Electronic Supplementary Information

Ballistic ion transport through hierarchically-ordered-structure polymer binder

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Supplemental Experimental Method

Ion Milling Cross-section and SEM Sample Preparation

The ion milling experiments were performed at Molecular Foundry, Laurence Berkeley National Laboratory. All electrode samples were cut into square shaped pieces with a dimension of 1 cm x 1 cm. The electrodes were affixed to a Fischione cross-section mask using carbon tape. The edges of electrodes protruded approximately 100 μ m above the mask, which were later subjected to ion milling. The ion milling process was conducted by using Fischione SEM Milling (Model 1061). Two steps of ion milling procedures were performed. The initial step is to utilize ion milling to eliminate the edges with a voltage of 6 kV, an angle of 0 degree, a beam focus of 50%, and a milling rock angle of 10 degrees for 12 hours. Subsequently, while keeping the other settings unchanged, the voltage was lowered to 4 kV to clean the surfaces and maintain pristine properties for SEM imaging.

The SEM experiments were performed at University of California, Berkeley and Molecular Foundry, Laurence Berkeley National Laboratory. All surface and cross-sectional SEM images were acquired at high vacuum using FIB-SEM machine (FEI Quanta) with the voltage ranging from 5 kV to 15 kV and approximately 10 mm working distance. Some samples with poor electrical conductivity were coated with an ultra-thin gold on surface via gold sputtering to access better quality SEM images. All samples were characterized with SEM at different magnifications and locations to capture comprehensive surface and crosse-sectional details. Those air-sensitive samples, which were compressed against Li metal, Na metal, and K metal, were prepared inside Argon-filled glovebox and sealed in a vacuum bag to transport to ion milling and SEM machine. However, the samples were still exposed shortly in air when loading samples into SEM machine. This might result in unflatten cross-sectional SEM images in some lithiated samples. Besides, we discovered that the samples treated with Na metal or K metal were much more air sensitive. The short air-exposure was sufficient to cause serious damage on cross-sectional morphology of Na-ion doped and K-ion doped samples. Thus, we didn't include these Na-ion and K-ion doped samples prepared by Fischione ion milling machine.

Electrochemical Impedance Spectroscopy (EIS) Characterization

PFM Film Preparation: A 5wt% PFM in chlorobenzene solvent was applied on copper (Cu) or aluminum (Al) foil with doctor blade and was dried in air. The dried PFM film was heated under vacuum at 80 °C for 15 hours and cooled down to room temperature. Then, the PFM film was heated again under argon flow to 500 °C with 4 °C/min ramp rate, and was maintained at 500 °C for 10 min. After cooling down to room temperature, the PFM film was carefully peeled off from the Cu or Al foil to obtain free-standing HOS-PFM film.

Electrochemical Lithiation: The free-standing PFM and HOS-PFM film was assembled into a 2032 coin cell with lithium foil counter electrode and Celgard 2400 separators (Celgard). The electrolyte used was 1.2 M LiPF6 in ethylene carbonate/ethyl methyl carbonate EC/EMC (3:7 w/w, Tomiyama Pure Chemical Industries, LTD). The cell was discharged using linear sweep voltammetry (LSV) from open-circuit voltage (OCV) to 0 mV vs Li/Li+ at the rate of 0.1 mV s–1, followed by voltage holding at 0 mV vs Li/Li+ for at least 24 hours. Upon cell disassembly. The lithiated PFM (Li⁺/PFM) and HOS-PFM (Li⁺/HOS-PFM) film was thoroughly washed with EMC solvent and dried under vacuum. The dried Li⁺/PFM and Li⁺/HOS-PFM film was cut into 12 mm

diameter disks. All sample films were controlled at a thickness of 12 μ m for ionic conductivity measurement.

Conductivity Measurement: a polyether ether ketone (PEEK) Split Cell with 12 mm internal diameter (MSE Supplies) was used for ionic conductivity measurement. 0.16 g of lithium phosphorus sulfur chloride (LPSCl) powder was pressed at 350 MPa (4 tons in hydraulic compressor reading) to produce a bottom LPSCl pellet, and subsequently a sample film disk (PFM, Li⁺/PFM, HOS-PFM, or Li⁺/HOS-PFM) was positioned above the LPSCl pellet in a flat manner. Then, another 0.16 g of LPSCl powder was added on top of the sample film and compressed using the identical pressure. The Electrochemical Impedance Spectroscopy (EIS) measurement was performed with a VMP-3e potentiostat (Biologics) in the frequency range of 0.1 Hz to 1 MHz with an amplitude of 20 mV, and the cell pressure was about 150 MPa (~ 1.7 tons in hydraulic compressor reading). The cells were measured at variable temperatures of 70, 60, 50, 40, 30, 20, 10, 0, -10, -20, and 30°C. For reference cells without Li-PFM film, the protocol was identical except that no Li-PFM film was added.

X-ray Diffraction Experiments

All X-ray diffraction experiments were performed using Bruker D2 Phaser XRD machine at Laurence Berkeley National Laboratory. Samples, each measuring 1 cm x 1 cm, were prepared and sealed within Bruker Air-tight specimen holders (Model: A100B33) in a glovebox filled with Argon gas. The Sn(PFM) and Sn(HOS-PFM) single-layer electrode samples were compressed against Li metal with a one-ton force for one day. The PFM/Sn and HOS-PFM/Sn double-layered electrode (DLE) samples were compressed against Li metal, Na metal, or K metal, with a one-ton force for durations of 3, 12, and 5 days, respectively.

After compressing these metals (Li, Na, or K), the upper PFM layers of PFM/Sn DLEs were easily peeled off. Thus, negligible XRD patterns of the metals appeared in those PFM/Sn DLEs. In comparison, after compressing the metals, the copper substrates of HOS-PFM/Sn DLEs were readily peeled off in most cases. Therefore, after compressing the metals, some HOS-PFM/Sn DLE samples featured no XRD patterns of copper.

4-D STEM Characterization

Conductive polymer samples for Four-Dimensional Scanning Transmission Electron Microscopy (4D-STEM) experiments were prepared using spin-casting, where a solution of PFM in chlorobenzene (2 mg ml–1) was used to form a uniform thin film on quantifoil carbon TEM grids (1500 r.p.m. for 1 min). The samples were dried at 80 °C in vacuum overnight. To form HOS-PFM, the samples were annealed at 500 °C in a tube furnace under Argon environment and then naturally cooled down to room temperature. Li⁺- ion doping was achieved by pressing the HOS-PFM TEM grids against lithium in the presence of Gen 2 electrolyte, which contained 1.2 M lithium hexafluorophosphate (LiPF₆) dissolved in mixed solvent of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) with a weight ratio of 3:7. The potential gradient between HOS-PFM polymer and Li metal drove Li⁺ ions to insert into the polymer matrix. Similar approaches were applied to prepare Na⁺ and K⁺ ion doping, using 1 M sodium trifluoromethanesulfonimide and 1 M potassium trifluoromethanesulfonimide, respectively. These samples were slightly compressed for one day and followed by washing in EC solvent three times to remove any residual salt within the samples. Then, the doped samples were dried under vacuum for 12 hours. Consequently, they were transferred from the glove box to the microscope in a Fischione 2560 air-

free transfer holder. 4D-STEM datasets were collected using a K3 direct detection camera on a ThermoFisher TEAM1 microscope operated at 300 kV and analyzed using the py4DSTEM software package.^{1, 2}

Capacity Measurement

The PFM or HOS-PFM on copper foil were punched out as electrodes with a diameter of 9/16 inch. Lithium chips (MTI Co.) with a 16 mm diameter, were cleaned on surface using a nylon brush to eliminate any impurities until a shiny surface was achieved. Celgard 2400 separators (Celgard) were placed between lithium chips and PFM or HOS-PFM electrodes. The Gen2 electrolyte, obtained from Argonne National lab, contained 1.2 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate EC/EMC (3:7 w/w). Each battery assembly consumed 60 μ l of Gen2 electrolytes. Coin cells (CR 2032, Hosen Co.) were assembled inside an Argon glovebox. These batteries underwent circling at current densities of 12.5, 50, 100, and 167 mA/g for five cycles each.

Solid-State Battery Assembly and Testing

The cathode composite was prepared by taking an NMC811 cathode coated with 1 wt% lithium niobium oxide (LiNbO₃) and LPSCl electrolyte in a mortar inside a glove box, with a weight ratio of 80:20. Subsequently, 2 wt% of vapor-grown carbon fiber was added, and proper mixing was achieved using a pestle.

Part I: thin *Si/HOS-PFM electrodes*

Additionally, for the fabrication of the Si nanoparticle-HOS PFM composite anode, a specified quantity of PFM polymer was dissolved in a specific amount of chlorobenzene solvent to create a homogeneous and viscous solution. Subsequently, the active material, Si nanoparticles, was added and ground thoroughly for 30 minutes at room temperature. The weight ratio of PFM to Sinanoparticles was maintained at 50:50. The resulting slurry was applied to a copper foil using a doctor blade to achieve a thickness of approximately 50 μ m. Following this, the coated electrode was dried and subjected to baking at 500 °C in a tube furnace, resulting in a total mass loading of approximately 0.18 mg/cm² and a thickness of approximately 1.2 μ m. After the 500 °C thermal treatment, the weight ratio of HOS-PFM to Si nanoparticles was approximately 40:60.

For NMC811||LPSCl electrolyte||Si-HOS PFM full cell testing, the process began with the pressing of approximately 0.2 g of LPSCl electrolyte into a pellet using a pressure of around 348 MPa. Subsequently, the cathode composite material was uniformly distributed on the surface of the electrolyte plate and subjected to a pressure of about 348 MPa. On the opposite side of the electrolyte, a Si-HOS PFM anode on a copper foil was pressed, applying a similar pressure of approximately 348 MPa. The cathode composite material had an approximate mass loading of 12 mg, yielding a negative active material (NAM) (Silicon + HOS-PFM) capacity to positive active material (PAM) (NMC811) to ratio of approximately 0.7. This extra capacity of NMC811 cathode is intended to mitigate the irreversible capacity loss that occurs during the first SEI formation cycle. It is important to note that the upper cutoff voltage was limited to 4.0V, resulting in the NMC811 capacity not being fully used. The results of NMC811|| lithium cell shows that the NMC811 cathode is capable of delivering 120 mAh/g when charged to 4.0V, as shown in Fig. S38. Therefore, an NMC811 capacity of 120 mAh/g is used to calculate the N/P ratio when the full-cell batteries are cycled up to 4.0 V (Note S15). The resulting pellet was sandwiched between

two stainless steel (SS) rods. All of these procedures were conducted within an argon-filled glove box. Galvanostatic constant current discharge (CD) tests were performed using a Biologic system located in Claix, France, at a temperature of 25 °C and under an applied pressure of 150 MPa. The operating voltage range extended from 2.7 to 4.0 V (vs. Li⁺/Li).

For Si-HOS PFM||LPSCl electrolyte||Li-metal half-cell testing, the procedure involved pressing 0.2 g of LPSCl electrolyte into a pellet using an approximate pressure of 348 MPa. Subsequently, the Si-HOS PFM was evenly distributed on the surface of the electrolyte plate and subjected to a pressure of around 348 MPa. On the opposite side of the electrolyte, a Li metal foil was pressed, applying an approximate pressure of 50 MPa. The resulting pellet was placed between two stainless steel (SS) rods. All of these processes were conducted within an argon-filled glove box. Galvanostatic constant current discharge (CD) tests were carried out using a Biologic system located in Claix, France, at a temperature of 25 °C and under an applied pressure of 50 MPa. The operating voltage range covered the range from 0.01 to 1 V (vs. Li⁺/Li).

Part II: Thick Si/HOS-PFM electrodes:

To prepare high-loading or thick Si/HOS-PFM electrodes, PFM polymers were dissolved in chlorobenzene solvent to prepare a 7.5 wt% PFM solution. An equal amount of Si nanoparticles was then introduced to the PFM solution to prepare a slurry with PFM to Si weight ratio of 50: 50. The slurry was coated on a 16 µm copper foil using 200 µm doctor blade. The resulting Si/HOS-PFM electrodes had a total mass loading of approximately 1.05 mg/cm² or a thickness of approximately 4 to 5 µm. These thick Si/HOS-PFM electrodes, paired with 18 mg of NMC811 cathodes, were tested at a cycling rate of 0.2 C and a temperature of 30 °C, with an N/P ratio of approximately 1.4. In this case, the cathode capacity is a limiting factor. Several attempts were made to increase the cathode mass loading. However, when the cathode mass loading was more than approximately 20 mg, soft short circuits were observed. When a soft short circuit occurs, the battery is unable to charge to 4.0V, instead exhibiting a voltage plateau around 3.8-3.9V, as shown in Fig. S39. Thicker electrodes, whether in the anode or cathode, face increased resistance and transport issues. Thus, the soft short circuit occurred when the mass loading of the cathode material was too high. Therefore, the N/P ratio was set to 1.4 for the thick Si/HOS-PFM electrodes when paired with the NMC811 cathode.

Part III: Thick Si/PVDF/PEO/carbon black electrodes:

The Si/PVDF/PEO/carbon black electrodes were composed of 60 wt% Si, 10 wt% PVDF, 20 wt% PEO, and 10 wt% carbon black. First, 0.2 g PEO was dissolved in 2.4 ml N-Methyl-2-pyrrolidone (NMP) solvent with continuous stirring on a hot plate at 70 °C inside an argon-filled glovebox. An approximate amount of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was then added to mix with the PEO solution to achieve a molar ratio of EO: Li = 20 : 1. Next, 0.1 g PVDF was dissolved in 1.2 mL NMP solvent in a separate 20 ml glass vial. This PVDF solution was then transferred to mix with the PEO solution. To prepare the slurry, 0.6 g Si and 0.1 g carbon black were added to the solution. The slurry underwent three mixing cycles, each consisting of 5 minutes of ball milling and then followed by a resting period of 5 minutes. The slurry was coated on a 16 μ m copper foil using 50 μ m doctor blade. The resulting Si/PVDF/PEO/carbon black electrodes have a mass loading of approximately 0.95 mg/cm² and a thickness of approximately 6 μ m. These thick Si/PVDF/PEO/CB electrodes, paired with 15mg of NMC811 cathodes, were tested at a cycling rate of 0.2 C and a temperature of 30 °C, with an N/P ratio of approximately 1.4.

Nanoindentation Characterization

PFM or HOS-PFM polymers were coated on the surface of stainless-steel spacers for direct nanoindentation measurements or subsequent lithiation or delithiation treatments. Coin cells were assembled with the HOS-PFM coated spacers as the positive electrode, Celgard 2400 separators, lithium chips as the negative electrode, and Gen2 electrolytes. Before lithiating the polymers, the coin cells were at rest for 4 hours. Subsequently, the polymers were lithiated from open circuit potential (OCV) to 0 V using linear sweep voltammetry at a rate of 0.1 mV/s and then held at 0 V for 100 hours to ensure complete lithiation. To prepare delithiated polymers, the fully lithiatetd polymers were delithiated from 0 V to 2.5 V utilizing linear sweep voltammetry at a rate of 0.05 mV/s and then maintained at 2.5 V for 100 hours. The coin cells were disassembled with a Hohsen cell disassembly tool in an argon-filled glovebox. The lithiated and delithiated samples were washed by electrolyte-level solvent to remove electrolyte salts. Then, the samples were dried in a vacuum chamber to remove any residual solvents.

The nanoindentation experiments were conducted inside an argon-filled glovebox, which prevented lithiated polymers from reactions with water and oxygen. An Agilent G200 nano-indenter with a diamond Berkovich tip was used to study the elastic modulus and hardness using depth controlled continuous stiffness method (CSM) at a constant indentation strain rate.

This method measures the contact stiffness (S) as a function of indentation depth (h_c) by applying the oscillatory force to the tip, $P = P_0 e^{i\omega t}$ and measuring the displacement amplitude and phase $h_c = h_0 e^{i\omega t + \varphi}$ using lock-in amplifier. The elastic modulus and hardness are then calculated based on Oliver & Pharr method using equation 1, 2, and 3.

$$E_r = \frac{\sqrt{\pi S}}{2\beta \sqrt{A}} \tag{1}$$

$$\frac{1}{E_r} = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i}$$
(2)

$$Hardness(H) = \frac{P_{max}}{A}$$
(3)

where E_r is the reduced modulus, $\beta = 1.034$ for the Berkovich tip, A is the projected contact area determined through a calibration procedure performed on a fused silica positioned at the center of the sample holder, S is stiffness of the sample, E and v are the Young's modulus and Poisson's ratio of the sample, E_i and v_i are the Young's modulus and Poisson ratio of the indenter and P_{max} is the maximum force during indentation.

The indentation depth was selected to be 2 μ m and was found to be significantly greater than the surface roughness for every sample. This was important to ensure the surface roughness did not influence the resulting modulus and hardness. The indentation strain-rate, harmonic displacement, and frequency was selected to be 0.05 s⁻¹, 1 nm, and 45 Hz respectively. Each sample underwent

10 measurements with more than 500 μ m spacings between each indent to probe the surface homogeneity.

PVDF/Sn and PEO/Sn Double Layer Electrode (DLE) Preparation

An appropriate amount of PEO polymer was dissolved in NMP to prepare a 10 wt% PEO viscous solution at 60 °C. The double-layer electrodes were prepared by applying an additional PEO layer to the Sn(HOS-PFM) single-layer composite electrodes. A doctor blade with a height of 100 μ m was used to apply a homogeneous film on the surface of the Sn(HOS-PFM) single-layer composite electrodes. After vacuum drying overnight at 40 °C, the resultant double-layer electrode sample was named PEO/Sn double-layered electrodes (DLEs).

Following a similar method, PVDF polymer was dissolved in NMP solvent to prepare a 10 wt% PVDF solution. A doctor blade with a height of 100 µm was used to apply a homogeneous PVDF film on the surface of the Sn(HOS-PFM) single-layer composite electrodes. After vacuum drying overnight, the resultant double-layer electrode sample was named PVDF/Sn DLEs.

Elemental Analysis at Different Lithiation Stage

For each sample, a 5 mg sample of PFM was coated onto a stainless-steel spacer and thermally processed at 500°C to produce HOS-PFM. These samples were then assembled into Li||HOS-PFM coin cells and underwent lithiation under various conditions. For HOS-PFM-OCV, the sample was assembled without lithiation. For HOS-PFM-0V, the sample was reduced to 0V (vs. Lithium) using Linear Sweep Voltammetry (LSV) at a rate of 0.1 mV/s and then held at 0V for 24 hours. Other samples (HOS-PFM-0.01V, HOS-PFM-0.1V, HOS-PFM-0.2V, HOS-PFM-0.5V, HOS-PFM-1V) were prepared by adjusting the target voltage for lithiation accordingly. To prepare a delithiated HOS-PFM (2.5V) sample, the sample was first discharged to 0 V (vs. Li/Li⁺) using the LSV method at a rate of 0.1 mV/s, held at 0 V for 24 hours, and then recharged to 2.5 V at the same rate with the LSV method.

Post-lithiation, the HOS-PFM samples were initially washed with anhydrous ethyl methyl carbonate (EMC) and then digested in a solution containing 3% w/v HCl and 1% w/v HNO3 for subsequent elemental analysis. This analysis was conducted using a Perkin Elmer Inductively Coupled Plasma (ICP) Optima 7000 DV Spectrometer. Standard solutions for ICP, with concentrations ranging from 0.01 ppm to 100 ppm, were prepared by diluting lithium and phosphorus stock solutions. Yttrium solution was used as an internal standard, and emission measurements were taken at wavelengths of 670.784 nm and 610.362 nm for lithium, and 213.617 nm and 214.914 nm for phosphorus.

Supplemental Note

Note S1

This Li⁺ ballistic transport, in a solid-state environment, distinguishes itself from existing ion transport mechanisms, such as vehicle transport mechanism in liquid electrolytes and ion hopping transport via segmental motion.³ The well-aligned conjugated backbone structures of HOS-PFM facilitate creation of long-range and high-speed channels within the interlayers between neighboring backbone for ballistic ionic transport (Fig. 1c). Within the HOS, positively charged Li⁺ ions are dynamically counterbalanced by negatively charged electrons along the conjugated backbone to reach overall charge neutrality and achieve system stability. Electrons possess much faster migration velocities than ions and can migrate through π - π conjugated polymer backbones. Dynamically balanced with electrons, Li⁺ ions are capable of diffusing through the interspaces between polymer chains. This ballistic ion transport plastic exhibits much higher ionic conductivity below ambient temperature over polymer electrolyte based conventional segmental motion transport mechanisms. Moreover, the HOS-PFM polymers also demonstrated ballistic transport capability for Na⁺ and K⁺ similar to the Li⁺ transport mechanism.

Ballistic ion transport is defined as the movement of lithium ions through a polymer medium without significant collisions or scattering. Apparently, conventional lithium-ion diffusion via polymer segmental dynamics is not considered ballistic ion transport since the Li⁺ ions frequently collide with or interact with polymer chains during movement. Alternatively, this ion diffusion mechanism relies on polymer dynamics, where the polymer chains drive the movement of the ions. Therefore, this conventional ion transport highly depends on temperature. Increased polymer softness results in higher ionic conductivity. Thus, ion transport via polymer segmental motion faces a tradeoff between mechanical strength of polymer and ionic conductivity. In addition, the frequent collisions between ions and polymer chains or surrounding atoms can lead to a more random movement path and sluggish transport, especially in solid-state environments. In comparison, ballistic ion transport does not rely on polymer segmental motion to drive ion movement. Thus, it avoids the trade-off between polymer mechanical strength and ionic conductivity. In addition, owing to fewer collisions with polymer chains or surrounding atoms, ions can move more smoothly and achieve higher mobility, leading to superionic conductivity.

There are four primary reasons supporting our belief in the ballistic ion transport in hierarchicallyordered-structure (HOS) PFM polymer: (1) different transport mechanisms, (2) superionic conductivity, (3) overcoming the trade-off between ionic conductivity and mechanical strength, and (4) excellent battery performance compared to that of PEO. Please see the detailed explanations below. Points (2), (3), and (4) are discussed more in the main text in later sections.

Different transport mechanisms: As shown in Fig. 1a and 1b, after thermal processing at 500 °C, the long alkyl side chains were thermally cleaved, resulting in densely packed polymer conjugate chains. These densely packed conjugate chains are rigid and have limited mobility, thereby significantly suppressing their polymer dynamics. The ssNMR results provide evidence that ion transport within the HOS-PFM does not depend on polymer dynamics. When lithium ions travel through the HOS polymers matrix, their positive charges are balanced by the electrons along the conjugated polymer backbones. The interactions between electrons and lithium ions limit the random motion of lithium ions, and well-defined, well-organized HOS polymer structure decreases collisions between lithium ions and other polymer chains. It is important to point out that the HOS-

PFM polymers retain their HOS feature after doping lithium ions, as evidenced by the results of 4D-STEM experiments (Fig. 2d). This highly stacked polymer structure features distances of several hundred nanometers (Fig. 2d), which ensures ballistic ion transport without significant collisions along this distance. In comparison, the diffusive Li⁺ transport by polymer segmental motion involves frequent collision or interactions with the polymer chains. In this mechanism, Li⁺ ions move through the polymer medium by diffusing or hopping from one segment of polymer chains to another.⁴ Thus, this polymer segmental motion mechanism typically leads to random motion of ion diffusion. Its ion transport depends on and is limited by the dynamics of polymer segmental motion and the frequency of scattering events, which typically result in low ionic conductivity.

Superionic conductivity: Solid polymer electrolytes, such as PEO with lithium salts, have an approximate ionic conductivity (σ^+) in the range of 10⁻⁸ to 10⁻⁵ S/cm at room temperature, inadequate for practical applications.⁴⁻⁶ Polymer melt of PEO and lithium salts above melting temperature (~60 °C) possesses an approximate σ^+ of 10⁻⁵-10⁻⁴ S/cm.^{5, 7} The PEO polymer gains substantial improvement in ionic conductivity above its melting temperature owing to higher polymer dynamics in the molten state.

In comparison, the 100% Li⁺-doped HOS-PFM exhibited a superior σ^+ at room temperature, approximately 10⁻⁴ to 10⁻³ S cm⁻¹. At room temperature, the ionic conductivity of Li⁺-doped HOS-PFM is at least one to two orders of magnitude higher than that of salt-mixed PEO. Besides, the ballistic ion transport within HOS-PFM followed Arrhenius temperature variation $\sigma \sim \exp(-E_{\sigma}/kT)$, demonstrating solid-like transport mechanism.⁸ In comparison, the ionic conductivity of PEO based on polymer segmental motion does not closely follow the Arrhenius temperature equation, especially near the glass transition temperature.

Overcoming the tradeoff between ionic conductivity and mechanical strength: Polymer is soft and pliable above its glass transition temperature (T_g) due to polymer segmental motion, whereas below T_g , the polymer segmental motion reduces to minimum, thus the polymer is glassy and hard. Ionic conductive polymers, such as PEO, feature moderate lithium ionic conductivity (σ^+) at temperatures above T_g .^{4, 9} However, as the temperature drops below T_g . The σ^+ decreases by several orders of magnitude, and reduces to near zero. In addition, since partial crystallinity of the polymer restrains polymer segmental motion, the σ^+ of polymer can drastically decrease in the presence of crystalline domains. Therefore, the Arrhenius relationship between temperature and conductivity of a conventional polymer bents down at every phase transition of the polymer from polymer melt to partially crystalline states, and to glassy state.^{4, 8, 9} Additionally, these polymers confront a tradeoff between σ^+ and mechanical strength. Specifically, the softer the polymers, the higher the σ^+ , and vice versa. Therefore, achieving high σ^+ at ambient to low temperatures faces tremendous challenges in a mechanically robust polymer host.

In comparison, the HOS-PFM polymer achieves a synergistic effect in ionic conductivity and mechanical strength. After doping lithium ions, the ionic conductivity of HOS PFM improved by nearly three orders of magnitude (Fig. 2f). Meanwhile, the elastic modulus and hardness of lithiated HOS-PFM increased by approximately 725% and 433%, respectively, compared to the undoped HOS-PFM (Fig. 2e).

The HOS-PFM film electrodes have a thickness of approximately 2 to 3 μ m, which is slightly thick. A thick polymer film can face the resistance and mass transport issues encountered during electrochemical cycling, particularly at higher C rates. To avoid this issue, the cells containing HOS-PFM electrodes were initially tested at low cycling rates. In the Li || HOS-PFM half-cell configuration, the discharge capacity represents the amount of Li⁺ ions inserted into the HOS-PFM, the charge capacity indicates the amount of Li⁺ ions that can be extracted from the HOS-PFM. Since some Li⁺ ions can become trapped within the HOS-PFM polymers, the charge capacity reflects its usable or practical capacity.

Testing at a lower C-rate enables the measured capacity to more accurately reflect the theoretical lithium-ion capacity of the materials. As shown in Fig. S2, at the current of 12.5 mA/g, the highest charge capacities of two cells are approximately 800 mAh/g and 1100 mAh/g, respectively, yielding an average of specific capacity of 950 mAh/g. When measured at a current of 5.0 mA/g, the HOS-PFM polymer exhibits a charge capacity of approximately 1200 mAh/g (Fig. S3). When the current rate is decreased from 12.5 mA/g to 5 mA/g, there is no significant increase in charge capacity, indicating that the maximum capacity of HOS-PFM ranges between 1100 mAh/g and 1200 mAh/g. Given that a discharge/charge current of 12.5 mA/g corresponds to a cycling rate of 0.02 C, the estimated maximum capacity of HOS-PFM is approximately 1000 mAh/g. When the current increased from 12.5 mA/g to 50 mA/g, the reversible capacity of the HOS-PFM polymer dropped to approximately 400 mAh/g.

Although PFM polymer features conjugated backbone, its long alkyl side chains significantly disrupt the π - π stacking and influence the inter-chain electron migration. While electrons may migrate effectively along a single PFM conjugated backbone, migrating across different polymer chains can be challenging, thus affecting its bulk electronic conductivity. Therefore, PFM demonstrates significantly three orders of magnitude lower electronic conductivity compared to HOS-PFM.¹⁰ The positive lithium ions (Li⁺) within the polymers must be balanced by negative charges, which are provided by electrons on the conjugated backbone. During ballistic ion transport, the Li⁺ ions move through the polymer matrix, with their cationic charges balanced by electrons on the conjugated backbone. Thus, the Li⁺ ions and electrons move together, maintaining charge neutrality in the system. The inductively coupled plasma (ICP) experiments showed that no phosphorus (P) was detected when the HOS-PFM was lithiated (Table S1). This suggests that the PF₆⁻ ions from the LiPF₆ electrolyte did not significantly enter the HOS-PFM polymer matrix along with the lithium ions. Therefore, the inserted Li⁺ ions are highly dependent on electrons to achieve charge neutrality within the system. Poor electronic conductivity of PFM is one of major factors limiting ions transport and capacity. Besides, the flexible long and nonpolar alkyl side chains of PFM may disrupt ion transport.

In addition, the long alkyl chains of the PFM polymer reduce its overall polarity. The electrolytes used in this work consist of 1.2 M LiPF₆ in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a weight ratio of 3:7 (EC/EMC). Both EC and EMC are polar solvents, resulting in unfavorable interactions with the less polar PFM polymer. This may reduce the extent to which lithium ions enter the PFM polymer.

The structure of PFM underwent a sequence of thermal radical cleavage in its side chains upon increasing temperature. Previous works demonstrated that temperatures above 400 °C initiated the thermal cleavage process of bulky alkyl side chains, and the ester side chains experienced a gradual thermal decomposition with further temperature increase.¹⁰ Fig. 2a and 2b showed the ¹H spin-echo and ¹H \rightarrow ¹³C CPMAS solid-state NMR (ssNMR) spectra of PFM and HOS-PFM, respectively.

In these CPMAS experiments, the ¹H polarization is transferred to nearby ¹³C nuclei, enhancing the detected ¹³C signals and making protonated carbon significantly more intense than non-protonated carbon, such as quaternary carbon sites. As a result, CPMAS experiments are not quantitative, and interpreting signal intensities in ¹³C CPMAS spectra is challenging.

Solid-state ¹³C NMR analysis for PFM

Fig. 2b showed the non-quantitative ¹³C ssNMR recorded on PFM and HOS-PFM using ¹H \rightarrow ¹³C CPMAS experiment. A precise assignment of these carbon sites is challenging due to the limited resolution of our ssNMR ¹³C spectra rising from the close chemical shift values expected for (i) the ¹³C sites in the alkyl chain and (ii) the many aromatic ¹³C sites forming the polymer backbone. Despite this, a few ¹³C signals were well resolved in PFM (Fig. 2b) at 192 (site *a*), 169 (site *b*), 152 (site *c*), 55.7 (site *d*), 51.5 (site *f*) and 40.6 ppm (site *e*).

As shown in Fig. 1a (i), the sites *a* and *b* of PFM correspond to the carbon sites of the ketone and ester groups in its fluorenone and methylbenzoic ester monomer blocks, respectively. The low intensity observed for these two sites is attributed to the difficulty of polarizing ¹³C sites through CPMAS transfer due to their lack of close-by ¹H nuclei. Site *c* correspond to the two aromatic carbons bonded to the carbon site *d* anchoring the alkyl side chain of the 9,9-dioctylfluorene monomer block, while site *e* is attributed to the first carbon in that alkyl side chain (Fig. 1a(i)). Finally, site *f* correspond to the terminal methyl in the ester group of the methylbenzoic ester monomer block (Fig. 1a(i)).

Among these ¹³C signals, the well-resolved site *d* at 55.7 ppm is particularly interesting. As stated above, this ¹³C signal corresponds to a quaternary carbon, resulting in a weaker ¹³C signal compared to the protonated ¹³C nuclei of the alkyl side chains in the ¹H \rightarrow ¹³C CPMAS spectrum. This reduced intensity is due to (i) the ratio of the alky carbon site to quaternary *d* carbon that favors the first one and (ii) the lower ¹H polarization transfer efficiency in the ¹H \rightarrow ¹³C CPMAS experiment for the quaternary ¹³C nuclei *d*. In the alkyl side chain, the closer a carbon site is to the carbon site *d*, the more deshielded it is, resulting in a higher chemical shift value. This effect is typically known as the less alkyl substitution effect and explains why the carbon ^{*e*} have a chemical shift value near 40.6 ppm while the end carbon (-CH₃) in the alkyl chain has a chemical shift value of around 14.4 ppm.

Solid-state NMR analysis for HOS-PFM

The HOS-PFM featured noticeable differences in ¹³C ss-NMR spectra due to loss of alkyl side chains. Besides, the loss of hydrogen atoms nearby carbon atoms also resulted in difficulty obtaining sharp ¹³C NMR signals due to a poor CPMAS transfer efficiency. First, the site *a*' corresponds to the ketone carbon site in the fluorenone monomer blocks of HOS-PFM after heat treatment and is difficult to observe due to the limited CPMAS transfer efficiency for such carbon,

worsened by the lower ¹H concentration in HOS-PFM, as evidenced by the ¹H spectrum. Second, only one weak signal d' is observed in the non-aromatic carbon region of the spectrum at 36.5 ppm and indicates the loss of the alkyl sidechain as pictured in Fig. 1a (ii). Compared to PFM, the peaks in the 14.4 ppm to 40.6 ppm range disappeared in HOS-PFM (Fig. 2b top spectra), indicating the thermal decomposition and loss of the alkyl side chains that results in the formation of a single ¹³C site d' at 36.5 ppm in the HOS-PFM material (Fig. 2b, top spectra). The alkyl side chains are easier to cleave owing to a relatively lower carbon-carbon single bond dissociation energy of approximately 347-356 kJ/mol.¹¹ In comparison, the carbon-carbon (C–C) bond between d and c is not readily cleaved because of π electron delocalization, which contributes to a higher C–C bond dissociation energy of around 516-540 kJ/mol.¹¹ During the heat treatment, the cleavage of C-C bond between d and e induced the formation of an unstable radical site on the carbon d. To form a stable compound, the carbon d interacts with a radical hydrogen to form a relatively stable C-H bond (Fig.1a (ii)). The bond formation between the carbon d and a hydrogen radical result in a carbon site d' with a lower chemical shift value owing to the electron donation and shielding effect caused by hydrogen atom. This effect induces a peak shift of carbon d from 55.7 ppm (in PFM) to 36.5 ppm in HOS-PFM, and referred as carbon d'. Similarly, the signal of carbon c at 152 ppm is no longer easily resolved and can be explain by (i) the reduced efficiency of the CPMAS transfer after heat treatment caused by the reduction of ¹H content in the material and (ii) a shift of the signal toward the bulk aromatic carbon regions (from 110 to 160 ppm) induced by the protonation of the carbon d.

The carbonyl carbon-oxygen double bond (C=O) attributed to the ¹³C signals *a* and *a'* at 192-193 ppm (Fig. 2a, 2b) appears to be mainly unaffected by the thermal treatment. Such behavior is expected for carbonyl sites for which the high dissociation energy C=O bond (around 720 kJ/mol)¹¹ would require a much higher temperature to break. After heat treatment, the disappearance of the ¹³C signals *f* (at 51.5 ppm) suggested thermal cleavage of -CH₃ groups due to a relatively low bond dissociation energy of the C–O bond, 351 kJ/mol.¹¹ The removal of these - CH₃ groups significantly reduced the amount of neighboring ¹H of carbon *b'*, which made it challenging to observe the ¹³C signals in the carbon *b'* in HOS-PFM (Fig. 2b) due to a lower ¹H->¹³C transfer efficiency from the CPMAS experiments.

During the thermal treatment, the long alkyl side chains at site b' were cleaved and the carbon b' were reconnected with hydrogen atom to achieve molecular structure stability. Similarly, at site f, the -CH₃ groups were cleaved due to a weak low bond dissociation energy of the C–O bond, 351 kJ/mol.¹¹ With the presence of silicon, after the covalent bonds broken between the oxygen atom and -CH₃, the -COO- can react with -OH group on silicon surface via esterification reaction , which provide a covalent binding adhesion for silicon-based battery.

These findings in ssNMR suggested that the PFM polymer underwent thermal radical cleavage in its alkyl side chains, as well as at the terminal methyl groups on the ester side chains. The resultant HOS-PFM maintained the backbone polymer structure and adhesive functional moieties. The polymer nature of HOS-PFM distinguishes it from carbon materials and offers an innovative polymer processing strategy to engineer multifunctional polymer.

After lithiation or delithation, the mechanical properties of the PFM polymer remained nearly unchanged owing to its negligible Li⁺ ion capacity. In contrast, the HOS-PFM featured a capacity of approximately 1000 mAh/g capacity. As a result, lithiated and delithiated HOS-PFM exhibited significant changes in elastic modulus and hardness relatively to the pristine HOS-PFM.

The PFM featured large plastic deformation behavior while the HOS-PFM exhibited significant elastic recovery or rubber-like deformation attributes after unloading (Fig. S10). The PFM possessed flexible alkyl side chains, which softened structures and led to plasticization effect. After thermal removal of the alkyl side chains, the HOS-PFM featured densely stacked and well-defined polymer structures, acting as resilient leaf springs for elastic recovery. Due to PFM's negligible Li⁺ capacity, its load-displacement behavior remained unchanged and stable by either lithiation or delithiation. In comparison, both lithiation and delithiation resulted in significant changes in the load-displacement curves in the HOS-PFM polymers. The pristine HOS-PFM displayed elastic recovery or rubber-like deformation features, but the lithiated HOS-PFM lost these features and exhibited plastic deformation behavior. Following delithiation, the delithiated HOS-PFM partially recovered elastic recovery attributes. In summary, compared to the HOS-PFM, the PFM exhibited more stable load-displacement behavior across pristine, lithiated, and delithiated states due to its negligible Li⁺ capacity.

Polyethylene oxide (PEO) is a representative example of polymer electrolytes. When salts, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), are added into the polymer electrolytes, both positive and negative ions integrate into the polymer matrix. These ions interact with polymer chains, disrupting polymer chain packings and creating defects. Therefore, an increase of salt concentration break down crystalline regions of polymers and transform them into amorphous regions, thus leading to a decrease in crystallinity.¹² In addition, these salts functions as plasticizers, reducing the interaction between adjacent polymer chains, thus making the polymer chains more flexible and decreasing mechanical strength of the polymers. Traditional polymer electrolytes depend on polymer segmental motion to facilitate Li⁺ ion transport. Therefore, these polymer electrolytes adhere to the principle that softer polymer exhibit higher ionic conductivity.

In comparison, the HOS-PFM polymer preserves its hierarchically ordered structure after lithiation, as observed in the 4D-STEM experiment (Fig. 2d). When Li⁺ ions are inserted into the polymer matrix, electrons also enter and migrate along the conjugate backbone chains, thereby achieving overall charge neutrality in the system. Therefore, the negatively charged electrons along the conjugated backbone chains can form electrostatic interactions with the positively charged Li⁺ ions. When a lithium ion dynamically interacts with two or more adjacent negatively charged polymer chains, it can serve as a reversible and dynamic ionic cross-link, pulling chains closer together. These reversible ionic cross-links provide additional interactions and bonding between the polymer chains, thereby enhancing their mechanical strength. The interactions between lithium ions and HOS-PFM polymers are reversible. Therefore, the elastic modulus and hardness of HOS-PFM polymers increase substantially after lithiation and decrease upon delithiation. In comparison, in the PEO/LiTFSI system, the PEO chains do not carry electrons, thus there is no electrostatic interaction between Li⁺ ion and PEO chains.

Owing to high σ^+ , the LPSCl exhibited a straight line across all the frequencies in Nyquist plots (Fig. S13-16), and its ionic resistance (R_{LPSCl}) was determined at high frequencies. In comparison, the doped HOS-PFM samples featured an additional semicircle, which reflected the interface resistances between the LPSCl and HOS-PFM polymers.

The total ionic resistance ($R_{LPSCI+HOS-PFM}$) of HOS-PFM and LPSCl, also observed at high frequencies, were slightly larger compared to the LPSCl. The ionic resistance of doped HOS-PFM ($R_{HOS-PFM}$) was determined by subtracting R_{LPSCI} from $R_{LPSCI+HOS-PFM}$ (Fig. S14-16). The $R_{HOS-PFM}$ was significantly lower than R_{LPSCl} , mainly due to the thinner thickness of HOS-PFM (~12 µm) compared to the LPSCl (0.32g ~2 mm) (Table S3, 4)

The 90% Li⁺-doped HOS-PFM polymer exhibited similar σ^+ , illustrating the formation of interconnected ion pathways under this doping condition.

Pristine PFM/Sn and HOS-PFM/Sn DLEs featured distinctive sharp peaks corresponding to crystalline Sn nanoparticles and copper (Cu) substrate (Fig. 3a). These phenomena demonstrated that the X-ray successfully penetrated the electrode materials, enabling the capture of crystallinity information from copper substrate. Simultaneously, the X-ray was cable to detect the crystallinity of any remaining Sn particles within the electrodes, thereby monitoring the crystallinity changes of Sn particles before and after compressing alkali metal (Li, Na, and K).

Tin (Sn) nanoparticles were chosen over Si nanoparticles for experimental characterization due to four major reasons.

First, Sn has a higher density (7.29 g/cm³) compared to Si (2.33 grams/cm³). Therefore, Sn will occupy a smaller volume for the same mass. When fabricating an electrode with 50 wt% Sn and 50 wt% PFM polymers, the interparticle spacing between Sn particles is significantly greater than that between Si particles under identical conditions. This was intentionally designed from the beginning to ensure that alkali metal ions must travel through the HOS-PFM polymer to react with Sn. The alkali metals can potentially puncture the top PFM or HOS-PFM layer through a pinhole under pressure. Therefore, the large inter-particle distance added another layer of security, ensuring that even if the alkali metal punctured the top HOS-PFM or PFM layer, it still had to travel through the HOS-PFM located between adjacent particles to react with Sn.

Second, Sn featured several peak positions at 30.6°, 32.0°, 43.9°, and 44.9°. In comparison, Si particles only feature two major peak positions at 28.4° and 47.3°. In addition, The XRD peaks of Sn particles are much sharper than that of Si particles, which make it easy to track the changes after compressing the lithium metal.

Third, after lithiation, both Sn particles and Si particles undergo approximately 300% volume expansion. Under compressing lithium metal, we observed that Sn particles within the Sn/HOS-PFM electrodes could maintain their spherical structure after the volume expansion. However, Si particles nearly lost their structural integrity under the same compression conditions after lithiation. Similar phenomena involving Si were also observed in another study.¹³

Fourth, Sn can react with lithium, sodium, and potassium. However, it is well known that Si has difficulty reacting with sodium.

Why is Sn not used for solid-state battery testing? Sn was not selected for electrochemical performance in solid-state batteries due to its low theoretical specific capacity of 994 mAh/g. In comparison, silicon, with a theoretical capacity of approximately 3700 mAh/g, has attracted increasing research attention and has emerged as a potential anode material for solid-state batteries.¹⁴ Besides, Sn is more expensive and less abundant than silicon. Therefore, silicon was chosen to fabricate electrodes with HOS-PFM polymers to demonstrate the potential of these polymers in solid-state battery applications.

After compressing sodium metal, a few small peaks appeared between 30° and 40° in the XRD patterns of the sodium HOS-PFM/Sn samples. This phenomenon was observed in several sodium HOS-PFM/Sn samples. These small peaks are primarily attributed to Na₁₅Sn₄ and NaOH.

The original Na metal and HOS-PFM/Sn samples did not exhibit these small peaks. These peaks emerged following the compression experiments, indicating that they likely originated from the reaction product formed during the compression experiment. In our experimental setup, an excess of sodium metal is used to ensure the complete reaction of all the tin (Sn). During sodiation process, sodium ions were inserted into the Sn metal and experience alloying process.

Ellis *et al.* observed the $Na_{15}Sn_4$ as the final product through in situ XRD experiments performed during the sodiation process.¹⁵ Wang *et al.* performed the in-situ TEM experiments and proposed a slightly different reaction mechanism.¹⁶ However, both Elllis and Wang observed the formation of crystallized $Na_{15}Sn_4$ after complete reaction. This $Na_{15}Sn_4$ phase forms in the presence of excess sodium sources, which matches with our experimental conditions.

As shown in Fig. S23, the standard XRD pattern of $Na_{15}Sn_4$ (PDF#31-1327) exhibited five peaks between 30° and 40°, specifically at 31.92°, 33.38°, 34.80°, 37.46°, and 39.98°. Those small XRD peaks (31.92°, 33.38°, 34.80°, and 37.46°) of the sodium HOS-PFM/Sn sample matched well with the standard XRD patterns of $Na_{15}Sn_4$. This confirms that $Na_{15}Sn_4$ is the primary compound contributing to the small peaks.

In addition, a minor peak is observed around 38.3° , which deviates slightly from the standard peak position of Na₁₅Sn₄ (PDF#31-1327). There are two possible reasons. First, this peak measured in the experiments might have experienced a slight peak shift compared to the theoretical value due to technical issues or potential another phase of Na_xSn alloy. Second, the NaOH may form during the compression experiment, during the XRD measurement process, or during both. Sodium metal is highly reactive and reacts with moisture in the air to form NaOH.

Although air-free sample holders (Bucker Airtight Sample holder: A100B33, Fig. S24B) were used for these XRD experiments, they are not perfectly sealed. Each XRD experiment took around one hour by using the Brucker D2 Phaser XRD machine (Fig. S24C). Occasionally, a color change in the metal was observed after the XRD measurement. This suggests that the sample holders may have experienced some air leakage, leading to the reaction of sodium with moisture to form NaOH. The minor peak at 38.3° matches well with the standard values of NaOH (PDF#35-1009). Besides, three minor peaks observed between 53° to 56° in the sodium HOS-PFM/Sn sample also closely align with the theoretical values of NaOH (PDF#35-1009).

The absence of potassium peaks in the XRD patterns of potassium HOS-PFM/Sn samples is due to two reasons. Pure potassium metal foil (size: 1×1 cm) has very weak XRD crystalline peaks, as shown in Fig. S24. This potassium metal was purchased from Sigma Aldrich without any further treatment. The potassium metal was cut into a 1×1 cm foil, and its XRD patterns were then measured. This commercial potassium metal had weak XRD patterns, with its highest intensity peak having nearly the same intensity as the air-free sample holder (Fig. S24). Two potassium HOS-PFM/Sn samples exhibited the similar patterns, in which their potassium peak didn't show up. We think there are two possible reasons resulting in this phenomenon. First, compared to lithium and sodium, the pure potassium metal exhibited very weak XRD crystalline peaks. Following the procedure described in Fig. S17 to remove the copper foil and prepare the samples for XRD experiment, some potassium metal residues remained on the samples. However, the quantity of residual potassium was significantly less than that of pure potassium foil. Given that even the pure potassium metal displayed poor peaks, the small amount of residual potassium exhibited almost no detectable peaks in the XRD experiments. Second, it was observed that the air-free sample holder (Bucker Airtight Sample holder: A100B33) is not perfectly airtight after one hour of measurement in the XRD machine, as shown in Fig. S24B,C. Therefore, the air leakage from the sample holder can further reduce the quantity of potassium metal residues, as potassium metal can react with air. This makes the potassium residues even more difficult to detect due to their low quantity.

In addition to experiencing the crystalline-to-amorphous transition, the Sn nanoparticles would also undergo volume expansion owing to lithiation. Initially, this morphological evolution was visualized by the cross-sections of HOS-PFM/Sn DLEs prepared by an ion milling machine (Fig. S27, S28). However, this method involved a short exposure of samples (~1 minute) to air during transfer. To avoid air exposure, the HOS-PFM/Sn DLEs were fabricated on 4.5-µm thick copper substrates (Fig. 3b), which were accessible for focused ion beam (FIB) milling to create cross-sectional views under vacuum.

As shown in Fig. 3c and Fig. S25, for the original HOS-PFM/Sn DLEs, the interspace among isolated Sn nanoparticles were filled with HOS-PFM polymers. One approximate 2-µm thick HOS-PFM layer was engineered on the Sn layer, eliminating possible direct contact between Li and Sn during the compression. The energy dispersive X-ray spectroscopy (EDS) image confirmed spatial distribution of Sn nanoparticles within HOS-PFM polymer matrix and no clear interfacial boundary between the Sn and HOS-PFM layer. After the compression, both SEM and EDS images confirmed the volume expansion of Sn nanoparticles (Fig. 3d). Despite large volumetric expansion of Sn particles, the HOS-PFM polymers demonstrated mechanical flexibility to accommodate this volume expansion and maintained electrode integrity and avoided structural pulverization owing to its binding function.

Polyvinylidene fluoride (PVDF) and polyethylene oxide (PEO) are two commonly used polymers. We followed the same methods used for making HOS-PFM/Sn double-layer electrodes (DLEs) to prepare PVDF/Sn and PEO/Sn DLEs. These PVDF/Sn or PEO/Sn DLEs contain a top and a bottom layer. As shown in Fig. S29, the bottom layer of these DLEs shares the same composition, which contains approximately 60 wt% Sn and 40 wt% HOS-PFM polymers. The top layer is PEO or PVDF, with a thickness of approximately 2 to 4 micrometers. After compressing lithium metal for three days, both PVDF/Sn and PEO/Sn DLEs preserved the XRD diffraction peaks of Sn particles at 30.6°, 32.0°, 43.9°, and 44.9° (Fig. S29). In addition, after the compression of lithium metal, the cross-sectional profiles of PEO/Sn and PVDF/Sn measured by FIB-SEM showed that Sn particles averaged between 300 nm and 500 nm, similar to the particle sizes in the pristine electrodes. These results are expected due to required conditions for lithium ions to react with Sn particles in this experimental setup. As shown in Fig. 1d, first, during the compression of Li metal, a redox reaction between the Li metal and the polymers must occur to produce lithium ions. Second, these lithium ions must migrate through the polymers to reach the Sn particles and initiate reactions. Neither PVDF nor PEO can initiate a redox reaction with lithium metal under these reactions. Therefore, the Sn particles within PVDF/Sn or PEO/Sn electrodes retained their XRD diffraction peak patterns and maintained similar particle sizes after lithium metal compression.

Most silicon thin film electrodes of ASSBs featured a nanometer-ranged thickness (typically < 150 nm).^{13, 17, 18} In recent years, one cutting-edge strategy is to incorporate solid-state electrolytes, such as garnet-type electrolyte¹⁸ and LPSCl¹⁹, with silicon particles, to create sufficient ionic pathways. Such strategies can enhance the thickness of Si-based electrodes to micrometer regime but often face cycling stability issues due to limited control for Si volume changes during battery cycling or require a large compression force.

In this context, we proposed an alternative strategy for engineering Si-based anodes, which enhanced cycling performance while avoiding the need for a large compression force. The anode electrodes contained only HOS-PFM polymer and Si particles, without the need for any electronically or ionically conductive additives. The HOS-PFM polymers played the roles of electronic and ionic conductors, creating electronic and ionic pathways bridging active material Si with current collector and solid electrolytes, respectively. Moreover, the HOS-PFM functioned as polymer binders, which not only maintained structural integrity and accommodated drastic volume change of Si but also ensured good electrical and ionic contact with Si material regardless of its volume expansion and shrinkage during battery cycling. The cycling performance of half-cell validated these advantages of HOS-PFM (Fig. S35). Moreover, owing to these advantages, the ASSBs full cells with thin Si/HOS-PFM electrodes retained approximately 70% capacity after undergoing 100 cycles at 0.2 C rate (Fig. S36). This manifested that HOS-PFM polymers effectively controlled volume variation of Si, maintained electrical connections and ionic pathways with active Si materials, even under harsh conditions. Additionally, the binding function of HOS-PFM preserved electrode integrity and minimized 'dead' Si throughout battery cycling process.

The capacify loss of solid-state batteries can occur in several parts, including the cathode, solid electrolyte, and anode. To focus on the anode, we prepared Si/HOS-PFM on a 4.5 µm thick copper foil, which can be ion-milled using FIB-SEM. The standard 16 µm copper foil is too thick to cut through with FIB-SEM. As shown in Fig. S37, when the Si/HOS-PFM electrodes underwent 25 cycles in combination with an NMC811 cathode, cracks were observed in the cross-sectional SEM images. These cracks are one of the reasons contributing to capacity fade. The half cells experienced faster capacity lost not only due to the Si/HOS-PFM electrodes but also because of the unstable interface between the LPSCl solid electrolytes and lithium metal.

In summary, the polymers containing HOS structures featured high σ^+ based ballistic ion transport, presenting a promising polymer engineering solution to address the poor σ^+ bottleneck within ASSB electrodes.

Why choose an upper operating voltage of 4.0 V instead of 4.2 V?

The cycling performance of full cells is influenced by several factors, including negative electrode, solid electrolytes, and positive electrode. We assembled a NMC811 || Si/HOS-PFM full cell, which were cycled to higher operating voltages of 4.0V, 4.2 V, 4.3 V, 4.4 V, and 4.5 V for five cycles each (Fig. S40, S41). With a lower voltage fixed at 2.7 V, the cell was cycled to 4.0 V for 5 cycles, then 4.2 V, 4.3 V, 4.4 V, and 4.5 V. We observed that using a higher upper operating voltage can release more capacity of NMC811 materials, but it also results in significant capacity fade. For example, when the cells were cycled to 4.0 V, they exhibited 99.29% capacity retention after 5 cycles (Fig. S40). In comparison, cycling the cell to 4.2 V resulted in a capacity retention of 96.79% after 5 cycles (Fig. S40). As the upper operating voltage increased to 4.3 V, 4.4 V, and 4.5 V, the capacity retention progressively decreased (Fig. S40, S41).

The cathode composite electrodes were composed of NMC811, LPSCl, and carbon nanofiber in a weight ratio of 80 : 20 : 2, and were mixed using a pestle and mortar. We chose to cycle at 4.0 V rather than 4.2 V to prioritize the investigation of the Si/HOS-PFM anode's performance and to minimize the effects of other influencing factors. In our self-prepared cathode materials, faster capacity fade at higher operating voltages can be attributed to several factors, including the structural degradation of NMC811 material and the poor electrochemical stability between NMC811/LPSCl interface. Additionally, the absence of a polymer binder in our cathode composition may contribute to the reduced structural integrity when cycling at higher voltages. The primary goal of the NMC811||Si/HOS-PFM full cells, containing approximately 60 wt% Silicon and 40 wt% HOS-PFM, is to demonstrate the feasibility of ballistic ion transport in solid-state battery systems. Therefore, we used a high loading of HOS-PFM polymers to isolate the Si particles.

Supplemental Figure



Figure S1. (A) Thermogravimetric analysis (TGA) of PFM polymer. The experiment started at 40°C and ramped up to 800 °C with a heating rate of 4 °C per minute. The polymer structures showed no noticeable changes prior to reaching 200 °C. According to the TGA results, the structural changes of PFM polymer began around 400 °C. Upon reaching 500 °C, the polymer experienced a weight loss of approximately 40%, which aligns with the atomic weight percentage of alkyl side chains in the PFM polymers. (B) FTIR measurement of PFM polymer structural changes at different processing temperatures. The PFM samples were heat to the desired temperature with a ramp rate of 4 °C per minute in a tube furnace. The SP³ C-H stretch peaks between 2750 and 3000 cm⁻¹ were mainly contributed from the alkyl side chains and the - CH₃ group from the ester chain. When the temperature reached 400 °C, most of these SP³ C-H stretch peaks disappeared due to thermal decomposition. By 500 °C, those peaks had almost completely vanished. Both the TGA and FTIR experiment results were consistent with our previous solid-state NMR findings.



Figure S2. Lithium-ion capacity characterization of HOS-PFM polymer at four different current densities. (A and B) Cyclic voltage versus time at the current densities of 12.5, 50, 100, and 167 mA/g for (A) Coin Cell #1 and (B) Coin Cell #2. (C and D) Specific capacity versus cycle number at the current densities of 12.5, 50, 100, and 167 mA/g for (C) Coin Cell #1 and (D) Coin Cell #2.



Figure S3. Lithium-ion capacity measurement of HOS-PFM at a current density of 5 mA/g. (A) Voltage versus time. (B) Voltage versus specific capacity.



Figure S4. Lithium-ion capacity characterization of PFM polymer at four different current densities (C rates). (A and B) Cyclic voltage versus time at the current densities of 12.5, 50, 100, and 167 mA/g for (A) Coin Cell #1 and (B) Coin Cell #2. (C and D) Specific capacity versus cycle number at the current densities of 12.5, 50, 100, and 167 mA/g for (C) Coin Cell #1 and (D) Coin Cell #2.



Figure S5. (A and B) Schematics of original (A) PFM/Sn and (B) HOS-PFM/Sn double layer electrodes (DLEs). (C and D) Schematics illustrating the volumetric changes of Sn nanoparticles within the (C) PFM/Sn and (D) HOS-PFM/Sn DLEs after compressing Li metal.



Figure S6. Surface SEM image of PFM/Sn DLE surface. The smooth SEM surface image demonstrated that the top PFM layer completely covered the bottom Sn layers, thereby preventing direct contact between Sn and the alkali metals (Li, Na, or K) during the compression process.



Figure S7. Surface morphology of HOS-PFM/Sn DLEs. This surface SEM image reflected that the top HOS-PFM layer fully encapsulated the bottom Sn layers, thereby preventing direct contact between Sn and the alkali metals (Li, Na, or K) during the compression process.



Figure S8. Soft X-ray absorption spectroscopy (sXAS) experimental illustration for HOS-PFM polymer characterization post-compression with Li metal, Na metal, or K metal. The HOS-PFM in this experiment featured the thickness of around 2 μ m. These alkali ions and electrons must travel through the HOS-PFM layer in order to be detected on another side of surface, also reflecting that Li⁺ ions, Na⁺ ions, and K⁺ ions could travel through the 2- μ m-thick HOS-PFM film.



Figure S9. The high-efficiency carbon *K*-edge RIXS maps collected from (A) HOS-PFM, (B) Li⁺/HOS-PFM, (C) Na⁺/HOS-PFM, and (D) K⁺/HOS-PFM.



Figure S10. Nanoindentation load-displacement behaviors of (A) PFM, (B) HOS-PFM, (C) Lithiated PFM, (D) Lithiated HOS-PFM, (E) Delithiated PFM, and (D) Delithiated HOS-PFM.



Figure S11. Comparison of elastic modulus and indentation hardness for PFM and HOS-PFM polymers in pristine, lithiated, and delithiated states. (A) Elastic modulus. (B) Indentation hardness.


Figure S12. (A) Illustration of solid-state ionic conductivity experimental set-up. (B) Equivalent circuit for pure LPSCI. (B) Equivalent circuit for doped HOS-PFM. The Total referred to LPSCI + Li^+/HOS -PFM, and the Int referred to interface.



Figure S13. Nyquist plots of 0.32g LPSCl, pristine PFM, doped Li⁺/PFM, pristine HOS-PFM, 90% Li⁺/HOS-PFM, and 100% Li⁺/HOS-PFM across various temperatures. (A) 70 °C, (B) 60 °C, (C) 50 °C, (D) 40 °C, (E) 30 °C, (F) 20 °C, (G) 10 °C, (H) 0 °C, (I) -10 °C, and (J) -20 °C. The LPSCl had a weight of 0.32 g. The pristine PFM, doped Li⁺/PFM, pristine HOS-PFM, 90% Li⁺/HOS-PFM, and 100% Li⁺/HOS-PFM films were measured with incorporating a total of 0.32 g LPSCl, in which 0.16g LSPCl was equally distributed in two sides of the film. All films had a thickness of approximate12 μ m and area of 1.13 cm².



Figure S14. Nyquist plots of 0.32g LPSCl and 100% doped HOS-PFM film across various temperatures. (A) 70 °C, (B) 60 °C, (C) 50 °C, (D) 40 °C, (E) 30 °C, (F) 20 °C, (G) 10 °C, (H) 0 °C, (I) -10°C, and (J) -20°C. The LPSCl had a weight of 0.32 g. The doped HOS-PFM samples were measured with incorporation of 0.32 g LPSCl, which was equally distributed in two sides of the doped HOS-PFM film. The resistances were summarized in Table S3.



Figure S15. Nyquist plots of 0.32g LPSCl and 90% doped HOS-PFM film across various temperatures. (A) 70 °C, (B) 60 °C, (C) 50 °C, (D) 40 °C, (E) 30 °C, (F) 20 °C, (G) 10 °C, (H) 0 °C, (I) -10°C, and (J) -20°C. The LPSCl had a weight of 0.32 g. The 90% doped HOS-PFM samples were measured with incorporation of 0.32 g LPSCl, which was equally distributed in two sides of the doped HOS-PFM film. The resistances were summarized in Table S3.



Figure S16. Nyquist plots of 0.2g LPSCl and doped HOS-PFM film across various temperatures. (A) 70 °C, (B) 60 °C, (C) 50 °C, (D) 40 °C, (E) 30 °C, (F) 20 °C, (G) 10 °C, (H) 0 °C, (I) -10 °C, and (J) -20 °C. The LPSCl had a weight of 0.2 g. The doped HOS-PFM samples were measured with incorporation of 0.2 g LPSCl, which was equally distributed in two sides of the doped HOS-PFM film. The resistances were summarized in Table S4.



Figure S17. Demonstration of sample preparation for XRD characterization. (A) Removing top PFM and alkali metal. (B) Removing the bottom copper substrate. The alkali metal layers were thick and blocked the X-ray peneration. Therefore, the goal of this sample preparation procedure was to maximize the exposure of Sn-based electrode material for effective X-ray characterization, which could detect any remaining crystalline Sn particles. The objective of this XRD experiment was to examine the changes in Sn particle crystallinity before and after compression of Li metal. It was expected that the peaks of copper would not be observed when using method 2 for sample preparation.



Figure S18. XRD patterns of Sn(PFM) and Sn(HOS-PFM) single-layer composite electrodes before and after compressing Li metal.



Figure S19. Cross-sectional SEM images of Sn(PFM) single layer electrodes (A) before and (B) after compressing Li metal. Those Sn particles were isolated from each other in the pristine Sn(PFM) single layer electrodes, with the gaps between the Sn particles filled with PFM polymers. After one-day Li metal compression, only the partial Sn particles near the contact surface underwent volume expansion, suggesting that the reactions were confined to the contact surface area. This phenomenon suggested that PFM polymer featured poor capability to transport Li⁺ ions.



Figure S20. Cross-sectional SEM images of Sn(HOS-PFM) single layer electrodes (A) before and (B) after compressing Li metal. Those Sn particles were isolated from each other in the pristine Sn(HOS-PFM) single layer electrodes, with the gaps between the Sn particles filled with HOS-PFM polymers. After compression of Li metal, the Sn particles within the electrodes experienced significant volume expansion and resulted in significant morphological changes. This indicated that Li⁺ ions could travel through the gaps filled with HOS-PFM polymers. We used the 20 μ m lithium coating on a PEI film (Applied Materials) for this experiment. There are two reasons causing no apparent sign of lithium metal that was pressed against the polymer. One is that when we remove the PEI film from the samples prior ion milling, some lithium metal may be detached from the sample. Second, the majority of lithium metal reacted with Sn and HOS-PFM, resulting in a reduced thickness.



Figure S21. XRD patterns of original PFM/Silicon and HOS-PFM/Silicon DLEs and their corresponding phase after compressing Li metal. Si particles feature two major peak positions at 28.4° and 47.3°. In addition, the intensities of these peaks are relatively weaker compared to those of Sn. Consequently, this is one of the reasons why Si was not selected for the experimental characterization. After compressing Li metal, the silicon XRD patterns disappeared in the Si/HOS-PFM electrodes but remained in the Si/PFM electrodes. These results are consistent with those observed in the Sn/PFM and Sn/HOS-PFM electrodes, suggesting that Li⁺ ions can diffuse through the HOS-PFM polymer but not through the PFM polymer.



Figure S22. Crystalline-to-amorphous phase transformation of Sn nanoparticles after compressing Na metal and K metal. (A) XRD patterns of original PFM/Sn and HOS-PFM/Sn DLEs and their corresponding phase after compressing Na metal. (B) XRD patterns of original PFM/Sn and HOS-PFM/Sn DLEs and their corresponding XRD features after compressing K metal.



Figure S23. XRD patterns of HOS-PFM/Sn DLEs and their corresponding phase after compressing Na metal. The theoretical XRD patterns of $Na_{15}Sn_4$ and NaOH are included to analyze the new small peaks that appeared after compressing Na metal. These sodium peaks closely match the characteristic peaks of $Na_{15}Sn_4$,²⁰ which are products after sodium ions traversed the HOS-FPM and reacted with Sn particles. In addition, these airtight samples are not perfectly sealed. Thus, air leakage can cause sodium to react with moisture, resulting in the formation of NaOH. The observed XRD peaks at 38.3° and between 53° and 56° closely match the theoretical diffraction peaks of NaOH.



Figure S24. (A) XRD patterns of pure potassium metal, original HOS-PFM/Sn DLEs and two samples after compressing K metal. The XRD patterns of pure potassium metal (dimensions: 1 cm \times 1 cm) exhibit low intensity. Therefore, the detection of potassium XRD peaks in potassium HOS-PFM/Sn samples is challenging due to the small amount of residual potassium present. Additionally, potential air leakage from the airtight sample holder may lead to the reaction of potassium with air or moisture, further diminishing the intensity of their XRD patterns. Consequently, potassium diffraction peaks were not detected in any of the potassium PFM/Sn and potassium HOS-PFM/Sn samples. (B) Bucker airtight sample holder (Model: A100B33). (C) Bruker D2 Phaser Diffractometer.



Figure S25. Cross-sectional FIB-SEM images of original HOS-PFM/Sn DLEs at different length scale of (A) 20 μ m, (B) 10 μ m, (C) 5 μ m, and (D) 2 μ m.



Figure S26. Cross-sectional FIB-SEM images of HOS-PFM/Sn DLEs after compressing Li metal at different length scales of (A) 20 μ m, (B) 10 μ m, (C) 5 μ m, and (D) 2 μ m.



Figure S27. Cross-sectional SEM images of PFM/Sn DLE (A) before and (B) after compressing Li metal. The negligible volumetric changes of Sn nanoparticles indicated that the PFM polymer possessed limited capability to facilitate Li⁺ ion transport.



Figure S28. Morphological changes in cross-sectional profile of HOS-PFM/Sn DLEs: (A) before and (B) after compression of Li metal. The volumetric expansion of Sn nanoparticles after compressing Li metal demonstrated that HOS-PFM polymer featured the ability to facilitate Li⁺ ions transport.



Figure S29. (A) Schematics showing the procedure to prepare lithium PVDF/Sn or lithium PEO/Sn double layer electrodes. (B) XRD patterns of original electrodes, lithium PFM/Sn, lithium PEO/Sn, and lithium PVDF/Sn. All the double layer electrodes shared a same bottom layer, which contained approximate 60 wt% Sn and 40 wt% HOS-PFM. Therefore, the XRD patterns of original electrodes are similar. (C and D) FIB-SEM cross-sectional image of (C) lithium PEO/Sn and (D) lithium PVDF/Sn. After compressing lithium metal for three days, both PVDF/Sn and PEO/Sn DLEs preserved the XRD diffraction peaks of Sn particles at 30.6°, 32.0°, 43.9°, and 44.9°. In addition, after the compression of lithium metal, the cross-sectional profiles of PEO/Sn and PVDF/Sn measured by FIB-SEM showed that Sn particles averaged between 300 nm and 500 nm, similar to the particle sizes in the pristine electrodes. These results are expected due to the required conditions for lithium ions to react with Sn particles in this experimental setup. First, during the compression of Li metal, a redox reaction between the Li metal and the polymers to reach the Sn particles and initiate reactions. Neither PVDF nor PEO can initiate a redox reaction with lithium metal under these conditions. Therefore, the Sn particles within PVDF/Sn or PEO/Sn electrodes

retained their XRD diffraction peak patterns and maintained similar particle sizes after lithium metal compression.



Figure S30. (A, B) Surface morphology and (C, D) Cross-sectional SEM images of pristine Si/PVDF/PEO/Carbon black electrodes with mass loading around 0.95 mg/cm² at different scales, measured using FIB-SEM.



Figure S31 (A, B) Surface morphology and (C, D) Cross-sectional SEM images of pristine Si/HOS-PFM electrodes with mass loading around 1.05 mg/cm² at different scales, measured using FIB-SEM.



Figure S32. (A) Linear sweep voltammetry measurements of steel electrodes, free-standing HOS-PFM, and free-standing PFM polymers from the open-circuit potential to 0 V at a scan rate of 0.2 mV/s. (B-D) Cyclic voltammetry of steel electrodes, free-standing HOS-PFM, and free-standing PFM polymers between 0 V and 5 V for (B) the first cycle, (C) the second cycle, and (D) the fifth cycle. Lithium metal and LPSCl were used as the counter electrodes and solid electrolytes, respectively, in these experiments. The LSV and CV results indicated the presence of small peaks between 0 and 2.5 V for both PFM and HOS-PFM, which overlapped with the peaks of the steel electrodes at the same potential positions. The diameter of these free-standing PFM or HOS-PFM polymer film disks is 11 mm. The inner diameter of our solid-state cells is approximately 12 mm, slightly larger than the PFM or HOS-PFM polymer film disks. Therefore, when measuring the free-standing PFM or HOS-PFM polymer films, a small area of the LPSCl solid electrolyte can come into contact with the steel electrodes. Therefore, the small peaks observed for PFM and HOS-PFM, which overlapped with the steel electrodes at the same potential positions, are attributed to the steel electrodes. Additionally, the current density values of the steel electrode are significantly higher than those of PFM and HOS-PFM. Thus, PFM and HOS-PFM exhibited a broad ESW ranging from 0 V to 5 V.



Figure S33. (A) Linear sweep voltammetry measurements of copper (Cu) disk electrodes, HOS-PFM coated on Cu (HOS-PFM/Cu), and PFM coated on Cu (PFM/Cu) from the open-circuit potential to 0 V at a scan rate of 0.2 mV/s. (B-D) Cyclic voltammetry of Cu electrodes, HOS-PFM/Cu, and PFM/Cu electrodes between 0 V and 5 V for (B) the first cycle, (C) the second cycle, and (D) the fifth cycle. Lithium metal and LPSCl were used as the counter electrodes and solid electrolytes, respectively, in these experiments. These results indicate that the LPSCl solid electrolyte underwent side reactions with the copper electrodes. Both PFM and HOS-PFM featured a few small peaks that overlapped with the peak positions of the Cu disk. In this experiment, the PFM and HOS-PFM polymers were coated onto a 16 μ m thick copper foil, which was then cut into disks with a diameter of 11 mm using an electrode cutter. The inner diameter of our solid-state cells is approximately 12 mm, which is slightly larger than the PFM/Cu and HOS-PFM/Cu electrodes. Therefore, the LPSCl solid electrolytes can come into contact with the sides or edges of the copper within the PFM/Cu or HOS-PFM/Cu electrodes, leading to these side reactions and exhibited the similar peak locations. In addition, these CV results show the broad electrochemical stability window of PFM and HOS-PFM.



Figure S34. (A) SEI formation cycles for NMC811||Si/HOS-PFM full cells cycled at 0.05 C under 30 °C. (B) SEI formation cycles for NMC811|| Si/HOS-PFM full cells cycled at 0.05 C under 30 °C.



Figure S35. Battery performance of Li||LPSCl||Si-HOS PFM half cells at room temperature and a 0.2 C rate. (A) Voltage profiles. (B) Specific capacity and Coulombic efficiency of Li||LPSCl||Si-HOS-PFM. These anode electrodes have a diameter of 12 mm. The specific capacity is calculated based on the total weight of Si and HOS-PFM polymers. The experimental specific capacity is lower compared to that of pure Si due to the dilution effect of the HOS-PFM polymer.



Figure S36. (A) Surface and (B, C) Cross-sectional SEM images of Si/HOS-PFM electrodes, with an average electrode thickness of approximately 1.2 μ m. Cycling performance of NMC811||Si/HOS-PFM all-solid-state full cell at a cycling rate of 0.2C at room temperature. (D) Voltage profiles. (E) Galvanostatic cycling results over 100 cycles. These anode electrodes have a diameter of 12 mm. The specific discharge capacity is calculated based on the total weight of Si and HOS-PFM polymers. The experimental specific capacity is lower compared to that of pure Si due to the dilution effect of the HOS-PFM polymer.



Figure S37. (A, B) Cross-sectional SEM images of pristine Si/HOS-PFM electrodes on 4.5 μ m copper foil. (C, D) Cross-sectional SEM images of Si/HOS-PFM electrodes after undergoing 25 cycles, in combination with an NMC811 cathode, at an N/P ratio of 1. These cross-sectional FIB-SEM images indicate that electrochemical cycling can lead to cracks within the Si/HOS-PFM, which is one of reasons for capacity fading.



Figure S38. Cell voltage versus specific capacity for NMC811 || lithium solid-state batteries. This result suggests that the NMC811 material can reach approximately 120 mAh/g when charged to 4.0 V in the first cycle.



Figure S39. Cathode mass loading test for NMC811||Si/HOS-PFM full cells. (A) Voltage profile for 20 mg cathode materials (N/P ratio ≈ 1.3) (B) Voltage profile for 24.6 mg cathode material (N/P ratio ≈ 1.06). The anodes used in these tests are the thick Si/HOS-PFM electrodes with a total mass loading of approximately 1 mg/cm² or a thickness of approximately 4 to 5 µm. Based on these results, an N/P ratio of approximately 1.4 was used for the full cell test for the thick Si/HOS-PFM electrodes and the thick Si/PVDF/PEO/carbon black electrodes.



Figure S40. Capacity retention of NMC811||Si/HOS-PFM all-solid-state full cells following five cycles with upper voltage limits of (A) 4.0 V, (B) 4.2V, and (C) 4.3 V.



Figure S41. Capacity retention of NMC811||Si/HOS-PFM all-solid-state full cells following five cycles with upper voltage limits of (A) 4.4 V and (B) 4.5 V.

Supplemental Table

Table S1. Elemental analysis results of the HOS-PFM sample (3 mg) at different lithiation and delithiation conditions. The delithiated (2.5V) sample refers to the HOS-PFM that was first discharged to 0V and then charged to 2.5 V.

| Voltage | Li 670.784 | Li 610.362 | P 213.617 | P 214.914 |
|---------------------------------|--------------|--------------|--------------|--------------|
| Open Circuit Potential (OCV) | Not detected | Not detected | Not detected | Not detected |
| 0V | 280 µg | 283 µg | Not detected | Not detected |
| 0.01V | 217 µg | 217 µg | Not detected | Not detected |
| 0.1V | 48.1 μg | 39.7 μg | Not detected | Not detected |
| 0.2V | 1.59 μg | 1.94 μg | Not detected | Not detected |
| 0.5V | Not detected | Not detected | Not detected | Not detected |
| 1V | Not detected | Not detected | Not detected | Not detected |
| Delithiated (2.5V) | 111 µg | 104 µg | Not detected | Not detected |

| Voltage | C/ Li Ratio (mol/mol) |
|--------------------|-----------------------|
| OCV | Not detected |
| 0 V | 3.12:1 |
| 0.01 V | 4.02:1 |
| 0.1 V | 20.1:1 |
| 0.2 V | 498.7:1 |
| 0.5 V | Not detected |
| 1 V | Not detected |
| Delithiated (2.5V) | 10.8:1 |

Table S2. The carbon/lithium (C/Li) ratio of the HOS-PFM sample (3 mg) at different lithiation and delithiation conditions.

| | LPSC1 | 90% Li ⁺ /HOS-PFM | 100% Li ⁺ /HOS-PFM |
|-------------|---------------------|---------------------------------|---------------------------------|
| Temperature | $R_{LPSCl}(\Omega)$ | $R_{LPSCl + HOS - PFM(\Omega)}$ | $R_{LPSCl + HOS - PFM(\Omega)}$ |
| (°C) | (0.32g LPSCl) | (0.32g LPSCl) | (0.32g LPSCl) |
| | | Thickness: 12µm | Thickness: 12µm |
| 70 | 14.4 ± 0.16 | 16.29 ± 0.33 | 17.72 ± 0.31 |
| 60 | 20.32 ± 0.20 | 22.71 ± 0.38 | 22.82 ± 0.32 |
| 50 | 29.93 ± 0.25 | 33.67 ± 0.52 | 33.48 ± 0.38 |
| 40 | 45.16 ± 0.28 | 47.9 ± 0.42 | 48.85 ± 0.40 |
| 30 | 70.76 ± 0.31 | 74.7 ± 0.59 | 75.98 ± 0.47 |
| 20 | 115.1 ± 0.36 | 121.2 ± 0.90 | 122.9 ± 0.63 |
| 10 | 194.4 ± 0.56 | 205.5 ± 1.73 | 207 ± 1.09 |
| 0 | 343.2 ± 1.59 | 367.7 ± 4.58 | 366.9 ± 3.08 |
| -10 | 616.5 ± 2.17 | 634.7 ± 6.87 | 640.5 ± 3.01 |
| -20 | 1167 ± 2.17 | 1197 ± 12.99 | 1223 ± 10.35 |

Table S3. Summary of resistances collected in EIS experiments. All these samples contained 0.32g LPSCl. The surface area of HOS-PFM was 1.13 cm², and its thickness was around 12 μ m.

| Temperature | LPSC1 $R_{LPSCl}(\Omega)$ | 100% Li ⁺ /HOS-PFM $R_{LPSCl + HOS - PFM(\Omega)}$ |
|-------------|------------------------------|--|
| (°C) | (0.2g LPSCl) | (0.2g LPSCl) Thickness: 12 μm |
| 70 | 9.17 ± 0.13 | 11.06 ± 0.82 |
| 60 | 12.92 ± 0.18 | 14.65 ± 0.35 |
| 50 | 18.67 ± 0.12 | 21.81 ± 0.48 |
| 40 | 28.13 ± 0.14 | 32.92 ± 0.64 |
| 30 | 43.92 ± 0.24 | 47.81 ± 0.59 |
| 20 | 71.05 ± 71.03 | 77.46 ± 0.80 |
| 10 | 118.3 ± 0.29 | 131.1 ± 1.20 |
| 0 | 208.6 ± 0.30 | 232.2 ± 2.34 |
| -10 | 382.9 ± 0.83 | 403.5 ± 3.13 |
| -20 | 728.9 ± 0.82 | 761.5 ± 7.32 |

Table S4. Summary of resistances collected in EIS experiments. All these samples contained 0.20g LPSCl. The surface area of HOS-PFM was 1.13 cm², and its thickness was around 12 μ m.

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