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Interface design for all-solid-state lithium batteries

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The operation of high-energy all-solid-state lithium-metal batteries at low stack pressure is challenging owing to the Li dendrite growth at the Li anodes and the high interfacial resistance at the cathodes¹⁻⁴. Here we design a Mg₁₆Bi₈₄ interlayer at the Li/Li₆PS₅Cl interface to suppress the Li dendrite growth, and a F-rich interlayer on LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathodes to reduce the interfacial resistance. During Li plating-stripping cycles, Mg migrates from the Mg₁₆Bi₈₄ interlayer to the Li anode converting Mg₁₆Bi₈₄ into a multifunctional LiMgS_x-Li₃Bi-LiMg structure with the layers functioning as a solid electrolyte interphase, a porous Li₃Bi sublayer and a solid binder (welding porous Li₃Bi onto the Li anode), respectively. The Li₃Bi sublayer with its high ionic/electronic conductivity ratio allows Li to deposit only on the Li anode surface and grow into the porous Li₃Bi sublayer, which ameliorates pressure (stress) changes. The NMC811 with the F-rich interlayer converts into F-doped NMC811 cathodes owing to the electrochemical migration of the F anion into the NMC811 at a high potential of 4.3 V stabilizing the cathodes. The anode and cathode interlayer designs enable the NMC811/Li₆PS₅Cl/Li cell to achieve a capacity of 7.2 mAh cm⁻² at 2.55 mA cm^{-2} , and the LiNiO₂/Li₆PS₅Cl/Li cell to achieve a capacity of 11.1 mAh cm⁻² with a cell-level energy density of 310 Wh kg⁻¹ at a low stack pressure of 2.5 MPa. The Mg₁₆Bi₈₄ anode interlayer and F-rich cathode interlayer provide a general solution for all-solid-state lithium-metal batteries to achieve high energy and fast charging capability at low stack pressure.

All-solid-state lithium-metal batteries (ASSLBs) with NMC811 cathodes can meet the high-energy-density and safety requirements for electric vehicles and large-scale energy storage systems. However, the operation of Li||NMC811 cells at a high capacity and a high rate under a low stack pressure has been restricted by the Li dendrite growth and electrolyte reduction on the Li anode side, and the formation of a highly resistive interphase on the cathode^{5,6}. On the Li anode side, introducing a dense interlayer with a high electronic conductivity (Au, Al and so on)⁷⁻⁹, a high lithiation potential (versus Li⁺/Li, Si, Sn, Sb, In and so on) $^{\rm 10-14}$ or lithiophobicity (W and so on) $^{\rm 8}$ at the solid-state electrolyte/ Li (SSE/Li) interface cannot simultaneously prevent SSE reduction and suppress Li dendrite growth. On the cathode side, the coating of LiNbO₃ on the NMC811 cathode cannot prevent NMC811 from reacting with the electrolyte owing to the evolution of cracks in LiNbO₃@NMC811 cathodes during charge-discharge cycles^{15,16}. Therefore, the rational design of interphases at Li/SSE and NMC811/SSE interfaces to enable NMC811||Li ASSLBs to achieve superior performance at a low stack pressure is highly desired.

In this work we designed a $Mg_{16}Bi_{84}$ interlayer between the Li anode and Li_6PS_5Cl , and a F-rich layer on the surface of NMC811, which simultaneously solved the challenges associated with both Li anodes and NMC811 cathodes (Fig. 1a-c). During the initial annealing and Li platingstripping activation cycles, the $Mg_{16}Bi_{84}$ interlayer converted into a multifunctional LiMgS_x-Li₃Bi-LiMg triple interlayer enabling Li plating at the LiMg surface and penetrating into the porous Li₃Bi (Supplementary Fig. 1), and the surface F-rich NMC811 converted into F-doped NMC811 (F@NMC811) cathodes (Fig. 1a,b) at a high potential of 4.3 V owing to the electrochemical migration of F anion from the surface to the bulk of NMC811. The Mg₁₆Bi₈₄ anode interlayer and F-doped NMC811 cathode enable NMC811||Li ASSLBs to achieve superior performance at a low stack pressure, paving the way for the commercialization of ASSLBs.

Formation of LiMg-Li₃Bi-LiMgS_x/Li₆PS₅Cl

Mg–Bi alloys (Mg_xBi₈₄; x = 0, 2, 8, 16, 24) with different compositions were synthesized by ball-milling of Bi and Mg powders at different weight ratios (Supplementary Table 1). As Mg₁₆Bi₈₄ enables Li₆PS₅Cl to achieve the highest critical current density (CCD), 1.9 mA cm⁻² at 1.9 mAh cm⁻² (Supplementary Fig. 2 and Supplementary Discussion 1), it was selected to investigate the Mg migration process during the Li plating–stripping activation process.

At the Li/Mg₁₆Bi₈₄ interface, the Li reacts with the Mg₁₆Bi₈₄ forming a Li₃Bi compound and a Li_xMg solid solution (Supplementary Fig. 3). The formed Li₃Bi does not convert back to Bi during Li stripping owing to the high potential of Li₃Bi as demonstrated by the X-ray powder diffraction patterns (Supplementary Figs. 4 and 5 and Supplementary Discussion 2). The formation of the Li_xMg solid solution is attributed to the high solubility of Mg in Li metal (Supplementary Fig. 3).

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Fig. 1| Design principle, characterization and modelling of in situ transformation of Li₆PS₅Cl/Mg₁₆Bi₈₄/Li to Li₆PS₅Cl/LiMgS_x/Li₃Bi/LiMg. **a**-c, Illustrations of the in situ formation of F@NMC811/Li₆PS₅Cl/LiMgS_x/Li₃Bi/ LiMg. **d**, Cross-sectional scanning electron micrographs and EDS images of the Li₃Bi/Li interface (converted from the Mg₁₆Bi₈₄/Li interface) after the tenth Li plating cycle at 1.0 mA cm⁻² and 1.0 mAh cm⁻². Scale bars, 20 μ m. The white dashed line represents the Li/LiMg interface. The area between red and green dashed lines is rich in Mg and poor in Bi, demonstrating that Li₃Bi was bonded to Li by LiMg. **e**, Distributions of Li⁺, Mg⁺ and Li₂MgS₂²⁺ along the depth of the Mg₁₆Bi₈₄ to the bottom Li. **f**,**g**, Simulated Li concentration distribution in a

solid-solution alloy (**f**; for example, Li–Mg alloy) and an intermetallic spherical particle (**g**; for example, Li–Zn and Li–Bi intermetallic compounds) at the 1,000th time step. Blue (intensity: 0) represents no implanted Li⁺ in M; increasing intensity from 0 (blue) to 1 (red) represents the increase in implanted Li⁺ amount in M; a.u., arbitrary units. **h**, Potential evolution in Li₆PS₅Cl/LiMgS_x/Li₃Bi/LiMg, **i**, Diffusion path of Mg or Zn (orange spheres) on the surface of Li₃Bi (purple spheres represent Bi atoms and green spheres represent Li atoms). **j**, The diffusion energy barrier of Zn and Mg on the Li₃Bi (110) surface from nudged elastic band calculations.

Energy-dispersive spectroscopy (EDS) images (Fig. 1d) show that most Mg moved to the Li₃Bi/Li interface after Li plating, strongly welding the porous Li₃Bi to the Li anode, and Li₃Bi maintained its interlayer position. As we cannot map Li in EDS images, we assume the Mg to be Li_xMg alloy and the Bi to be Li₃Bi. The Li₃Bi formed in situ has a much higher ratio of ionic/electronic conductivity (Supplementary Fig. 6) compared with $Mg_{16}Bi_{84}$ (Supplementary Fig. 7), which allows Li plating at the Li/Li₃Bi interface (rather than at the Li₆PS₅Cl/Li₃Bi interface) and then penetration into the porous Li₃Bi (Fig. 1d). The O intensity in the Li₃Bi layer is much higher than that in the Li layer after Li plating (Fig. 1d; O is an indicator for Li owing to Li oxidation during sample transfer

for scanning electron microscopy (SEM) and EDS tests), evidencing Li penetration into the Li₃Bi layer after Li plating as the O intensity of the porous Li₃Bi is similar to that of Li (Supplementary Fig. 8). After Li stripping, the Li_xMg remained at the Li₃Bi/Li interface (Supplementary Fig. 8), and strongly bonds the porous Li₃Bi to the Li ensuring a low contact resistance during Li plating–stripping.

At the $Mg_{16}Bi_{84}/Li_6PS_5Cl$ interface, the $Mg_{16}Bi_{84}$ reacts with the Li_6PS_5Cl forming a LiMgS_x solid electrolyte interphase (SEI). As shown in Fig. 1e and Supplementary Figs. 9 and 10, the intensities of Mg^+ and $Li_2MgS_2^{2+}$ were high at the interlayer/ Li_6PS_5Cl interface, and then quickly decreased along the depth of the interlayer (Fig. 1e), confirming that the

reaction between Mg and Li₆PS₅Cl forms a LiMgS_x layer at the Li₆PS₅Cl/Mg₁₆Bi₈₄ interface, and the other Mg migrated to the Li/Li₃Bi interface forming porous Li₃Bi. The LiMgS_x SEI can suppress reduction of Li₆PS₅Cl (ref. 17) even if Li fully penetrates into the pores of Li₃Bi. When further sputtered from the LiMgS_x SEI to the Li₃Bi, the Mg content dropped to zero whereas the Li content was maintained in the interlayer, demonstrating that Mg completely migrated into the Li anode (Fig. 1a-c).

The migration capability of Mg in porous Li_3Bi is mainly attributed to the formation of the Li_xMg solid solution. The migration kinetics of metal elements under an electric field is affected by the amount of electrochemical implanted Li^* in the metal and the migration energy barrier of the metal across the interlayer. To investigate the migration mechanism of metal elements under an electric field, the Li_xZn intermetallic compounds¹⁸ were selected to compare with the Li_xMg solid solution.

The amount of electrochemically implanted Li⁺ in metal

Li⁺ can electrochemically implant into nano-M (M = solid solution or intermetallic compound) forming $(LiM_x)^+$ in the interlayers with low electronic conductivity because the $(LiM_x)^+$ has lower total energy than the neutral compound (Supplementary Fig. 11, Supplementary Table 2 and Supplementary Discussion 3). The amount of positive charge implanted is affected by the Li⁺ solubility in M, the lithiation potential of M and the lithiophobicity of the lithium compounds.

Regarding the Li⁺ solubility in M, Fig. 1f shows that Li can successfully diffuse into the core of solid-solution metal (for example, Mg). However, lithium accumulation was observed only at a thin surface layer in an intermetallic particle (Fig. 1g). Therefore, intermetallic alloys including Zn (ref. 18) or Bi (ref. 19) take up only a small amount of positive charge and migrate in the electric field at a low rate. By contrast, solid-solution metal (Mg) that can take up more Li⁺ ions will be more positively charged than intermetallic alloy (Zn or Bi), which in turn facilitates its migration in the electric field (Supplementary Fig. 12 and Supplementary Discussion 4).

Regarding the lithiation potential of M, one Bi atom takes up three Li⁺ ions to form Li₃Bi at a high potential of 0.7 V (Supplementary Fig. 13a), whereas one Zn atom takes up only about 0.3 Li⁺ ions (Supplementary Fig. 13b) at a similar potential. Therefore, more positive charges accumulate at Bi particles (Supplementary Fig. 14), which facilitates their migration.

Regarding the lithiophobicity of lithium compounds, lithiophobic components such as LiF cannot take up positive charge on the basis of density functional theory calculations (Supplementary Table 3). Therefore, LiF cannot migrate. In summary, the mobility of Li alloys and compounds in the interlayer decreases in the order of Li–Mg > Li–Bi > Li–Zn > LiF. In the Mg₁₆Bi₈₄ interlayer, Mg migrates but Bi remains in the interlayer.

The migration energy barrier of the metal across the interlayer

The $(LiMg_{y})^{+}$ and $(LiZn_{y})^{+}$ migrate through the Li₃Bi surface to the Li anode under the electric field (during Liplating; Fig. 1h). The formed $(Li_xMg)^+$ cation can jump along bridge positions of the Li₃Bi (110) surface (Fig. 1i and Supplementary Figs. 15 and 16) and migrate to the Li anodes forming Li, Mg alloy on the Li surface. Nudged elastic band calculations show that Mg atoms can migrate on the surface of Li₃Bi with a much lower energy barrier (0.03 eV) than that of Zn atom (0.12 eV; Fig. 1j). After Mg migration, the formed LiMg alloy layer at the Li/Li₃Bi interface can promote Li atom diffusion^{2,20} (Supplementary Fig. 17) and weld the Li/Li₃Bi interface together, enabling cell operation at low stack pressure²¹ (Fig. 1c). The nano-Ag migration in the Ag@C interlayer²² can also be well explained by the migration principle of electrochemically implanted solid solution. The high solubility of Li in Ag²³ enabled Ag to migrate in the electric field. The potential gradient in Li₆PS₅Cl/LiMgS₃/ Li₃Bi/LiMg (Fig. 1e-h) is also important for Mg migration and Li₆PS₅Cl stability. As shown in Supplementary Fig. 18, during Liplating, the potential at the Mg₁₆Bi₈₄/Li₆PS₅Cl interface is about 0.7 V (Supplementary Discussion 5). The high potential at the Li₄PS₅Cl surface can protect the Li₆PS₅Cl from reduction and enhance Mg migration in the interlayer. When the Mg in $Mg_{16}Bi_{84}$ is replaced by Zn (ref. 18) or Al (ref. 24) that has low solubility in Li, the lithium dendrite suppression capability is substantially reduced, with the CCD of a Li/Li₆PS₅Cl/Li symmetric cell decreasing to 0.9 mA cm⁻² at 0.9 mAh cm⁻² for a ZnBi interlayer (Supplementary Fig. 19) and 0.7 mA cm⁻² at 0.7 mAh cm⁻² for an AlBi interlayer (Supplementary Fig. 20) because the near lack of migration of intermetallic compounds (Li, Al and Li, Zn) leads to crack formation in the interlayer after Liplating (Supplementary Fig. 21), which increases cell resistance and promotes lithium dendrite growth (Supplementary Figs. 22 and 23a-d). By contrast, the migration of Mg from the Li₃Bi interlayer to the deposited Li (Supplementary Fig. 24 and Supplementary Discussion 6) can generate free volume inside the Li₃Bi, which is beneficial for accommodating volume expansion of Bi, maintaining the structural stability of the interlayer (Supplementary Figs. 23e-h), and reducing the solid-solid contact resistance (Supplementary Figs. 25 and 26 and Supplementary Discussion 7) as Mg welds the Li₃Bi to the Li. Mg migration is also affected by particle size. When the particle size of the Mg16Bi84 increased from about 20 µm to about 40 µm (Supplementary Fig. 27), the CCD reduced to 1.1 mA cm⁻² at 1.1 mAh cm⁻² (Supplementary Fig. 28).

In summary, the merits of the $Mg_{16}Bi_{84}$ interlayer include the following: the formation of the LiMgS_x SEI protects the Li₆PS₃Cl from reduction and welds the Li₆PS₃Cl electrolyte to the Li₃Bi interlayer; the Mg migration into the Li anode welds the Li₃Bi interlayer to the Li anode; the porous Li₃Bi enables Li penetration into pores to reduce the stack pressure; the high potential (about 0.7 V) at the Li₃Bi/Li₆PS₅Cl interface further stabilizes the Li₆PS₅Cl electrolyte and accelerates Mg migration; the high ionic/electronic conductivity ratio of the Li₃Bi ensures that Li plates on the Li₃Bi/Li interface rather than on the Li₃Bi/Li₆PS₅Cl interface.

Li dendrite suppression of Mg₁₆Bi₈₄ interlayer

The synergetic function of the self-passivated LiMgS, SEI, porous Li₃Bi interlayer and LiMg anode effectively improves the lithium dendrite suppression capability. The CCDs of Li/Li₆PS₅Cl/Li symmetric cells using different anodes (Li versus LiMg) and SEIs (LiMgS, versus Li₂S-Li₃P-LiCl) were investigated. The CCD of the Li/Li₄PS₅Cl/Li cell without an interlayer is only 0.4 mA cm⁻² (Supplementary Figs. 29 and 30) because the in situ-formed Li₂S-Li₃P-LiCl SEI cannot suppress lithium dendrite growth. Using a LiMg alloy anode with a high lithium diffusivity can suppress the void formation at the Li/SEI interface during Li stripping², thus increasing the CCD of a LiMg/Li₆PS₅Cl/LiMg cell to 1.5 mA cm⁻² at a capacity of 0.5 mAh cm⁻² (Supplementary Fig. 31a), and 1.1 mA cm⁻² at an increased capacity of 1.0 mAh cm⁻² (Supplementary Fig. 31b). Notably, the Mg₁₆Bi₈₄ interlayer increased the CCD to 2.6 mA cm⁻² at the same capacity of 1.0 mAh cm⁻² (Supplementary Fig. 31c), and 1.6 mA cm⁻² at a capacity of 2.0 mAh cm⁻² (Supplementary Fig. 31d). A Li/Mg₁₆Bi₈₄-Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cell can be stably charged-discharged with 1.2 mA cm⁻² at 1.2 mAh cm⁻² for >2,700 h at 25 °C (Fig. 2a), and 6.0 mA cm⁻² at 6.0 mAh cm⁻² for 1,798 h at 80 °C (Fig. 2c and Supplementary Fig. 32). However, the Li/Li₆PS₅Cl/Li cell (without a Mg₁₆Bi₈₄ interlayer) was short-circuited at 1.1 mA cm⁻² and 1.1 mAh cm⁻ (Supplementary Fig. 33).

Li/Mg₁₆Bi₈₄-Li₆PS₅Cl/NMC811 full cell performance

The high interface resistance in NMC811–Li₆PS₅Cl composite cathodes also needs to be reduced for Li||NMC811 full cells. As Cl-doped single-crystal NMC811 (Cl@NMC811) prepared by annealing LiClcoated NMC811 at 500 °C for 1.0 h showed high stability during charging–discharging at 2.7–4.1 V (ref. 16), the performance of

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Fig. 2 | **Electrochemical performance of the Li/Mg₁₆Bi₈₄-Li₆PS₅Cl-Mg₁₆Bi₈₄/ Li symmetric cell. a**, Voltage profile of the Li/Mg₁₆Bi₈₄-Li₆PS₅Cl-Mg₁₆Bi₈₄/Li symmetric cell at 25 °C with stepwise current in the first 12 cycles and then galvanostatically charging-discharging at 1.2 mA cm⁻² in the following cycles. The time for each Li plating or stripping process was 1.0 h. b, Voltage profile of the Li/Mg₁₆Bi₈₄-Li₆PS₅Cl-Mg₁₆Bi₈₄/Li symmetric cell at step-increased current

to 6.0 mA cm⁻² at 80 °C. **c**, Voltage profile of the Li/Mg₁₆Bi₈₄–Li₆PS₅Cl–Mg₁₆Bi₈₄/Li symmetric cell at a constant current density of 6.0 mA cm⁻² at 80 °C after step-increased current to 6.0 mA cm⁻² in **b** (the corresponding voltage profile of the Li/Li₆PS₅Cl/Li cell with a Mg₁₆Bi₈₄ interlayer at 6.0 mA cm⁻²/6.0 mAh cm⁻² and 80 °C is shown in Supplementary Fig. 32). The time for each Li plating or stripping process was 1.0 h.



Fig. 3 | Electrochemical performance of the Cl@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li full cell.

a, Rate performance of the Cl@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cell with a high cathode loading of 5.1 mAh cm⁻² (25.5 mg cm⁻²) at increasing currents from 2.55 to 10.2 mA cm⁻² at 80 °C. **b**, Cyclic performance of the Cl@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cell at a high current density of 15.3 mA cm⁻² and at 80 °C. The cell was activated at a low current density of 2.55 mA cm⁻² in the first four cycles. The cutoff voltage of the cells was 2.7–4.1 V. The filled symbols in **a**, **b** are charge capacity (left axis) and specific capacity (right axis). The open symbols are discharge capacity (left axis) and specific capacity (right axis).





Cl@NMC811/Li₆PS₅Cl/Li cells with a Mg₁₆Bi₈₄ anode interlayer was evaluated and a high capacities of 4.3 mAh cm⁻² at 2.55 mA cm⁻² (0.5C; 1C = 200 mAh g⁻¹) and 1.5 mAh cm⁻² at 10.2 mA cm⁻² (2.0C) were achieved (Fig. 3a). When the current density was reduced back to 2.55 mA cm⁻², the capacity increased back to 3.5 mAh cm⁻², evidencing excellent rate capability. Cl@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cells at 80 °C also provided a reversible capacity of 1.5 mAh cm⁻² for 300 cycles at 3C (15.3 mA cm⁻²; Fig. 3b). The capacity retention at the 3C rate is 64.3% that at 0.5C (Supplementary Fig. 34), evidencing the superior fast charging capability of the cell with a Mg₁₆Bi₈₄ interlayer.

F doping on the NMC811 surface enables NMC811 to be charged to a high voltage of >4.1 V, enhancing the energy density. We doped F on the NMC811 surface (F@NMC811) by mixing 5.0 wt% LiBF₄ into NMC811 powders using ethanol, followed by annealing at 500 °C for 1.0 h (Supplementary Fig. 35). The element F is rich on the surface of pristine NMC811 (uncycled F@NMC811), where the area with intense O intensity

of the F@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cell at 1/3C (2.55 mA cm⁻²) under a high cathode loading of 7.64 mAh cm⁻² at 80 °C (1C = 200 mAh g⁻¹). The filled black circles in **g**, **h** are discharge capacity (left inner axis) and specific capacity (right axis). The open black circles are charge capacity (left inner axis) and specific capacity (right axis). The filled blue diamonds are energy density in the discharge process. The open blue diamonds are energy density in the charge process.

represents the NMC811 (Fig. 4b), and the element F (Fig. 4c) was only observed on the outer surface of the NMC811 particle. When charging to 4.1 V, the element F remained on the surface of the NMC811 (Supplementary Fig. 36). On further charging to 4.3 V, the F diffused from the NMC811 surface to the bulk as evidenced by the overlap of the F distribution (Fig. 4f) with the O distribution (Fig. 4e). The electrochemical migration of the element F from the surface to the bulk can improve the structural stability of the NMC811, as evidenced by the absence of cracks in the NMC811 after charging to 4.3 V (Fig. 4d). The F@NMC811/ $Li_6PS_5Cl-Mg_{16}Bi_{84}/Li$ cell with a cathode loading of 0.51 mAh cm⁻² can provide a capacity of 157.8 mAh g⁻¹ after 444 cycles (Fig. 4g) at 80 °C, and 86.1 mAh g⁻¹ after 681 cycles (Supplementary Fig. 37) at 60 °C at a rate of 5C (2.55 mA cm⁻²). When the cathode loading increases to 1.27 mAh cm⁻², the F@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cell provides a capacity of 69.8 mAh g⁻¹ at a rate of 3C (3.8 mA cm⁻²) after 300 cycles (Supplementary Fig. 38) at 60 °C. When the cathode loading was further

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increased to 7.64 mAh cm⁻² (38.22 mg cm⁻²), the F@NMC811/Li₆PS₅Cl-Mg₁₆Bi₉₄/Li cell at 80 °C can charge-discharge at 1/3C (2.55 mA cm⁻²) for 40 cycles with a capacity retention of 80% (Fig. 4h). However, the cell-level gravimetric energy density can reach only about 200 Wh kg⁻¹ owing to the low weight ratio (50%) of the F@NMC811 active material in the composite cathode layer and the low capacity of NMC811. To increase the cell energy density, NMC811 was replaced by LiNiO2. The reversible areal capacity of the LiNiO₂/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cell at the second cycle was 11.1 mAh cm⁻² (Supplementary Fig. 39), corresponding to the cell-level gravimetric energy density of 310 Wh kg⁻¹. In contrast to the previously reported cells that can achieve either fast charging performance²⁵, or high energy density at a high stack pressure^{13,22,26}, but not both, our ASSLBs can simultaneously achieve high energy density and fast charging at a low stack pressure 13,22,25,26 (Supplementary Table 4) owing to the Mg₁₆Bi₈₄ anode interlayer (Supplementary Fig. 40) and F doping on the NMC811 cathodes. The superior performance cannot be achieved by using a single lithiophilic Bi interlayer at the Li/SSE interface^{27,28}, as evidenced by the fast short circuit of the F@NMC811/ Li₆PS₅Cl/Bi/Li cell (Supplementary Fig. 41).

Generalization of Mg-Bi interlayer

The Li dendrite suppression capability of the Mg₁₆Bi₈₄ interlayer can be further enhanced by increasing the lithiophobicity through adding O and Cl elements in Mg16Bi84 (Supplementary Figs. 42 and 43 and Supplementary Discussion 8). As Li₂O and LiCl have high interface energy against Li (ref. 29), a Li||Li symmetric cell with a BiOCI-Mg interlayer achieved a higher CCD of 3.5 mA cm⁻² at 3.5 mAh cm⁻² (Supplementary Fig. 44a) than that with the Mg₁₆Bi₈₄ interlayer (1.9 mA cm⁻² at 1.9 mAh cm⁻²) at room temperature. The BiOCl-Mg interlayer also enabled a NCA/Li_3YCl_6/Li_6PS_5Cl/BiOCl-Mg/Li cell with a cathode loading of 2.5 mAh cm⁻² to stably charge-discharge at 1.0 mA cm⁻² for 150 cycles at room temperature (Supplementary Fig. 44b). The BiOCl-Mg interlayers can also suppress lithium dendrite growth of other solid electrolytes (Supplementary Discussion 9), including Li₃YCl₆ halide electrolyte (Supplementary Figs. 45 and 46), Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ (LLZTO) oxide electrolyte (Supplementary Fig. 47 and Supplementary Table 5) and LiFSI/PMMA-PVDF-HFP polymer electrolyte (Supplementary Figs. 48 and 49).

Conclusion

We designed a $Mg_{16}Bi_{84}$ anode interlayer and a F-doped NMC811 cathode enabling Li/Li₆PS₅Cl/NMC811 cells to achieve high energy and fast charging at a low stack pressure. The $Mg_{16}Bi_{84}$ interlayer converted into a passivated LiMgS_x SEI on the Li₆PS₅Cl surface, porous Li₃Bi sublayer and lithiophilic LiMg solid-solution alloy on the Li anode. The $Mg_{16}Bi_{84}$ interlayer enables F@NMC811/Li₆PS₅Cl-Mg₁₆Bi₈₄/Li cells to simultaneously achieve high capacity and high rate at a low stack pressure of 2.5 MPa. Furthermore, BiOCl-Mg interlayers can also further enhance the lithium dendrite suppression capability in different types of SSE. Such a general interphase design principle could expedite the commercialization of ASSLBs.

Online content

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Data availability

The data that support the findings of this study are available within this article and its Supplementary Information. Additional data are available from the corresponding author upon reasonable request.

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simulations. W.Z. prepared the polymer electrolyte and the CCD test for the polymer electrolyte. X.H. prepared the oxide electrolyte and the CCD test for the oxide electrolyte. All authors discussed the results, analysed the data and drafted the manuscript.

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Additional information

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