

Supporting Information

Designing ionic conductive elastomers using hydrophobic networks and hydrophilic salt hydrates with improved stability in air

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Experimental Section

Materials. The monomer, ethylene glycol methyl ether acrylate (MEA), the lithium salts perchlorate trihydrate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$), lithium bis(trifluoromethane)sulfonimide (LiTFSI) and lithium perchlorate (LiClO_4), were purchased from Shanghai Aladdin. The monomer, isobornyl acrylate (IBA) were purchased from Shanghai Macklin. The photoinitiator benzophenone was obtained from Nantong Feiyu. All the chemicals were used as received without further purification.

Preparation of stable ionic conductive elastomers (s-ICEs). Synthesis of the s-ICEs includes a few steps. Firstly, crystals of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and benzophenone (ultraviolet initiator) were mixed with a proper amount of liquid monomer of MEA. Then the mixture was stirred for 30-60 minutes to dissolve the $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ crystal. Thereafter, the liquid monomer of IBA was added to the mixture, obtaining a transparent precursor solution of the s-ICEs. The molar ratio of IBA to MEA was fixed to be 1:4. In the liquid binary mixture of MEA and IBA, the molar concentration of benzophenone relative to the binary mixtures of monomers was fixed at 0.0052 M;

the molar concentration of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ was varied from 0.25 M to 1 M in 0.25 M intervals, to obtain s-ICEs with different electrolyte salt concentrations. Finally, the precursor solution was transferred to release-film-coated glass molds and cured in 7.5 h by ultraviolet light irradiation (365nm) in a nitrogen atmosphere (oxygen content < 0.01 PPM, and water content < 0.01 PPM).

Preparation of ionic conductive elastomers (ICEs) for comparison. Liquid monomers of MEA and IBA were mixed at room temperature. The molar fraction of IBA in the binary mixture is 0.2. LiTFSI or LiClO_4 powder and photo-initiator benzophenone were then dissolved in the mixed liquid, forming a transparent precursor solution. The molar concentration of BP was fixed at 0.0052 M and the molar concentration of LiTFSI and LiClO_4 was fixed at 0.5 M. The mixed precursor solution was then poured into molds consisting of two glass plates that were separated by a 2 mm-thick fluoroelastomer spacer. The polymerization was performed in a nitrogen atmosphere (oxygen content < 0.01 PPM, and water content < 0.01 PPM) under UV light irradiation (365nm). The samples were irradiated for 7.5 h.

Mechanical characterizations. Materials to be tested were cut into dumbbell-shaped samples. The sample dimensions were specified by the JIS-K6251-7 standard, with the gauge length being 12 mm, width 2 mm, and thickness 2 mm. These samples were used in the uniaxial tension tests and cyclic loading-unloading tests. All these tests were conducted on a universal testing machine (Instron 3343) with a 50 N loading cell. A displacement rate of 100 mm/min, which yields a stretch rate of 0.14 s^{-1} , was used in all the tests.

Fracture toughness measurement. To determine the fracture toughness, we prepared two

sets of samples. One set of samples had no pre-crack, whereas the other set of samples was pre-notched. Each tested sample had a width (w_0) of 50 mm and a thickness (t_0) of 2 mm; and the distance between the two clamps was 5 mm. The precut sample was prepared by using a razor blade and had a 25 mm-long single-edge notch. The uncut sample was stretched for the measurement of the force-distance curve. When the two clamps were pulled to a distance of H , the area beneath the force-distance curve gives the work done by the applied force, $U(H)$. In addition, the precut sample was stretched until the notch turned into a running crack. The critical displacement H_c when the pre-notch started propagating was recorded. Then, the fracture toughness of the ionogels was evaluated using the formula $\Gamma = U(H_c)/w_0t_0$.

Measurement of adhesion energy. Samples of s-ICE-0.5 were used for testing, with the dimensions of 50 mm (L) \times 20 mm (W) \times 2 mm (T). By simply attaching s-ICEs to various substrates including VHB, glass, copper, and P(MEA-co-IBA), interfacial adhesion naturally forms between s-ICEs and the substrate materials. As required by the 90-degree peeling test, a 10 mm \times 30 mm polyester film was placed on the s-ICE/substrate interface to introduce a pre-crack at one end of the interface. After being stored under ambient conditions for one night, the prepared samples were tested using a universal testing machine (Instron 3343 with a 50 N load cell) with a 90-degree peeling fixture. All 90-degree peeling tests were performed with a constant peeling speed of 20 mm/min. The plateau value of the force-displacement curves was used to calculate the interfacial toughness: the plateau value divided by the width of the sample (i.e., 20 mm) gives the interfacial toughness (adhesion energy).

Electrical characterizations. A rectangular strip of s-ICEs (dimensions: 40 mm × 5mm × 2mm) was prepared using a cutter. The bulk resistance of the samples was measured using a desktop multimeter (Keithley, DAQ 6510). The conductivity of the s-ICEs was then calculated according to $\sigma = L/(AR)$, where L corresponds to the distance between the electrodes, A denotes the cross-sectional area of the sample, and R is the bulk resistance measured by the multimeter.

Characterization of water uptake. Round-shaped samples (diameter: 25 mm; thickness: 2 mm) of the s-ICEs were stored under ambient conditions. Then the weight of the samples were measured for a certain storage time (i.e., every 3.5 h for the first day, 12 h for the second day and 24 h for the following day). The weight change of each sample was monitored for 4 days (96 h) in ambient conditions with varying humidity for 7 days.

Thermal analysis. The DSC measurements were performed using a differential scanning calorimeter (TA Instruments Q200) in air. The temperature was scanned from -90 °C to 100 °C with a heating speed of 20 °C/min.

Computational methods. First, a LiClO₄ molecule and 20 water molecules (4 water molecules in the control model) were added to the simulation box, and the water molecules aggregated into cluster during relaxation stage for 20 ps. Then 56 MEA chains consisting of 192 atoms were used to uniformly encapsulate the water cluster. Then molecular dynamics simulations were carried out using the LAMMPS package at canonical (NVT) ensemble at 300K to study the water behavior as simulation time increases. Visualization was performed through OVITO

software. The OPLS-AA force field was used to model the bonded and non-bonded interactions of the MEA copolymer, the TIP4P/2005 model was used to account for the water interactions. For TIP4P/2005 water model, the bond lengths and bond angles were held fixed using the Shake algorithm to allow for using a time step of 2.0 fs. OPLS-AA parameters and atomic charges were obtained using LigParGen with the 1.14*CM1A-LBCC method. The LiClO₄ parameters were calculated by Patra et al. by density functional theory (DFT). The particle-particle-particle-mesh (PPPM) scheme has been employed for the calculation of the long-range electrostatic forces.

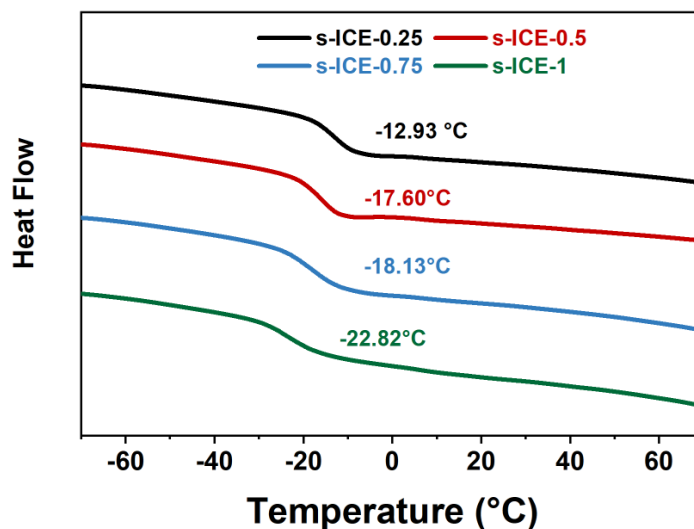


Figure S1. DSC scans of the synthesized s-ICEs with different hydrated salt concentrations.

The Tg of the s-ICEs decreased as the increased concentration of hydrated lithium salt, illustrating that the salt is dissolved in the polymer networks.

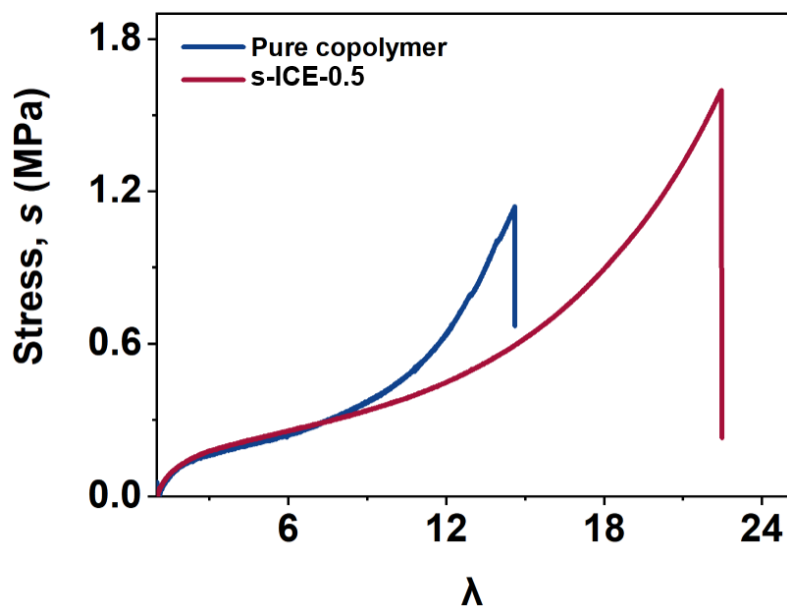


Figure S2. The comparison between P(MEA-*co*-IBA) copolymer and the s-ICE-0.5. The results show that P (MEA-*co*-IBA) copolymer of $F = 0.2$ (F denotes the molar fraction of IBA in the copolymer) exhibits a stretch at break about $\lambda_b = 14$, and the ultralow-water-content

s-ICE-0.5 demonstrates enhanced stretchability ($\lambda_b > 21$) and strength relative to the pure copolymers.

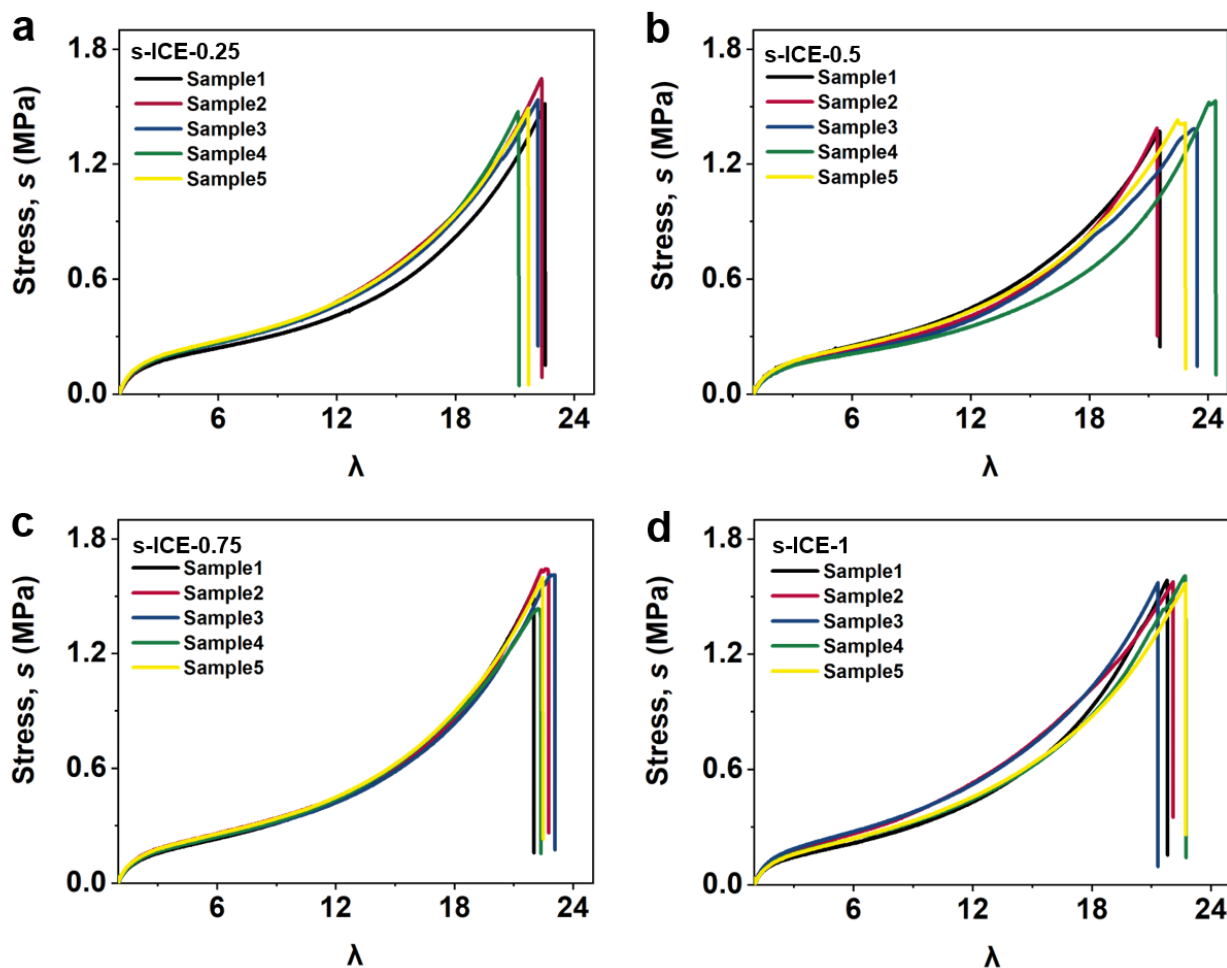


Figure S3. Representative stress-stretch curves of the s-ICEs containing different $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ contents. (a) 0.25 M, (b) 0.5 M, (c) 0.75 M, and (d) 1 M. All s-ICEs exhibit almost identical stress-strain behavior, regardless of the concentration of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$.

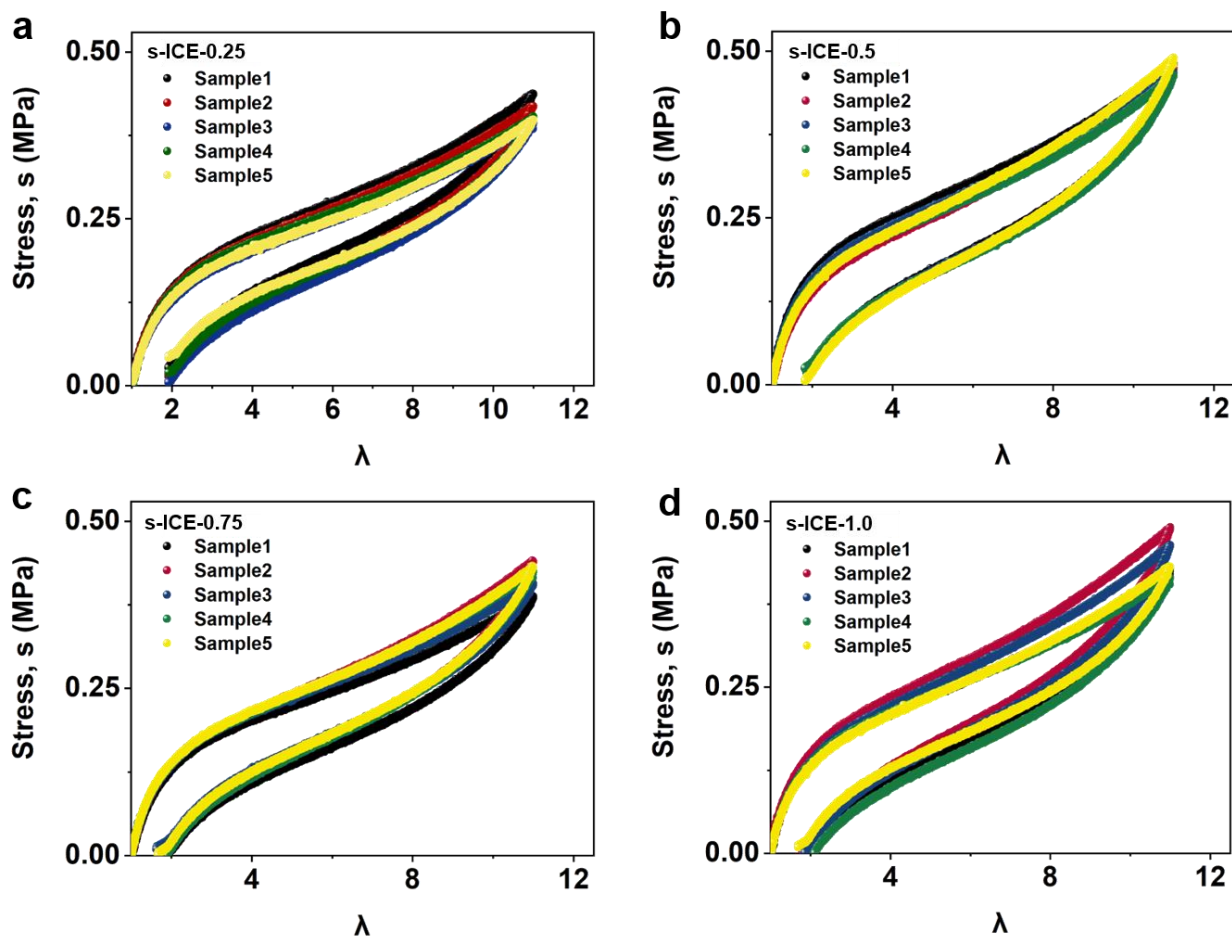


Figure S4. Cyclic loading-unloading stress-stretch curves of the s-ICEs with various $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ concentrations. (a) 0.25 M. (b) 0.5 M. (c) 0.75 M. (d) 1 M. The maximum stretch ratio $\lambda_{max} = 11$.

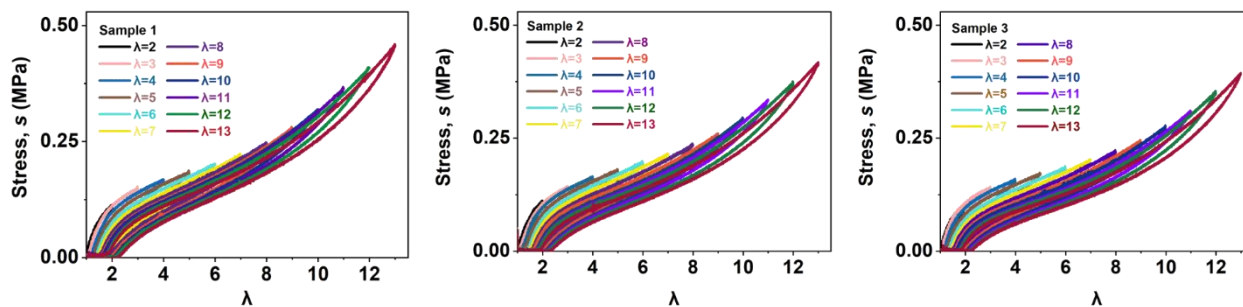


Figure S5. Cyclic loading-unloading stress-stretch curves of three s-ICE-0.5 samples subject to increasing cyclic stretches with λ_{max} increasing from 2 to 13. Note that data of

Sample 1 is also presented in Fig. 3f of the main text.

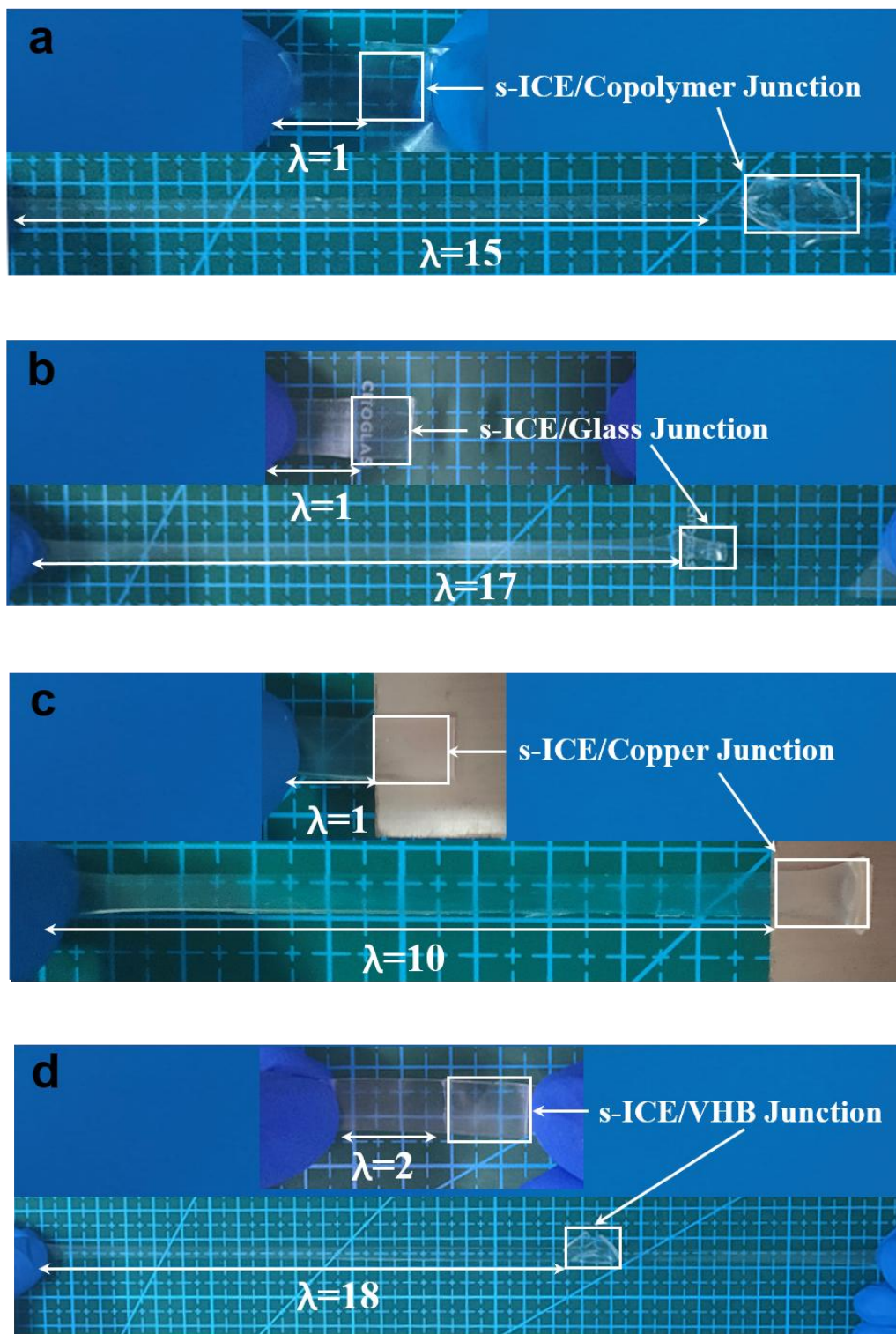


Figure S6. Photographs demonstrating instant and tough adhesion of the s-ICEs to various

materials. The junctions of (a) s-ICE/copolymer P(MEA-*co*-IBA), (b) s-ICE/glass, (c) s-ICE/copper, (d) s-ICE/VHB can sustain stretches larger than 10, without interfacial delamination.

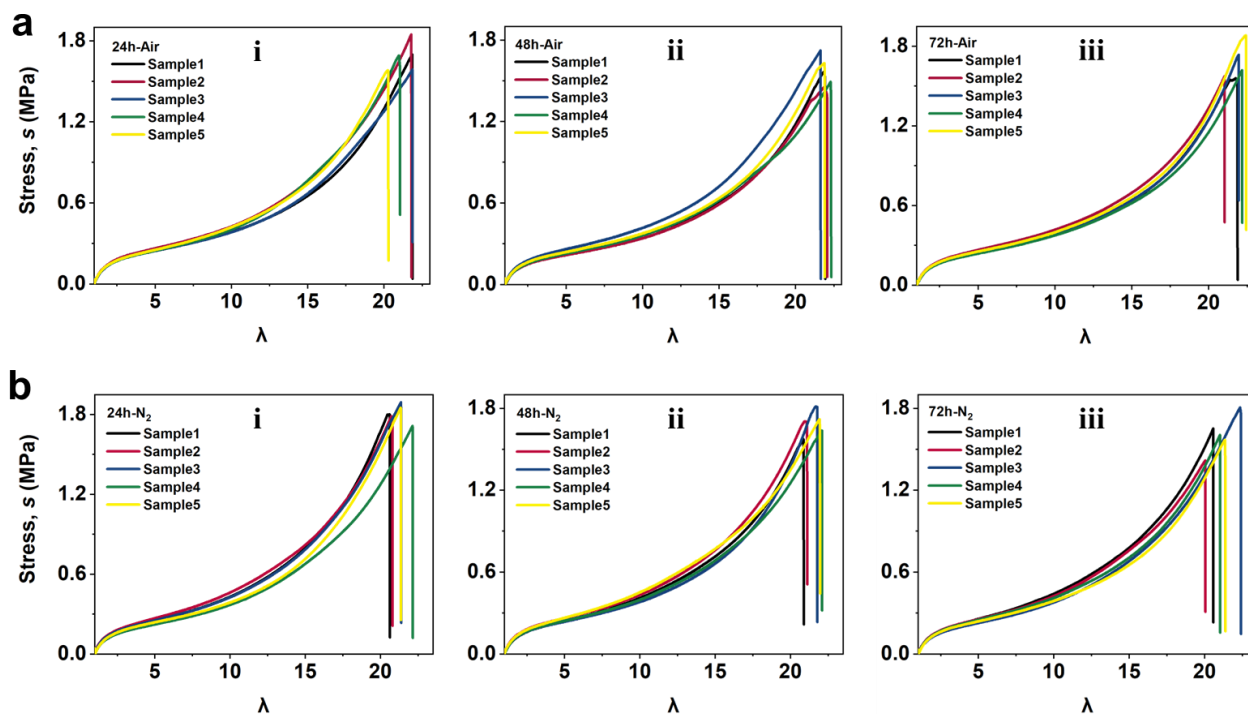


Figure S7. Stress-stretch curves of the s-ICE-0.5 samples stored at ambient and extremely dry conditions. (a) Stress-stretch curves of the s-ICE-0.5 samples exposed to ambient environments. (b) Stress-stretch curves of the nitrogen-stored s-ICE-0.5 samples. The columns i, ii, and iii correspond to the storage time of 24 h, 48 h, 72 h, respectively.

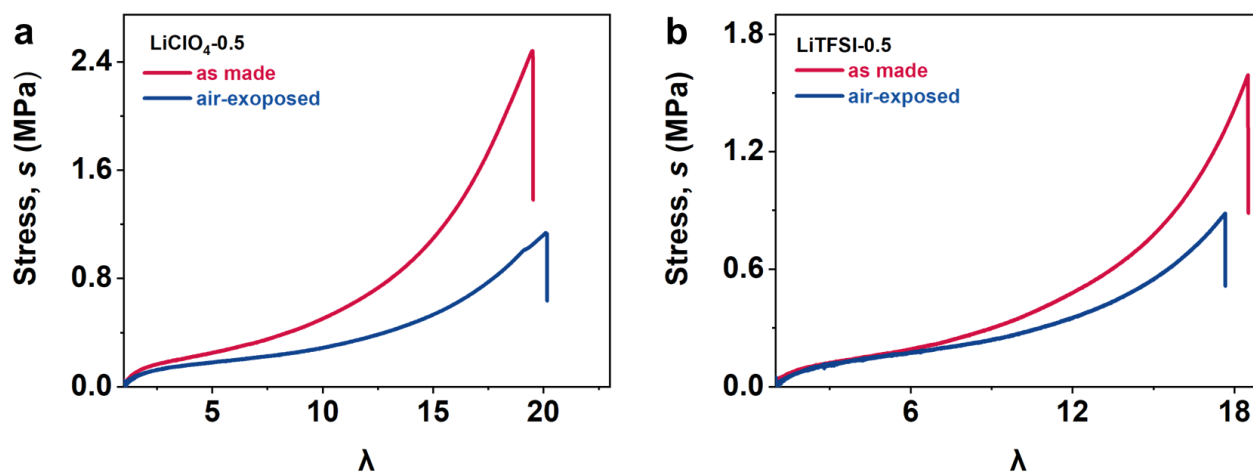


Figure S8. Air aging behavior of liquid-free ICEs. (a) Representative stress-stretch curves of as-made and air-aged liquid-free ICEs, namely, P (MEA-*co*-IBA) copolymer containing 0.5 M LiClO₄. (b) Representative stress-stretch curves of as-made and air-aged liquid-free ICEs, namely, P (MEA-*co*-IBA) copolymer containing 0.5 M LiTFSI. The air-aged samples are stored under ambient conditions for 24 h before testing. Both air-aged samples exhibit decreased stiffness and strength.

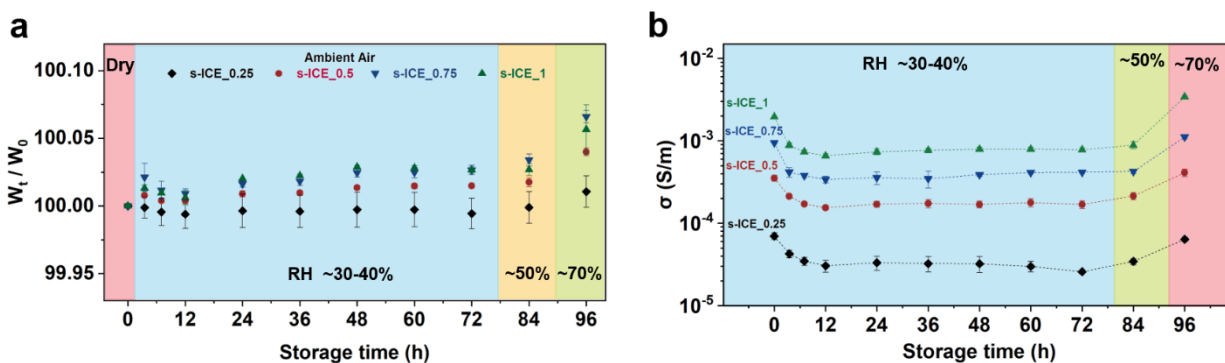


Figure S9. (a) Weight change of air-exposed s-ICEs with different salt concentrations under ambient conditions with RH changing from ~30% to ~70%. (b) Evolution of the conductivity over time under different humidity levels.

Table S1. Composition of <i>s</i>-ICEs synthesized in this work (in volume fractions)			
Sample name	$\phi_{MEA}(\%)$	$\phi_{IBA}(\%)$	$\phi_{Li-Hyd}(\%)$
s-ICE-0.25	69.27%	28.44%	2.28%
s-ICE-0.5	67.735%	27.81%	4.47%
s-ICE-0.75	66.25%	27.20%	6.55%
s-ICE-1.0	64.83%	26.62%	8.55%