

Supplementary Information

A quasi-solid-state rechargeable lithium–oxygen battery based on a gel polymer electrolyte with an ionic liquid

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Preparation of polymer electrolyte

IL–GPE films were prepared by using a solution casting method. P(VdF-HFP) ($M_w = 455,000$, Aldrich) was dissolved in *N*-methyl pyrrolidone (NMP). Then, LiTFSI and PYR₁₄TFSI were added to the P(VdF-HFP)–NMP solution, which was vigorously stirred overnight. The transparent and viscous solution was cast onto a polytetrafluoroethylene (PTFE) mold, followed by drying at 70 °C under vacuum. After removing the residual NMP solvent, a dimensionally stable, flexible, free-standing film composed of P(VdF-HFP), PYR₁₄TFSI, and LiTFSI (1:1:1 by weight) was obtained. All the procedures and the handling of materials were carried out in an argon-filled glove box.

Materials characterization

XRD patterns were recorded with an automated Rigaku diffractometer (2500 D/MAX, Rigaku) using Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation. The measurements were conducted over the scanning angle range of 10–80° at a scan rate of 5° min⁻¹ using a step size of 0.02°. Raman spectra were recorded using a DXR raman spectrometer (Thermo Fisher Scientific). A Nd:YVO₄ laser with a 532 nm line was used as an excitation source, and the resolution was set to 4 cm⁻¹. The morphology and microstructure were examined by SEM (Hitach X-4900). The chemical analysis was conducted using XPS (a Thermo MultiLab 2000 spectrometer with a monochromatic Al K α X-ray source). The ionic conductivity (σ) was determined by ac-impedance spectroscopy. The electrolyte film was sandwiched between two blocking electrodes of stainless steel. The impedance spectra were measured from 10⁶ to 0.1 Hz with an ac signal of 5 mV amplitude using an electrochemical impedance spectroscopy (Zhaner Zennium).

Electrochemical experiments

A Li–O₂ cell was constructed based on a symmetrical design of the IL–GPE and the cathode with respect to the Li anode as illustrated in Fig. 2(a), *i.e.*, cathode/IL–GPE/Li anode/IL–GPE/cathode. The sizes of the cathode, IL–GPE and Li anode were 3.6 × 3.6 cm², 4.0 × 4.0 cm², and 3.8 × 3.8 cm², respectively. The cathode was prepared by casting a mixture of Denka black and a binder (Kynar 2801) (80:20 in wt.%) in NMP on carbon paper, followed by vacuum drying at 70 °C for 24 h. The electrode loading was 1.1 mg cm⁻². Galvanostatic discharge–charge tests were performed at a current density of 0.25 mA cm⁻² (based on the cathode area) using a Maccor Series 4000, and cycling experiments were conducted with a 10 mAh capacity. **Unless otherwise noted, all of the electrochemical experiments were conducted at 50 °C by supplying a high-purity O₂ (99.99%) gas.**

Ionic conductivity of P(VdF-HFP)–LiTFSI and IL–GPE

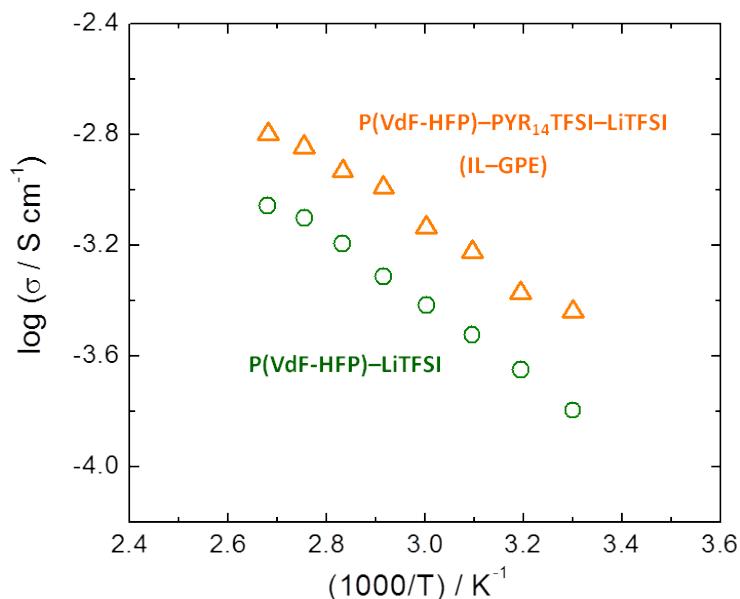


Fig. S1 Dependence of the ionic conductivity (σ) on the temperature determined from the P(VdF-HFP)–LiTFSI composite and IL–GPE.

Table S1 Ionic conductivity (σ) of the P(VdF-HFP)–LiTFSI composite and IL–GPE.

Specimen	$\sigma / \text{S cm}^{-1}$	
	30 °C	50 °C
P(VdF-HFP)–LiTFSI	1.6×10^{-4}	3.0×10^{-4}
IL–GPE	3.6×10^{-4}	5.9×10^{-4}

Comparative studies of IL-GPE and conventional liquid electrolyte

Fig. S2 presents typical Nyquist plots of the ac-impedance spectra for the symmetric cells (Li/electrolyte/Li) measured at various storage times. **The experiments were conducted at 30 °C.** In general, the magnitude of the first semi-circle in the high-frequency region represents the film resistance (R_f) between Li and electrolyte.¹ The value of R_f for the conventional liquid electrolyte used for Li-O₂ batteries (1 M LiTFSI in TEGDME impregnated into a glass fiber separator) continuously increases with time. On the other hand, R_f for the IL-GPE is considerably lower and remains nearly invariant with time. This means that the IL-GPE leads to the formation of more conductive and stable SEI compared with the liquid electrolyte.

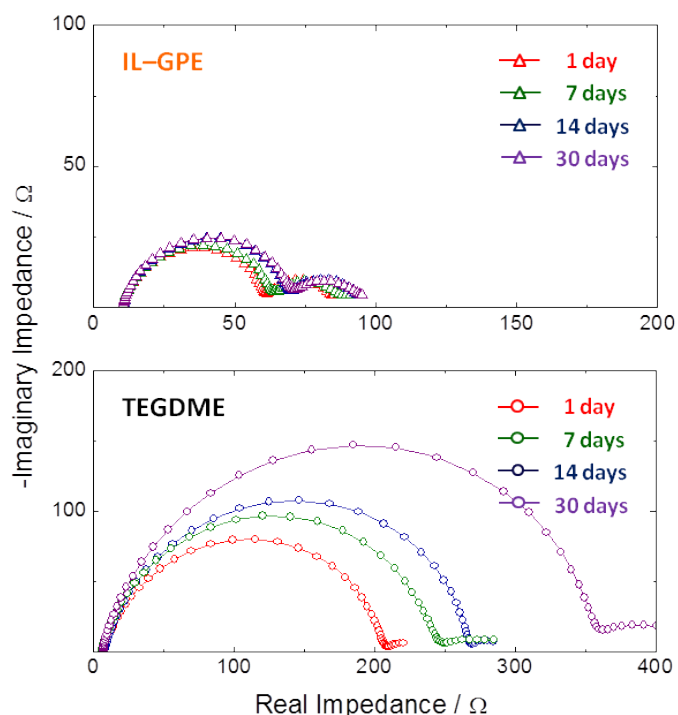


Fig. S2 Ac-impedance spectra of the Li/electrolyte/Li cells with different electrolytes as a function of storage time.

In addition, coin cells composed of Li/electrolyte/cathode/PTFE film were fabricated and stored in a constant humidity chamber (R.H. = 30 %, Temp. = 30 °C) for various times. Fig. S3 shows that the color of the Li anode in the liquid electrolyte turned abruptly from silver to black after 30 min. The anode in the IL-GPE, by contrast, remained almost stable for 60 min. This indicates that the IL-GPE provides a more effective barrier to water transport toward the Li anode.

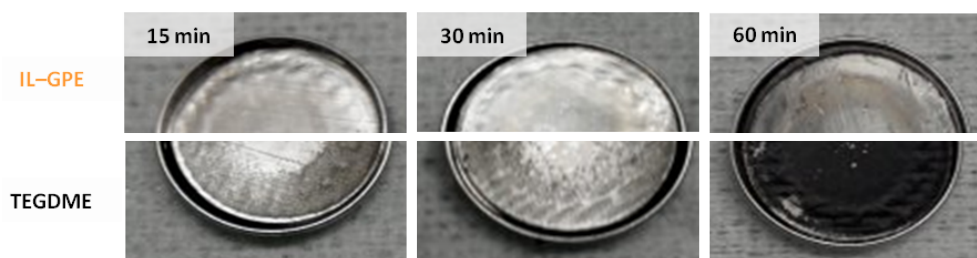
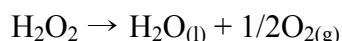
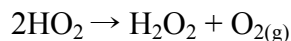
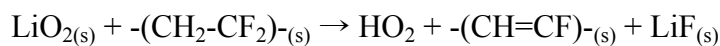


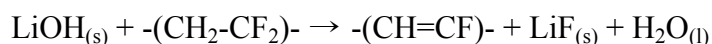
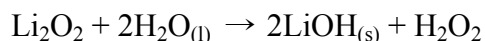
Fig. S3 Photographs of the Li metal anodes taken out of the full cells (Li/electrolyte/cathode/PTFE film) with different electrolytes after storage for various times inside a constant humidity chamber (R.H. = 30 % and Temp. = 30 °C).

Dehydrofluorination reaction and formation of by-products

- (a) P(VdF) undergoes dehydrofluorination due to attack by superoxide radicals, and as a result, by-products such as LiF and H₂O are formed:²



- (b) The discharge product (Li₂O₂) reacts with H₂O to produce LiOH, which can promote further dehydrofluorination:^{2,3}



References

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3. R. Crowe and J. P. S. Badyal, *J. Chem. Soc., Chem. Commun.*, 1991, 958.