3OCl interlayer, a piece of Li foil was directly attached to the Li_3OCl . Lastly, 7 mg of composite positive electrode powder (with a corresponding positive electrode material mass loading of 6.24 mg cm^{-2}) was uniformly distributed on the opposite side of the Li_3InCl_6 pellet to the Li foil. The assembled cell was then pressed uniaxially at 1.5 tons for 1 min. Following this step, the assembled cell was cycled at 303 K under the corresponding strain state, which was maintained by mechanically constraining the cell with stainless steel casing and bolts. A stack pressure of 1.5 tons (187.5 MPa) was applied, and this value was benchmarked against the literature (Supplementary Table 18). All assembly took place within an Ar-filled ($\geq 99.999\%$, Air Products) glovebox (Mikrouna, Super 1220/750) with O_2 and H_2O concentrations below 0.01 ppm. Cells were cycled using a LANHE CT2001A battery tester within an ESPEC, SU-242-5 temperature chamber, maintained at $303 \pm 1\text{ K}$. All batteries were cycled with a voltage window of 2.5–4.2 V (*vs.* Li/Li^+). Cycling currents were 0.85 mA (1 C, 1.09 mA cm^{-2}) for LiCoO_2 positive electrode, and 3.01 mA (3 C, 3.84 mA cm^{-2}) for $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ positive electrode.

At least three full cells of each configuration were assembled and tested to ensure the reliability of the results and reproducibility. Representative data, selected for both capacity and cycle stability, are presented here; the cycling performance of the remaining cells is shown in Supplementary Fig. 15.

Declaration of the use of generative AI and AI-assisted technologies in the writing process

The authors declare that the large language model Claude 3.5 Sonnet was utilized to streamline the language of this manuscript. Following the use of this tool, the authors thoroughly reviewed and revised the content as necessary. Dr. Mark Ellwood (Cantab) further refined the manuscript for clarity, grammatical correctness, and language accuracy. The authors assume full responsibility for the final content of the published article.

Data availability

The data generated in this study are provided in the Supplementary Information, Supplementary Data, and Source Data file. Additional data are available from the corresponding author upon request. Source data are provided with this paper.

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Author contributions

L.S. and F.C. conceived this research project and wrote the manuscript. L.S. performed the simulations and experiments, analyzed the data, and wrote the initial draft. F.C. supervised the study, designed the work, and led the subsequent writing and revision of the manuscript. Z.W., H.M.L., S.X., and Y.Z. contributed to the discussions and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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