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Solid-State Electrolytes

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Multiscale Engineered Bionic Solid-State Electrolytes Breaking the Stiffness-Damping Trade-Off

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Abstract: All-solid-state lithium metal batteries (LMBs) are regarded as next-generation devices for energy storage due to their safety and high energy density. The issues of Li dendrites and poor mechanical compatibility with electrodes present the need for developing solid-state electrolytes with high stiffness and damping, but it is a contradictory relationship. Here, inspired by the superstructure of tooth enamel, we develop a composite solid-state electrolyte composed of amorphous ceramic nanotube arrays intertwined with solid polymer electrolytes. This bionic electrolyte exhibits both high stiffness (Young's modulus = 15 GPa, hardness = 0.13 GPa) and damping (tan δ = 0.08), breaking the trade-off. Thus, this composite electrolyte can not only inhibit Li dendrites growth but also ensure intimate contact with electrodes. Meanwhile, it also exhibits considerable Li^+ transference number (0.62) and room temperature ionic conductivity $(1.34 \times 10^{-4} \, \text{S cm}^{-1})$, which is attributed to oxygen vacancies of the amorphous ceramic effectively decoupling the Li-TFSI ion pair. Consequently, the assembled Li symmetric battery shows an ultra-stable cycling (>2000 hours at 0.1 mA cm^{-2} at $60 \,^{\circ}\text{C}$, >500 hours at 0.1 mA cm^{-2} at $30 \,^{\circ}\text{C}$). Moreover, the LiFePO₄/Li and LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂/Li allsolid-state full cells both show excellent cycling performance. We demonstrate that this bionic strategy is a promising approach for the development of high-performance solid-state electrolytes.

Introduction

Rechargeable lithium metal batteries (LMBs) are considered as one of the most attractive options for high-energydensity energy storage. However, in conventional liquid

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LMBs, electrolyte leakage and uncontrollable Li dendrites growth tend to cause major safety incidents.^[1] Inorganic solid electrolytes (ISEs) with high stiffness (~6-200 GPa) and immobility inhibit Li dendrite growth to a certain extent and thus improve battery safety.^[2] However, their highly

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brittle properties make them susceptible to contact defects with the electrodes, ultimately resulting in failure.^[3] To promote solid state electrolytes (SSEs)/electrodes intimate contact, the development of composite solid-state electrolytes (CSSEs) is necessary, which usually incorporate high damping solid polymer electrolytes (SPEs) into ISEs, but the modulus of CSSEs is significantly lower than that of ISEs.^[4] Recent research has indicated that the Li dendrites growth can only be inhibited when the elastic modulus of the SSE is greater than 9 GPa.^[5] Frustratingly, the modulus of most CSSEs is considerably inferior to this value. Therefore, to break the stiffness-damping trade-off, it is necessary to develop SSE with both high stiffness comparable to ISEs and damping comparable to SPEs.

Apart from the mechanical properties, the ionic transport efficiency of the SSE is the most important factor. Typically, the crystallinity of SPE in CSSE can be reduced by fillers, which increases the movement of the polymer chain segments and facilitates Li⁺ transport.^[6] The strong Lewis acid-base reaction between the filler and SPE is another strategy, which promotes the Li salt dissociation and forms more free Li⁺.^[7] Furthermore, the morphology of fillers is also a factor that affects the SSE ionic conductivity. Commonly dispersed fillers,^[8] such as nanoparticles,^[9] nanowires,^[7] and nanosheets,^[10] tend to agglomerate with increasing content, which prevent them from forming effective interfaces with the polymer and affects ionconducting pathways.^[11] Comparatively, 3D-arrays fillerbased CSSE may be the most feasible option.^[6,12] It not only enlarges the effective interface between fillers and polymer, but also shortens the Li⁺ transport path. For example, vermiculite sheet array-based CSSE has an ionic conductivity of $1.89 \times 10^{-4} \, \text{S cm}^{-1}$ at room temperature (RT), which is 6.5 times higher than that of a disordered sheets-based CSSE. Therefore, preparation of a CSSE with highly ordered inorganic-organic interface would be of great importance to enhance ionic conductivity. Unfortunately, the mechanical modulus of this array-based CSSE is only 0.044 GPa.^[4b]

Enamel, consisting mainly of hydroxyapatite (HA) nanowires arrays and protein, is an ideal model for composites with high stiffness and damping.^[13] Here, inspired by the superstructure of tooth enamel, we develop a novel CSSE composed of amorphous ceramic nanotube arrays intertwined with SPEs. This CSSE exhibits a modulus higher than 9 GPa (Young's modulus = 15 GPa), high hardness (0.13 GPa), and damping comparable to that of polymer $(\tan \delta = 0.08)$, effectively inhibiting Li dendrite growth and ensuring mechanical compatibility with the electrodes. Meanwhile, the RT ionic conductivity $(1.34 \times 10^{-4} \, \text{S cm}^{-1})$ and Li^+ transference number (0.62) of the bionic CSSE (amorphous titania/poly(ethylene oxide)-lithium bis(trifluoromethanesulfonyl)imide, AT/PEO-LiTFSI) are 5.6 times and 2.0 times higher than those of PEO-LiTFSI. Both experiments and theoretical calculations confirm that polymer chain segments are more susceptible to diffusive motions in amorphous structure than in crystalline structure, thus facilitating Li⁺ migration. Furthermore, coordination unsaturation in the localized environment of AT leads to high concentration of oxygen vacancies (O_v s). O_v s serve as Lewis acid active sites to promote the dissociation of Li salts, while the highly ordered interface ensures rapid Li⁺ migration, thus synergistically improving the Li⁺ transport efficiency. Consequently, the assembled Li symmetric battery shows an ultra-stable cycling (>2000 hours at 0.1 mA cm⁻² at 60 °C, >500 hours at 0.1 mA cm⁻² at 30 °C). Moreover, the LiFePO₄/Li and LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂/Li allsolid-state full cells both show excellent cycling performance. A comparable methodology is employed in sodiumion SSEs, demonstrating the generalizability of this bionic strategy.

Results and Discussion

Design and Simulation for Bionic CSSEs

CSSEs with high stiffness and high damping were constructed by mimicking the hierarchical organization of tooth enamel to resist Li dendrites impact and maintain mechanical compatibility with electrodes (Figure 1a). For comparison, AT and crystalline titania (CT) nanotube arrays-based CSSEs were fabricated. Generally, the higher diffusion coefficient of the polymer chain segments on the inorganic filler surface is a prerequisite to ensure that Li⁺ can be transported efficiently. Molecular dynamics (MD) analysis showed the diffusion capacity of PEO chain segments on AT and CT surfaces. PEO chain segments on the AT surface $(0.16 \text{ A}^2/\text{ps})$ have 4 times higher diffusion coefficients than that on the CT surface (0.04 A²/ps) in the time evolution of the mean square displacement (MSD) in Figure 1b. Moreover, density functional theory (DFT) revealed the interaction mechanism of substances on inorganic-organic interfaces. The dissociation energy of AT for LiTFSI is the lowest at 3.57 eV (Figure S1a, Supporting Information). We further investigated the adsorption capacity of PEO, CT and AT on TFSI-. As shown in Figure 1c and Figure S1b (Supporting Information), the adsorption energy of AT for TFSI⁻ was the most negative (-1.54 eV), indicating that AT with O_v has the strongest adsorption ability for TFSI⁻. O_v serves as a Lewis acid active site to facilitate the dissociation of Li salts, while the vertical inorganic-organic interfaces minimize the tortuosity of Li⁺ diffusion path, thus synergistically empowering biomimetic CSSEs the excellent ionic transport efficiency (Figure 1d).

Fabrication and Characterization of Bionic CSSEs

The preparation of AT and CT nanotube arrays and their corresponding through-hole arrays are described in the Materials and Methods, Figures S2 and S3 (Supporting Information). As a representative example, the nanotube arrays obtained after 2 hours anodization of pure titanium foils at 60 V and RT are shown in Figure 2a and Figure S4a (Supporting Information), with a thickness of approximately 12 μ m and a uniform distribution of nanotubes. As the anodization time extended, the arrays remained essentially

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Figure 1. Design and simulation for bionic CSSEs. Design strategies for enamel-inspired CSSEs with high stiffness, high damping, and considerable ionic conductivity. a) The hierarchical structure of enamel has been mimicked in the design of CSSE, allowing it to resist external impacts and maintain mechanical compatibility with electrodes. b) Calculated MSD of PEO chain segments on AT and CT as a function of simulation time. It confirms the PEO chain segments exhibit a higher diffusion coefficient on the AT surface than on the CT surface. c) The adsorption energy of CT and AT for TFSI⁻. AT possesses abundant O_v that promotes dissociation of Li salts and anchoring of TFSI⁻ anion. d) The vertically oriented inorganic-organic interface in the CSSE minimizes the tortuosity of Li⁺ diffusion path.

constant in nanotube diameter, except for an increase in height (Figures S4b and S4c, Supporting Information), allowing precise tuning of the CSSE thickness. Then, the initially prepared titania arrays at RT were heat-treated, during which the color of the samples changed as shown in Figures S2 and S5 (Supporting Information). The differential scanning calorimeter (DSC) curves of the initial titania at RT also indicate that it is fully crystallized at temperatures above 280°C (Figure S6, Supporting Information). X-ray diffraction (XRD) revealed that the phase of the 150°C treated samples was amorphous structures, which are referred to as AT, and the 400 °C treated samples were transformed into anatase CT (JCPDS no. 21-1272) (Figure S7, Supporting Information). The heat treatment facilitates the penetration and separation of the nanotubes from the titanium substrate at high anodization voltages (120 V), resulting in through-hole arrays. The sample's morphology was further observed using transmission electron microscopy (TEM) (Figure 2b and Figure S8, Supporting Information). The nanotube diameter size of AT and CT is essentially the same. However, the AT nanotube was homogeneous, whereas the CT showed wrinkles and holes, probably due to severe atomic rearrangements during heat treatment. Atomic-level imaging of AT and CT was also characterized by spherical aberration corrected TEM (AC-TEM). As shown in Figure 2c, the high-angle annular dark-field (HAADF) image of AT exhibits a disordered atomic arrangement, and the overall distribution of Ti and O elements is uniform (Figure S9, Supporting Information), which contrasts to the regular atomic arrangement of CT (Figure S10, Supporting Information). Furthermore, selected area electron diffraction (SAED) images (Figure S11,

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Figure 2. Characterizations of nanotube arrays and different SSEs. a) Cross-session SEM image of initial titania nanotube arrays. b) TEM image of individual AT nanotube. c) Corresponding HAADF-STEM image of AT nanotube. Spectroscopy analyses of AT and CT: d) EELS spectra of the Ti $L_{2,3}$ -edge for AT and CT. e) Ti 2p XPS spectra. f) EPR spectra. g) Cross-session SEM image of AT/PEO-LiTFSI. h) XRD and i) DSC curves of different SSEs. j) Raman spectra of different SSEs in the wavenumber range of 720–760 cm⁻¹ and corresponding quantification results of the TFSI⁻ anion states in the electrolytes. There are two main states referring to TFSI⁻ anions in SSE: free TFSI⁻ (red) and ionic clusters (blue). k) ⁷Li solid NMR curves of different SSEs.

Supporting Information) reveal that AT is a diffuse halo ring, while the ring diffraction speckle pattern of CT indicates a polycrystalline structure, consistent with the XRD results.

To characterize the electronic structures of AT and CT, electron energy loss spectroscopy (EELS) was performed. The Ti-L_{2.3} EELS spectra of AT exhibits broader t_{2g} peaks, indicating the formation of $O_v^{[14]}$ and thus a mixed valence states of +3 and +4 (Figure 2d and Figure S10, Supporting Information). The Ti 2p XPS spectra of AT and CT are shown in Figure 2e. Compared to CT, the AT peak is significantly shifted to lower energies, confirming the presence of Ti^{3+} in the AT, which is caused by O_{v} .^[15] Electron paramagnetic resonance (EPR) signal observed at g=2.006 also confirmed the occurrence of O_v in the AT (Figure 2f).^[16] O_v can act as a Lewis acid active site to effectively promote the dissociation of LiTFSI and the anchoring of TFSI- anions.^[17] Therefore, the AT nanotube arrays as the inorganic part of the CSSE are expected to significantly improve the efficiency of Li⁺ migration.

The fabrication process of the different SSEs, including bionic CSSEs (AT/PEO-LiTFSI), CT/PEO-LiTFSI, and

Methods. Figure S12 (Supporting Information) shows digital pictures of these two CSSEs. The microstructure of AT/ PEO-LiTFSI reveals that the PEO and AT nanotubes are in intimate contact, confirming the formation of the desired continuous inorganic-organic interfaces (Figure 2g). Energy dispersive spectrometer (EDS) mapping of element C from PEO and elements S and F from LiTFSI further confirms that PEO-LiTFSI was distributed uniformly throughout the nano-channel, filling the entire nanotube (Figure S13, Supporting Information). A top view of bionic CSSE allows observation of the AT nanotube profile and the penetration of the SPE into the nanotube arrays (Figure S14, Supporting Information). The microstructure features of PEO-LiTFSI, CT/PEO-LiTFSI, and different thicknesses of AT/PEO-LiTFSI SSEs are shown in Figure S15 (Supporting Information), with the thinnest AT/PEO-LiTFSI being 13.7 µm. The thickness is significantly lower than most reported CSSEs, potentially increasing the energy density of all-solid-state LMBs (ASSLMBs).^[6,12a, 18]

PEO-LiTFSI, is described in detail in the Materials and

Then, the physicochemical characterization of SSEs was performed. Figure S16 (Supporting Information) shows the thermo gravimetric analysis (TGA) of them. It is noteworthy that the introduction of CT and AT nanotube arrays lowered the decomposition temperature of the electrolyte system, but it remained as high as ~280°C. To investigate the effect of inorganic arrays on the crystallinity of the polymers, different SSEs were characterized by XRD. As shown in Figure 2h, the PEO-LiTFSI exhibits two distinct peaks at 19° and 23°, consistent with the XRD of PEO powder in Figure S17 (Supporting Information).^[12a] In contrast, the sharp peak at 19° attributed to PEO becomes broadened (Figure 2h, insert) for CT/PEO-LiTFSI and AT/ PEO-LiTFSI, indicating that the nano channels have the potential to impede the crystallization of the polymer matrix due to spatial constraints.^[19] The reduction of polymer crystallinity facilitates the reduction of complexation of Li+ with the polymer and improves the Li⁺ transport efficiency.^[20] To further test the crystallinity of the different SSEs, glass transition temperatures (T_{o}) were evaluated via DSC. As shown in Figure 2i, the T_g of AT/PEO-LiTFSI significantly decreased to -54.8°C. These results suggest that AT reduces polymer crystallinity more significantly than CT, consisting to the MD analysis. Consequently, the amorphous inorganic-organic interface constructed based on AT is more favorable to promote Li⁺ transport.

The mechanism of the enhanced ionic motion after the introduction of inorganic ceramic arrays was subjected to further detailed analysis. Figure S18 (Supporting Informa-

tion) shows the Fourier transform infrared spectroscopy (FTIR) of different SSEs. The results demonstrated that both AT and CT nanotube arrays diminished the crystallinity of PEO and the presence of O_v on AT anchored TFSI⁻, resulting in increase in the concentration of mobile Li⁺. Raman measurements were performed to illustrate the origin of free Li^{+, [21]} As illustrated in the middle sector of Figure 2j, AT/PEO-LiTFSI achieves a free TFSI- content of 86%, suggesting that AT with O_v significantly activates Li salt dissociation, forming more free Li⁺ in the amorphous inorganic-organic interface. Solid-state nuclear magnetic resonance (NMR) was used to study the Li⁺ chemical environment in different SSEs. The characteristic peak position of 7Li for AT/PEO-LiTFSI is more pronounced negative shift (Figure 2k), indicating the lowest interaction around Li⁺.^[22] Therefore, the presence of O_v on AT generates more free Li⁺, thus facilitating efficient Li⁺ transport.

Mechanical Properties of Bionic CSSEs

To evaluate their potential to resist Li dendrites impact and mechanical compatibility with electrodes, we systematically tested the mechanical properties of samples at RT. The stiffness of them was obtained by quasi-static nanoindentation. As shown in Figures 3a and 3b, the Young's modulus



Figure 3. Mechanical properties of different SSEs. a, b) Nanoscale dynamic mechanical analysis (Nano-DMA) nanoindentation test of E_v and H. c, d) Quasi-static nanoindentation tests for the typical 3D contour maps of the E_v and H. e) Topography in situ SPM images of one representative indent in nano-DMA tests. f) Nano-DMA nanoindentation tests measuring the tan δ coefficient by a frequency sweep with a varied frequency range (ω , from 1–200 Hz). g) The comparison of mechanical properties, modulus $vs \tan \delta$, with previous work confirms the bionic CSSE with both high stiffness and high damping.

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(E_y) and hardness (H) of AT/PEO-LiTFSI were 15 and 0.13 GPa, which were 2.6 and 1.6 times higher than that of CT/PEO-LiTFSI, 11.5 and 6.5 times higher than that of the PEO-LiTFSI, and much higher than that of the previous reported CSSEs in Figure 3g. The E_Y of AT/PEO-LiTFSI is almost twice that of 9 GPa, thus possessing the ability to inhibit Li dendrite growth. Besides, typical 3D contour maps of E_v and H were constructed over a test area of 0.3 mm ×0.3 mm. Figures 3c and 3d show that AT/PEO-LiTFSI has good uniformity in mechanical stiffness. The nanoindentation zones of samples were analyzed by in situ scanning probe imaging (SPM) (Figure 3e). The permanent deformation zones of them exhibited a tetrahedral-like morphology but varied in size. AT/PEO-LiTFSI has the smallest area compared with those of CT/PEO-LiTFSI and PEO-LiTFSI, indicating the highest stiffness in the samples. To simulate the ability of different SSEs to resist the impact of Li dendrites, a systematic finite element (FE) modeling approach was employed to study the strain variation of them at the nanoscale under the same load. The results of FE indicate that AT/PEO-LiTFSI exhibits the greatest resistance to dendrite impacts due to its elevated stiffness and lowest strain (Figure S19, Supporting Information).

The damping^[23] (loss factor, $tan\delta$) of the samples were further investigated through dynamic mechanical analysis. The experimental results indicate that at various frequencies, the average tan δ of AT/PEO-LiTFSI (0.08) is 2 times higher than that of CT/PEO-LiTFSI (0.04), comparable to those of common polymers (PMMA (0.055) and PTFE (0.06)) and PEO-LiTFSI (tan δ =0.14), and much larger than that of ISEs (Figures 3f and 3g, and Table S1, Supporting Information). Consequently, AT/PEO-LiTFSI is comparable to ISEs in terms of stiffness and polymers in terms of damping. In enamel, the highly ordered array structure and high inorganic content (96 wt%) are the main factors that allow it to resist external impacts. Recently, the presence of inorganic amorphous calcium phosphates (ACPs) between the arrays has been discovered, and the interaction of these stabilized ACPs with proteins is critical to further improving the hardness of enamel.^[13] Similar to the hierarchical structure and multi-components of tooth enamel, the inorganic component accounts for 48 wt %, thus AT/PEO-LiTFSI has the property of high stiffness (Figure S16, Supporting Information). And AT lacks defects such as grain boundaries and morphology compared to the CT, which further improves the mechanical stiffness of AT/PEO-LiTFSI (Figures S8 and S20, Supporting Information).^[16a,24] Moreover, the interaction between HA and protein imparts high damping to the enamel, resulting in its high resistance to vibrational damage. Therefore, the high damping of AT/ PEO-LiTFSI is largely determined by the vertical interface between its amorphous inorganic and organic components. The reduced crystallinity of polymer also leads to an increase in the damping property of AT/PEO-LiTFSI. These results demonstrate that AT/PEO-LiTFSI may prevent Li dendrite penetration and improve contact stability with electrodes.

Performance and Analysis of Symmetric Cells

Electrochemical properties of the different SSEs were further investigated. The electrochemical stability window of the different SSEs was verified by linear sweep voltammetry (LSV) test. Figure 4a shows the electrochemical window of AT/PEO-LiTFSI is 5.30 V, higher than that of CT/PEO-LiTFSI (5.04 V). This is due to the strong Lewis acid-base interactions between O_v of AT and TFSI-, which can improve the AT/PEO-LiTFSI antioxidant ability under high voltage.^[25] As shown in Figures 4b, 4c and Figure S21 (Supporting Information), the Li⁺ transference number of AT/PEO-LiTFSI reached the high value of 0.62 (Figure 4c). The temperature-dependent ionic conductivity curves of the SSEs are plotted (Figure 4d), and the corresponding electrochemical impedance spectroscopy (EIS) are shown in Figure S22 and Table S2 (Supporting Information). Among them, AT/PEO-LiTFSI had the highest ionic conductivity at different temperatures. Its ionic conductivity is $1.34 \times 10^{-4} \,\mathrm{S \, cm^{-1}}$ at 30 °C, which is 2 times higher than that of the CT/PEO-LiTFSI. The higher diffusion coefficients of the polymer chain segment on the AT surface and vertically oriented inorganic-organic interface construct a continuous fully active Li⁺ conductive channel. Concurrently, an extended study was conducted by replacing LiTFSI with NaFSI to prepare bionic CSSEs. The results are essentially the same as those for Li-based bionic CSSEs (Figure S23 and Table S3, Supporting Information). Furthermore, given that the diameter of the nanotube may influence the ionic conductivity of AT/PEO-LiTFSI, we regulated the inner diameter of the nanotubes by varying the anodization voltages (50 V and 90 V) (Figure S24, Supporting Information). The results demonstrate that the CSSE corresponding to AT nanotube arrays prepared with an anodization voltage of 60 V exhibits the highest ionic conductivity (Figure S25 and Table S4, Supporting Information). The primary rationale for this may be attributed to the fact that the AT nanotube arrays prepared with an anodization voltage of 90 V exhibit the largest inner diameter of the nanotubes (~110 nm), and 90 V-AT/PEO-LiTFSI is filled with a greater quantity of PEO-LiTFSI, which aligns closely with the intrinsic properties of the polymer electrolyte. The inner diameter of AT nanotubes prepared with an anodization voltage of 50 V is approximately 60 nm. However, it is challenging to completely fill the nanotubes with PEO-LiTFSI, which affects the ionic conductivity (Figures S26 and S27, Supporting Information).

To demonstrate the stability of SSEs, the cycling tests of Li/Li symmetric cells were investigated with increasing current density of 0.02 mA cm^{-2} to 1.0 mA cm^{-2} (Figure S28, Supporting Information). The critical current density (CCD) of the Li/AT/PEO-LiTFSI/Li is 0.6 mA cm^{-2} , which is higher than those of the Li/PEO-LiTFSI/Li (0.14 mA cm^{-2}) and the Li/CT/PEO-LiTFSI/Li (0.24 mA cm^{-2}). To further test the stability of the SSEs with Li metal, the long cycling tests and high-capacity plating/stripping experiments of the Li/Li symmetric cells were carried out. Li/PEO-LiTFSI/Li showed shorting-circuiting at 387^{th} hour. In contrast, Li/CT/PEO-LiTFSI/Li and Li/AT/PEO-LiTFSI/Li exhibited excellent

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Figure 4. Electrochemical properties of different SSEs and analysis of corresponding symmetric cells. a) LSV curves. b) Current-time curves of AT/ PEO-LiTFSI Li symmetric cell, with the corresponding EIS curves before and after polarization shown in the inset. c) Comparison of Li⁺ transference numbers. d) Temperature dependency comparison of ionic conductivity for different electrolytes from 30°C to 80°C. Galvanostatic voltage profiles of Li/Li symmetric cells using different SSEs at 0.1 mA cm⁻² and 60°C e) and at 0.1 mA cm⁻² and 30°C f). g, h) Morphology and mechanical property of SEI layer formed in PEO-LiTFSI and AT/PEO-LiTFSI electrolytes-based symmetric cells measured by AFM. i) XPS measurements of Li electrode surface after cycled for 120 hours for both PEO-LiTFSI and AT/PEO-LiTFSI electrolytes, with the signals: Li 1s, O 1s, and F 1s.

cycling stability, with durations of 1800 hours and 2000 hours at 0.1 mA cm⁻² and 60 °C, respectively (Figure 4e). Scaling up the cycling curves in Figure S29 (Supporting Information) shows that the polarization voltages of both Li/AT/ PEO-LiTFSI/Li (68 mV) are smaller than those of the Li/ CT/PEO-LiTFSI/Li (80 mV) and the values of solid-state electrolytes summarized in Table S5 (Supporting Information). Moreover, as shown in Figures S30 and S31 (Supporting Information), the Li/AT/PEO-LiTFSI/Li can be stably cycled with plating/stripping capacity of 0.1 mAh cm⁻² (0.1 mA cm^{-2}) and 0.25 mAh cm^{-2} (0.5 mA cm^{-2}) . Figure S32 (Supporting Information) shows that at 0.2 mA cm^{-2} and 60°C, the Li/AT/PEO-LiTFSI/Li exhibits a long cycle time, approaching 600 hours, while the stable cycle of Na/AT/ PEO-NaFSI/Na also exceeds 400 hours (Figure S33, Supporting Information). We note that there is a gradual stabilisation of the overpotential at the beginning, which may be attributed to the long time required to form a stable electrolyte/electrode interphase in the Na/Na symmetric cell.^[26] Meanwhile, the Li/AT/PEO-LiTFSI/Li was able to cycle stably for 500 hours at 0.1 mA cm⁻² even at RT (Figure 4f). The aforementioned results demonstrate that

bionic CSSE possesses the capacity to impede the growth of alkali (Li and Na) dendrites and exhibit favorable interfacial compatibility with electrodes, which enhances the cycling performance of symmetric batteries.

Furthermore, we also investigated the capabilities of the SSEs to modulate Li⁺ deposition. Figure S34 (Supporting Information) shows the Li electrode morphology of the symmetric cell after 300 hours at 0.1 mA cm⁻². Compared to fresh Li metal, the surface of the Li electrode cycling in Li/ PEO-LiTFSI/Li showed obvious Li dendrite morphology (Figures S34I and S35, Supporting Information). Cracks appeared on the surface of Li electrode cycled in Li/CT/ PEO-LiTFSI/Li (Figure S34 II, Supporting Information). In contrast, the Li electrode surface of Li/AT/PEO-LiTFSI/Li after cycling showed neither obvious Li dendrites nor cracks (Figure S34 III, Supporting Information), indicating that Li⁺ stripping/plating was uniform.^[27] Li⁺ concentration and potential distributions in the different SSEs were carried out using COMSOL Multiphysics (Figure S36, Supporting Information).^[15,28] The 3D profile of the computational model shows AT nanotube arrays containing O_v can effectively mitigate ion aggregation and the associated potential gradient in AT/PEO-LiTFSI, which leads to the homogeneous deposition of Li^+ during the plating/stripping process.

The uniformity of Li⁺ deposition is regarded as a critical indicator of the electrolyte-induced solid electrolyte interphase (SEI).^[29] Using atomic force microscopy (AFM),^[29-30] we obtained the 3D morphology and mechanical properties of the SEI formed in Li/PEO-LiTFSI/Li and Li/AT/PEO-LiTFSI/Li after 300 hours. Figure 4g exhibits the image roughness (denoted as R_a) in AT/PEO-LiTFSI is 78 nm, much smaller than that in the PEO-LiTFSI (185 nm). The Li deposition in the AT/PEO-LiTFSI exhibits a compact layer with tiny grain-like deposits, which can effectively alleviate parasitic reactions with the electrolyte and greatly improve the utilization of the Li electrode. Figure 4h shows the elastic modulus of the SEI formed in the Li/AT/PEO-LiTFSI/Li (2.2 GPa) is much higher than that in Li/PEO-LiTFSI/Li (1.5 GPa). Then, we performed ex situ XPS measurements on the cycled Li electrodes of the PEO-LiTFSI- and AT/PEO-LiTFSI-based symmetric cells to determine the SEI composition. Typical O-C=O/R-OLi (531.2 eV for O 1s and 55.2 eV for Li 1s), Li₂O (582.2 eV for O 1s and 54.4 eV for Li 1s), LiF (684.6 eV for F 1s and 56 eV for Li 1s), and Li₂S (53.5 eV for Li 1s) peaks were observed on the surface of Li electrodes before and after etching (Figure 4i and Figure S37, Supporting Information).^[21a,31] In Figure 4i, we compared the XPS signals (etching 54 seconds) of the Li electrodes. The Li₂O amount increased after the introduction of AT^[32] and the characteristic peaks attributed to -C-F (-CF₂ and -CF₃) at 688.5 eV in the high-resolution F 1s spectra are almost absent.^[33] The O atoms at the end of the PEO segments near the Li electrode are susceptible to the formation of Li₂O. Moreover, O_v of AT can better adsorb TFSI⁻ anions, making it difficult for them to diffuse into the Li electrode. The degradation of TFSI- on the Li metal surface is mitigated preventing the conversion of Li₂O to Li₂CO₃. Consequently, Li₂O is the main SEI component (instead of passivated Li₂CO₃) in the AT/PEO-LiTFSI system. The significant increase of Li2O in the SEI enhances the migration of Li⁺ at the Li electrode interface, resulting in a significant reduction in interfacial resistance (IR) and voltage overpotential even after prolonged cycling and accounts for the high mechanical modulus of SEI.^[34] Hence, benefiting from O_v of AT, a stable SEI is formed between Li and AT/PEO-LiTFSI.

Performance and Analysis of All-Solid-State Full Cells

The performance of different SSEs was further evaluated with all-solid-state full cells. The rate performance of LiFe-PO₄ (LFP)/Li ASSLMB was evaluated over a range of 0.1 C to 5 C (Figure 5a). The specific capacity of the LFP/AT/PEO-LiTFSI/Li with a specific capacity of 127.8 mAhg⁻¹ was observed at 2 C, and even at 5 C, the specific capacity was maintained at 69.4 mAhg⁻¹. When the current density was switched back to 0.1 C, the capacity was almost restored to its original level, demonstrating excellent capacity recov-

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ery. In contrast, the specific capacity of the control groups decreased significantly with increasing current, with all specific capacities below 30 mAhg^{-1} at 5 C. The detailed charge/discharge curves of the LFP cathode at different rates are shown in Figure 5b. In comparison to PEO-LiTFSI- and CT/PEO-LiTFSI-based LFP/Li full cells, the LFP/AT/PEO-LiTFSI/Li exhibited a flat plateau that expanded slightly and remained stable as current increased. Figure S38 (Supporting Information) presents voltage distribution plots for comparative analysis. The polarization of the control group exhibited a notable increase with increasing current, suggesting a potential limitation in Li⁺ transport efficiency. As illustrated in Figure S39 (Supporting Information), the IR of the initial LFP/CT/PEO-LiTFSI/Li is 236.6 Ω , which significantly increases to 638.8 Ω after the rate test. In contrast, the IR of the LFP/AT/PEO-LiTFSI/Li cell only increases from 116.8 Ω to 164.9 Ω following the rate test. These results indicate better interfacial compatibility and fewer side reactions between AT/PEO-LiTFSI and electrodes. Based on the excellent Li⁺ transport performance of the AT/PEO-LiTFSI, the corresponding LFP/Li ASSLMB has demonstrated excellent cycling stability, maintaining 85.2% capacity retention after 200 cycles at 0.33 C (Figure S40, Supporting Information) and 72.6% capacity retention after 800 cycles at 1 C with a specific capacity of 105.1 mAhg⁻¹ (Figure 5c). In stark contrast, the specific capacity of LFP/Li ASSLMBs based on CT/PEO-LiTFSI and PEO-LiTFSI decreased rapidly after long cycling under the same conditions. Moreover, the coulombic efficiency of LFP/CT/PEO-LiTFSI/Li fluctuate after 550 cycles at 1 C, implying the presence of side reactions between the electrodes and the SSE. As mentioned above, O_v of AT can dissociate the Li salt and induce the formation of a stabilized SEI, thereby inhibiting side reactions at the electrode/SSE interface. Therefore, LFP/AT/PEO-LiTFSI/ Li in our work showed enhanced cyclic performance compared to the recently reported full cells assembled with CSSEs based on vertically oriented and disordered structures (Figure 5d).^[7,12b, 18, 35] Additionally, the cycling performance of LFP/Li ASSLMB with different SSEs was investigated at 0.1 C and at 30°C, as shown in Figure S41 (Supporting Information). The AT/PEO-LiTFSI-based LFP/ Li full cell had the highest initial discharge capacity of 98.7 mAhg⁻¹ at 30 °C, corresponding to about 62 % of the discharge capacity at 60°C. In contrast, a rapid capacity decay of LFP/CT/PEO-LiTFSI/Li was observed, as the low ionic conductivity of CT/PEO-LiTFSI at RT significantly decreases its reaction kinetics.

To further validate the capability of AT/PEO-LiTFSI at high voltage, we tested an ASSLMB with LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) at a charging cutoff voltage of 4.25 V. NCM811/AT/PEO-LiTFSI/Li delivers a specific capacity of 151 mAhg⁻¹ with an average Coulombic efficiency of 99 % after 100 cycles at 55 °C and 0.2 C (Figure 5e). Notably, the charge–discharge curves after the first, tenth, and ninetieth cycles exhibit a pronounced NCM characteristic plateau (Figure S42, Supporting Information). In contrast, for CT/PEO-LiTFSI and PEO-LiTFSI-based NCM811/Li full cells, the electrolyte and the NCM811 cathode underwent violent

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Figure 5. Electrochemical performance of all-solid-state full cells. a) Rate performance of LFP/Li all-solid-state full cells at different rates. b) Voltage profiles of LFP/Li all-solid-state full cells at different rates. c) Cycling performance of the LFP/Li solid-state full cells at 1 C and at 60 °C. d) Comparison of cycling performance of PEO-based CSSEs. e) Cycling stability of the NCM811/Li all-solid-state full cells at 0.2 C and at 55 °C. f) EIS curves of NCM811/Li solid-state full cells before and after 90 cycles.

side reactions, resulting in rapid failure of the batteries within 50 cycles and 5 cycles, respectively (Figures S43 and S44, Supporting Information). Moreover, the interfacial stability was characterized by determining the change in impedance of the full cell before and after cycling. As shown in Figure 5f, the IR of the NCM811/CT/PEO-LiTFSI/Li is 172.6 Ω , compared to the IR of the NCM811/AT/PEO-LiTFSI/Li (77.1 Ω) before cycling, indicating that the incorporation of AT nanotubes serves to suppress interfacial polarization. After the cycling process, the total resistance of the NCM811/AT/PEO-LiTFSI/Li was 107.8 Ω , lower than that of NCM811/CT/PEO-LiTFSI/Li at 237.2 Ω . The EIS results indicate a more stable interface in NCM811/AT/ PEO-LiTFSI/Li due to the high damping of AT/PEO-LiTFSI and high Li⁺ transport efficiency.

Conclusion

In conclusion, inspired by the hierarchical organization of tooth enamel, we construct a bionic CSSE consisting of amorphous ceramic arrays and polymers, which endows the CSSE with excellent mechanical properties, inhibiting Li dendrites growth and ensuring intimate contact with electrodes. Furthermore, the high diffusivity of polymer chain segments on AT and the highly oriented amorphous

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inorganic-organic interface accelerates Li-ion conduction. The abundance of O_v sites of AT promotes the dissociation of Li salts and the immobilization of anions to release more free Li⁺. The enamel-like CSSE exhibit high mechanical properties ($E_v = 15$ GPa, H = 0.13 GPa and $tan \delta = 0.08$), considerable RT ionic conductivity $(1.34 \times 10^{-4} \, \mathrm{S \, cm^{-1}})$ and high Li^+ transference number (0.62). Consequently, the assembled Li symmetric battery shows an ultra-stable cycling (>2000 hours at 0.1 mA cm⁻² at 60 °C, >500 hours at 0.1 mA cm^{-2} at 30 °C). Moreover, the LFP/Li and NCM811/ Li all-solid-state full cells both show excellent cycling performance. A similar approach has been applied in sodium-ion CSSEs, demonstrating the generalizability of this bionic strategy. Our work highlights that the bionic strategy provides a concise and effective approach for SSEs with complex requirements.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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