

Supporting Information

Experimental Section

Sample preparation

A commercial poly(ethylene carbonate) (PEC, QPAC®25, Empower Materials, USA, $M_w=250,000$), Poly(ethylene oxide) (PEO, Aldrich Co., $M_v=100,000$), and lithium bis-(trifluoromethanesulfonyl) imide (LiTFSI, battery grade, Kanto Chemical Co., Japan) were used as received. The PEC was dissolved in chloroform, and the solution was added to excess methanol. The precipitated PEC was dried in a vacuum oven at 60 °C. The concentration of LiTFSI was set at 5 mol% in PEO-lig CPE and 100 mol% in PEC-lig CPE. The concentration of LiTFSI to PEC and PEO mixtures which means the molar ratio of ethylene carbonate (EC) or ethylene oxide (EO) units to a Li^+ ion were all fixed at 100 and 5 mol%. A Japanese cedar SESC lignin powder was adopted and dried for more than 6 h before use. The PEO or PEC-based CPE specimens were named according to the lignin contents as PEO-LPE 0~1.0% or PEC-LPE 0~1.0%, where the percent represents the lignin wt.%. Fig. S2 shows the preparation process of PEO and PEC-based CPE with SESC lignin. The electrolyte sample was firstly prepared by a simple solution casting method as step (1). Defined amounts of polymer (PEO or PEC), LiTFSI, and various amounts of SESC lignin powder were weighed and stirred using a magnetic stirrer in acetonitrile (99%, Kanto Chemical Co., Japan) at room temperature. The solution was cast onto a plastic petri dish and dried under N_2 at 60 °C for 24 h to remove excess solvent. The dried sample was then introduced into a vacuum oven at 60 °C for 48 h to eliminate all volatile residues. Self-standing flexible films, PEO-LPE and PEC-LPE, were both obtained as pre-mixed solids. The color of the specimens

gradually changed from transparent to light yellow as the lignin content increased. The kneading machine (Imoto Machinery Co. Ltd, Japan) was further utilized to mix vigorously the pre-mixed solid at 55 °C to get a well-dispersed sample in step (2). The obtained solids were finally hot-pressed under 15 MPa for 15 min at 60 °C and cold-pressed for 15 min to mold into a fine film sample. The hot drying, mixing, and pressing were all carried out in a dry Ar-filled glovebox. The obtained CPE film exhibited a much more uniform surface than the pre-mixed film A shown in Fig. S2. The images of Fig. S5 also present the process of bending the obtained film from flattening to bending twice and then restoring to deformation which demonstrates the flexibility and applicability in all-solid-state batteries.

Characterization

The ionic conductivity measurement of all electrolyte samples was carried out using the electrochemical impedance spectroscopy (EIS) equipped with a potentiostat/galvanostat SP-150 (Bio-Logic Instrument, France) in a glove box filled with dry Ar gas. The sample cells were kept consisting of combining two stainless steel blocking electrodes and sandwiched the electrolyte with Teflon® spacer. Before measurement, the sample cells were under constant temperature at 50 °C for 6 h. All cells were measured from 80 to 40 °C in the frequency range 100 Hz to 1 MHz and were held constant for at least 20 min at 10 °C intervals, after which an impedance measurement was carried out. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a DSC7020 (Hitachi High-Tech Co., Japan) and a TG/DTA7200 (Hitachi High-Tech Co., Japan) for measurements of thermal properties for all electrolytes. The second heating of DSC was from -150 °C

to 150 °C at a scan rate of 10 °C min⁻¹. The TGA samples were heated from room temperature to 500 °C at a scan rate of 10 °C min⁻¹. All DSC and TGA samples were made in a dry Ar-filled globe box using Al pans and measured under dry N₂ flow. The 5% decomposition loss temperature (T_{d5}) was determined as an index of heat tolerance on the composites. All those measurements were taken on at least three samples for each test. Fourier transfer-infrared (FT-IR) spectra of all samples were recorded on an FT-IR spectrometer (FT/IR-4100, JASCO Co.) using an ATR unit (ZnSe lens) from 700 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ under dry N₂ flow. The surface morphology of composite electrolytes was observed by the scanning electron microscope (SEM), using a JCM-5700 (JEOL, Japan) operated at 10 kV. Before the SEM measurement, all samples were etched and sputtered by Au using an ion coater (Eiko Engineering, Co., Ltd.) on the surface.

Results and Discussion on Fig. S3

Fig. S3 a shows results of thermal measurements for PEO- and PEC-based electrolytes with different lignin contents. All PEO-lig CPE has a large peak at around 50 °C because of the semi-crystalline nature of neat PEO. These large peaks are due to the endothermic change of the melting peculiar to the PEO crystal phase with strong crystallinity, and the endothermic peak corresponding to the melting temperature of 0% PEO-LPE occurs at 50 °C. As an incorporation of lignin increased, the melting temperature was shifted to a lower temperature, and the area under the melting peak also decreased, which suggests a decrease in the degree of crystallinity. The PEO-lig electrolytes have also a clear glass transition which means T_{d5} at -43 °C (0%) and -45 °C (0.5%, 1%), and there were no obvious changes for T_g . As seen in the typical DSC

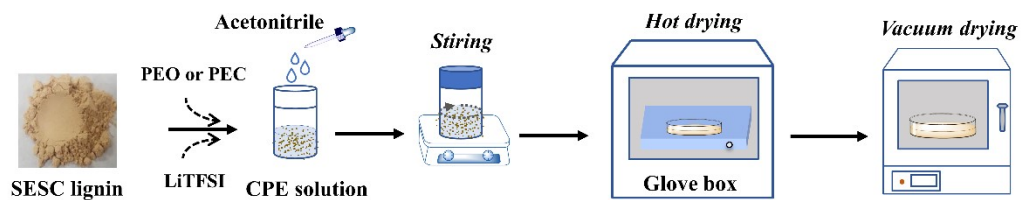
response of amorphous electrolytes in Fig. S3 c, there were no fusion peaks present in the temperature range $-90\sim 90$ °C which contrasts strongly with the PEO system. The absence of melting peaks is taken as evidence of a fully amorphous structure in the PEC system. On the other hand, the PEO-lig CPE has typical decomposition behavior as seen in Fig. S3 b, at which the first term occurs between $100\text{--}350$ °C, it was aroused from the degradation of functional groups, and in the second term between $360\text{--}450$ °C, it was associated with the pyrolytic degradation of PEO backbone. With the addition of lignin, the T_{d5} of PEO-lig CPE increased from the original value of 368 °C to the highest 385 °C for 0.5% . The PEO-lig CPE has a slightly better thermal stability by the addition of a very small amount of lignin and showed T_{d5} as 369 °C for 0.1% , 385 °C for 0.5% , 373 °C for 1% , and 368 °C for 0% with a char yield at 500 °C nearly 9.7% , 11% , 10.3% versus 8% , respectively. Furthermore, the weight loss of PEC-lig CPE is observed above 148 °C that was much higher than room temperature and processing temperature, demonstrating excellent thermal stability as shown in Fig. S3 d. The observation of TGA curves illustrates that there are two processes of the weight loss: one is the initial weight loss occurring in the temperature range from around 160 °C to 300 °C is mainly attributed to the PEC degradation, and the other is the weight loss at $370\text{--}380$ °C which may be aroused from the thermal decomposition reaction of dispersed lignin and TFSI anions. From the above comparative analysis, it is obvious that the addition of lignin expresses more excellent thermal properties than the original SPE, the initial decomposition temperature improved from 148 °C to 166 °C by the addition of 0.1% SESC lignin, thus the heat tolerance was enhanced. Previously, the improved heatproof property of PEC SESC lignin composites has been studied originated from the prevention of alkoxide back-biting due to the antioxidant nature of SESC lignin, as well

as SESC lignin could prevent hydrogen abstraction via the scavenging of oxygen radicals.¹

Reference

- 1 H. Sotome, K. Shikinaka, A. Tsukidate, Y. Tominaga, M. Nakamura and Y. Otsuka, *Polym. Degrad. Stab.*, 2020, **179**, 109273.

1. A simple solution casting method



2. Mechanical mixing and pressing

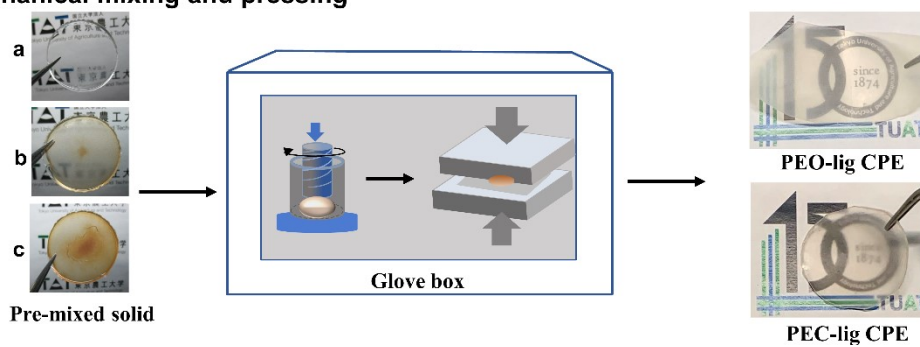
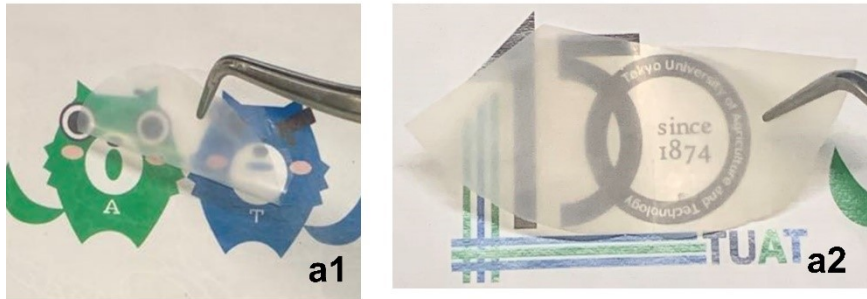


Fig. S1 Preparation process of composite electrolyte sample.

PEO-lig CPE



PEC-lig CPE

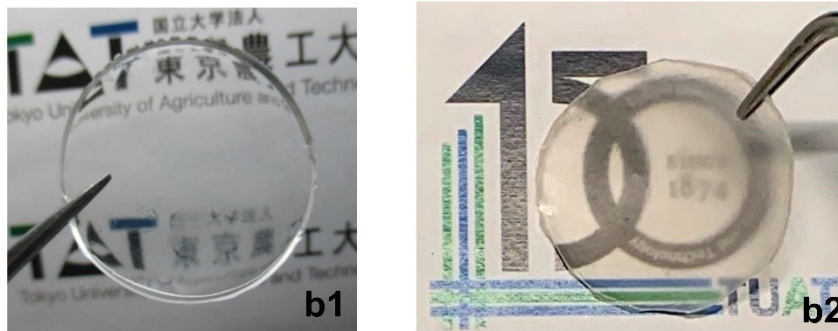


Fig. S2 Photographs of a1: PEO-lig CPE 0%, a2: PEO-lig CPE 0.1%, and b1: PEC-lig CPE 0%, b2: PEC-lig CPE 0.1%.

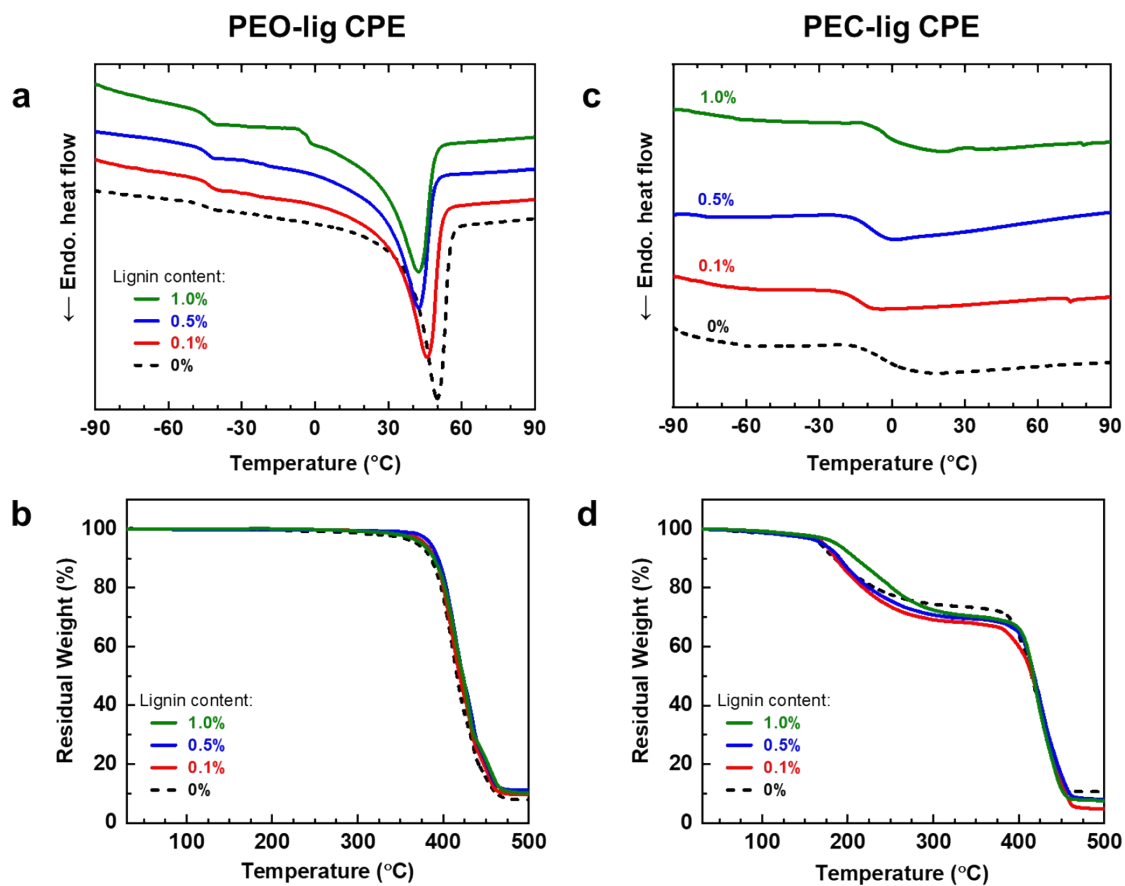


Fig. S3 DSC curves (a, c) and TG curves (b, d) of PEO and PEC-based electrolytes.

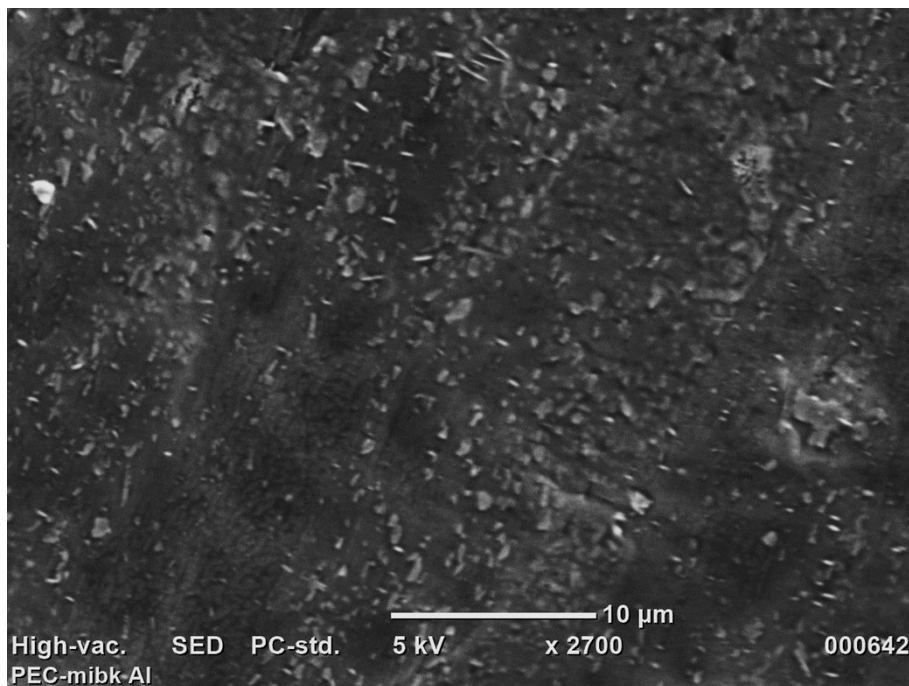


Fig. S4 A SEM image of section surface for PEC-lig CPE 0.1%.

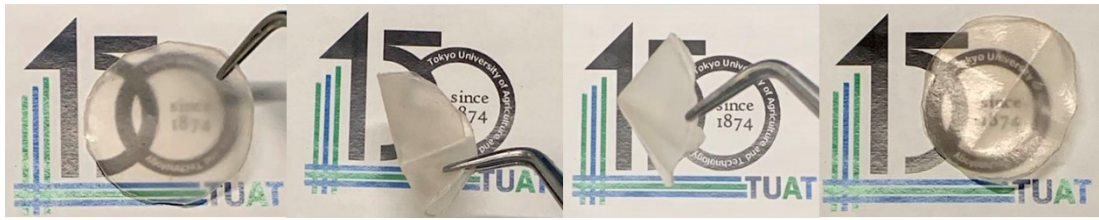


Fig. S5 The surface images of PEC-lig CPE film, from flattened to bent in half to bent again, and finally show the recovery of deformation after bending two times.