

Electronic Supplementary Information

High transference number enabled by sulfated zirconia superacid for lithium metal batteries with carbonate electrolytes

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Experimental Section

Synthesis of sulfated ZrO₂ superacid and ZrO₂ particles. 70 wt% zirconium *n*-propoxide (Sigma-Aldrich) in 20 mL of propanol (Sigma-Aldrich) was first mixed with 62.2 mL of anhydrous *n*-propanol (99.7% purity, Sigma-Aldrich). To this solution, 1.10 mL of sulfuric acid (99.999% purity, Sigma-Aldrich) and 14.81 mL of distilled water were added sequentially for 10 min at 50 °C until the vortex disappeared. The solution was then aged at the same temperature for another hour. Next, 100 mL of ethanol ($\geq 99.5\%$, Sigma-Aldrich) was added and the solution was centrifuged at 6000 rpm for 10 min to switch the solvent from water to alcohol to minimize particle growth during drying and calcination. This washing *via* centrifugation was repeated three times. The produced powder was dried at 80 °C for 12 hours to remove residual alcohol, followed by calcination at 600 °C for 3 hours to produce the designated crystal structure. For S-ZrO₂ with 2 and 6 wt% sulfate, the same procedure was adopted except that 0.28 and 0.55 mL of sulfuric acid was added, respectively. The bare ZrO₂ particles were synthesized based on the same procedure as S-ZrO₂ particles except that sulfuric acid was not added.

Coating of S-ZrO₂ and ZrO₂ particles on the separator. By benchmarking the existing coating process of ceramic particles onto the PE or PP separator, the PE separator (16 μm thick, Toray) was coated with the synthesized S-ZrO₂ and ZrO₂ particles by using the doctor blading technique with 33 wt% S-ZrO₂ or ZrO₂ solution. For this process, PVdF-HFP binder (Kynar2801, Arkema, MW=370,000) was used. The areal loading was 1.0 mg cm⁻² in both cases. For the thermal shrinkage test, separators with dimensions of 4.0×4.0 cm² were left in an oven at 125 °C for 1 hour and the dimensional changes were measured.

Electrochemical analysis. The symmetric cell tests were conducted by sandwiching various polyethylene separators between two sheets of Li foil (200 μm thick, Honjo Metal Co., Ltd.) and galvanostatically cycled at 3.0 or 6.0 mA cm⁻². Each charge or discharge was continued for 1 hour in the case of 3.0 mA cm⁻² and 0.5 hour in the case of 6.0 mA cm⁻². The electrolyte was 1 M LiPF₆ in EC/DEC (*v/v*=3/7) with 10 vol% FEC. The cells that were used for the asymmetric cell tests were prepared by using the same procedure

except that one side of the electrodes was replaced by Cu foil. For the full-cell tests, $\text{LiNi}_{0.82}\text{Co}_{0.07}\text{Mn}_{0.11}\text{O}_2$ cathodes were fabricated by first preparing a slurry consisting of the active material, Super P, and poly(vinylidene difluoride) (PVDF) in a weight ratio of 96:2:2 in *N*-methyl-2-pyrrolidone (NMP). The slurry was cast onto Al foil *via* the doctor blade method and dried at 120 °C for 12 hours. The areal loading of the active material was 15.5 mg cm⁻². The Li metal foil on the anode side was 40 μm thick. The electrolyte was the same as that used in the symmetric cells. The full-cells were pre-cycled at 0.1C and cycled at 1C (1C=200 mA g_{NCM}⁻¹) in subsequent cycles. The amount of the electrolyte was 80 μL for each coin cell. Both symmetric and full-cells were prepared in the form of 2032 coin cells by assembling the anode, cathode, and separator in a dry room. The ionic conductivity of each separator was assessed by performing EIS analysis, which was carried out in the frequency range of 10⁻²–10⁶ Hz with an amplitude of 10 mV. The ionic conductivity was retrieved from the *x*-axis intercept of each profile. The transference number was obtained by monitoring the change in the current when subjected to an applied voltage based on the following relation:^{1,2}

$$t_{\text{Li}} = \frac{I_{\text{SS}} \times (\Delta V - I_0 \cdot R_0)}{I_0 \times (\Delta V - I_{\text{SS}} \cdot R_{\text{SS}})}$$

where I_{SS} is steady state current, I_0 is initial current, R_{SS} is steady state resistance, R_0 is initial resistance, and ΔV is voltage applied (5 mV in the current study). I_0 was obtained by following the method by Galluzzo *et al.*³ Modified PITT analysis was conducted by applying constant voltage for one hour at every 2 mV while the current was monitored. The measured potential ranged from 0 to -50 mV vs. Li/Li⁺. To test the stability of the SEI layer, EIS analysis was performed after leaving the symmetric cells for a different number of days after undergoing one cycle of Li plating and stripping (C-rate=1C, capacity of each plating and stripping=3 mAh cm⁻²). These measurements were recorded in the frequency range of 10⁻²–10⁶ Hz with an amplitude of 10 mV.

Characterization of S-ZrO₂ and ZrO₂ particles. XRD (Empyrean, PANalytic) and FTIR (VERTEX 70, Bruker) analyses were carried out to characterize the crystal structures and chemical bonds of the S-ZrO₂ and ZrO₂ particles, respectively. TGA (TG/DTA 6300, PerkinElmer) was used to evaluate the sulfate content in S-ZrO₂. SEM analysis (JSM-7000F, JEOL) was performed to visualize the morphology of the Li metal

deposits on the surface. Raman analysis with a laser excitation wavelength of 532 nm (Senterra Grating 400, Bruker) was carried out for the electrolytes in which the different separators were soaked for 24 hours to monitor the ion-to-solvent interaction. ^{31}P solid NMR analysis (ASCEND, Bruker) was conducted for the S-ZrO₂ and ZrO₂ particles soaked in the electrolyte for 24 hours. The conditions for ^{31}P solid NMR analysis were such that the spinning frequency, dwell time, pre-scan delay, recycle delay, excitation pulse length, and excitation pulse power were 11 kHz, 6.3 msec, 6.3 msec, 0.5 sec, 5.0 msec, and 50 W, respectively. XPS (Scientific K-ALPHA, Thermo Fisher) was used to elucidate the SEI components.

DFT calculation. Geometrical optimizations and energy calculations were performed without symmetry restriction using the B3LYP hybrid density functional implemented in the GAUSSIAN 09 software package.⁴ The 6-311+G(d, p) basis sets were adopted for all the atoms. Frequency calculations at the same basis sets were performed to determine the nature of a stationary point as a true local minimum.

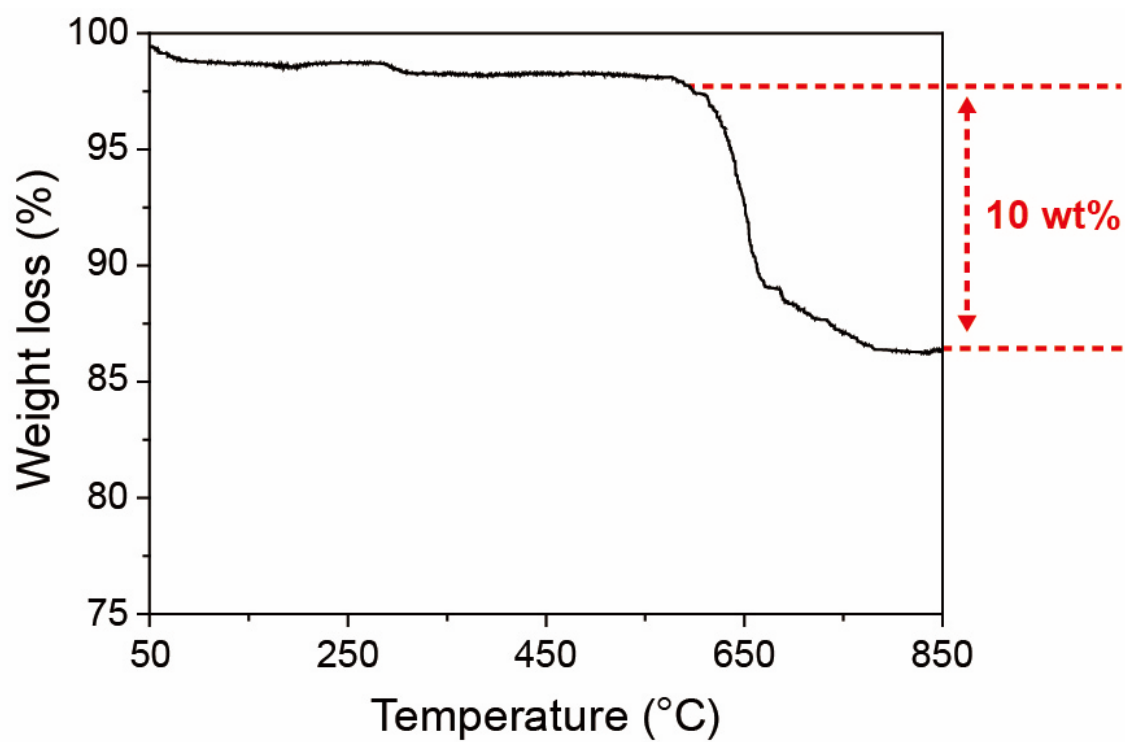


Fig. S1 TGA profile of S-ZrO₂ superacid.

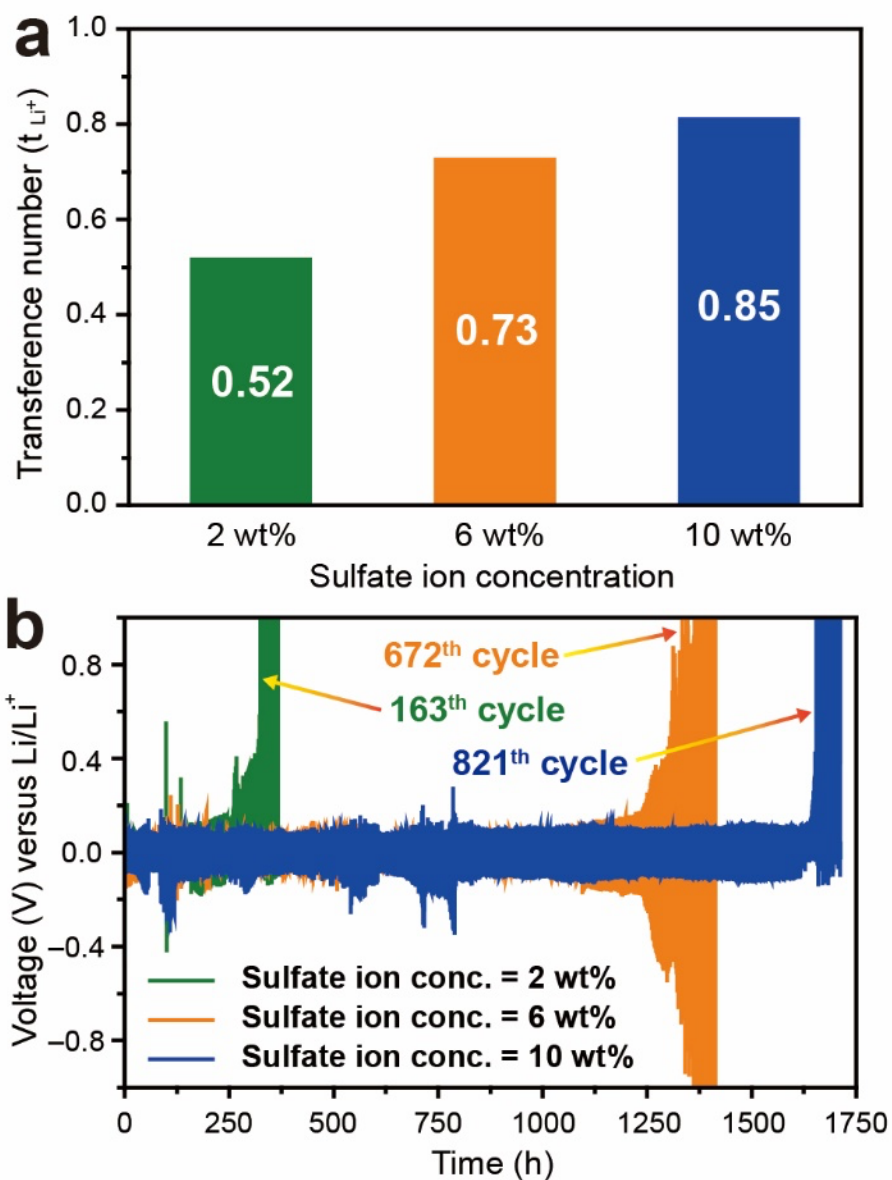


Fig. S2 (a) Transference numbers of the S-ZrO₂-coated PE separators with various sulfate contents. (b) Cycling results of the S-ZrO₂-coated cells with various sulfate contents when tested using a Li-Li symmetric cell setting. Current density = 3.0 mA cm⁻², 1 hour scanning for each Li plating and stripping.


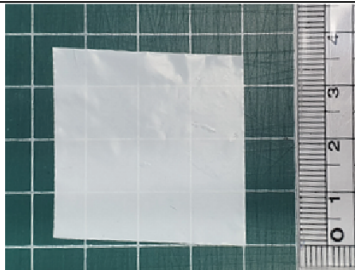

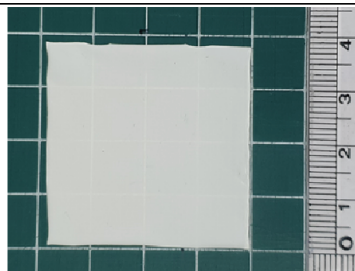
		Initial	125 °C for 1 h
a	PE separator		
		Area : 16 cm ² Thermal shrinkage : 0%	Area : 12.6 cm ² Thermal shrinkage : 21.3%
b	S-ZrO ₂ -coated PE separator		
		Area : 16 cm ² Thermal shrinkage : 0%	Area : 14.8 cm ² Thermal shrinkage : 7.4%

Fig. S3 Thermal shrinkage tests for (a) bare PE separator and (b) S-ZrO₂-coated PE separator before and after heat treatment in an oven at 125 °C for 1 hour.

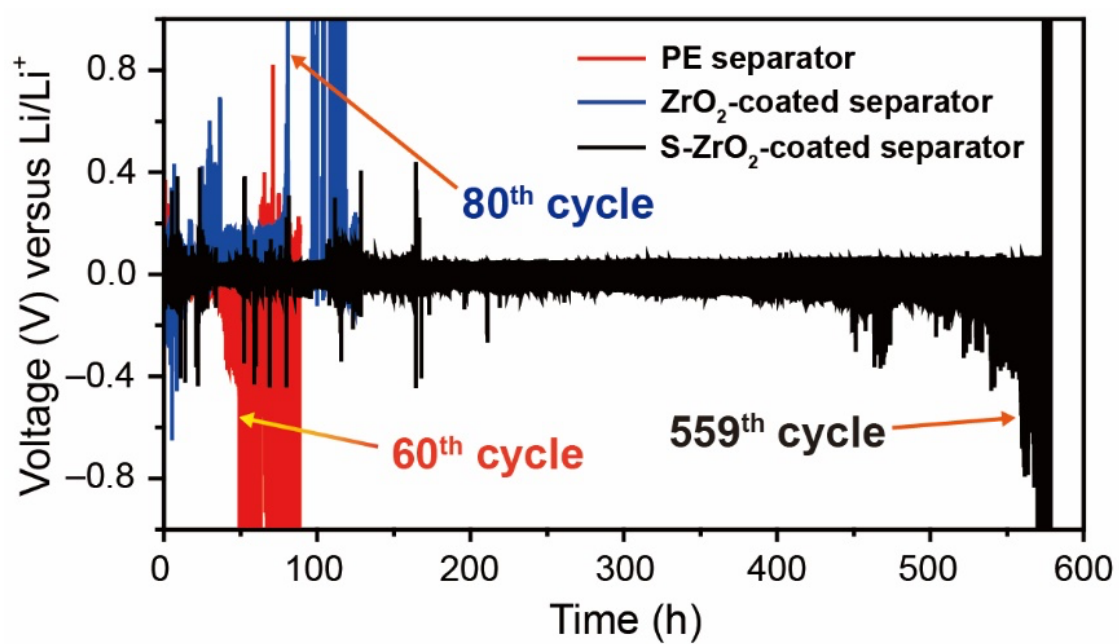


Fig. S4 Voltage profiles of the bare PE, ZrO₂-coated, and S-ZrO₂-coated symmetric cells when galvanostatically scanned at 6.0 mA cm⁻² for 0.5 hour for each plating and stripping.

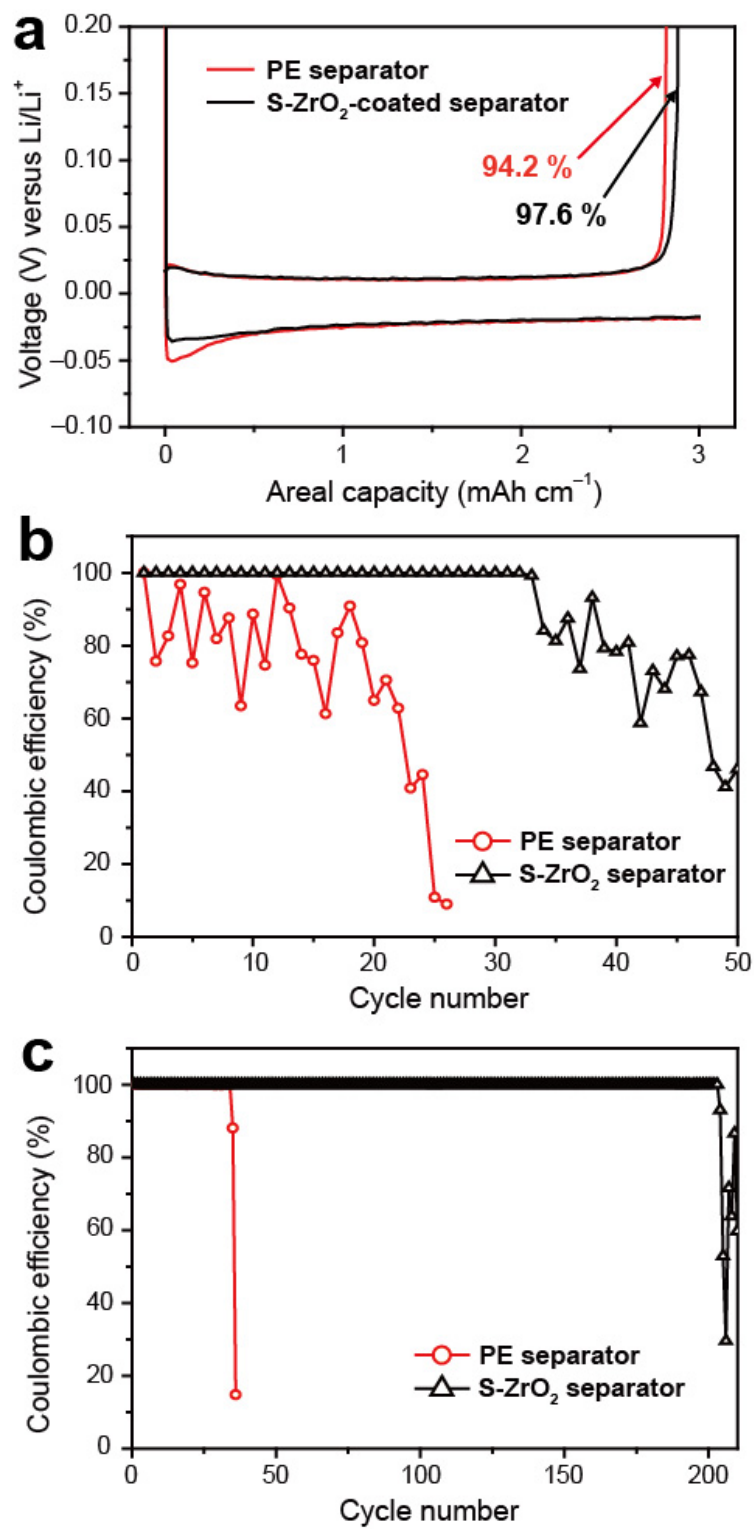


Fig. S5 Asymmetric cell tests. (a) Voltage profiles in the first cycle. Coulombic efficiencies over cycling with (b) 0% and (c) 200% Li reservoir.

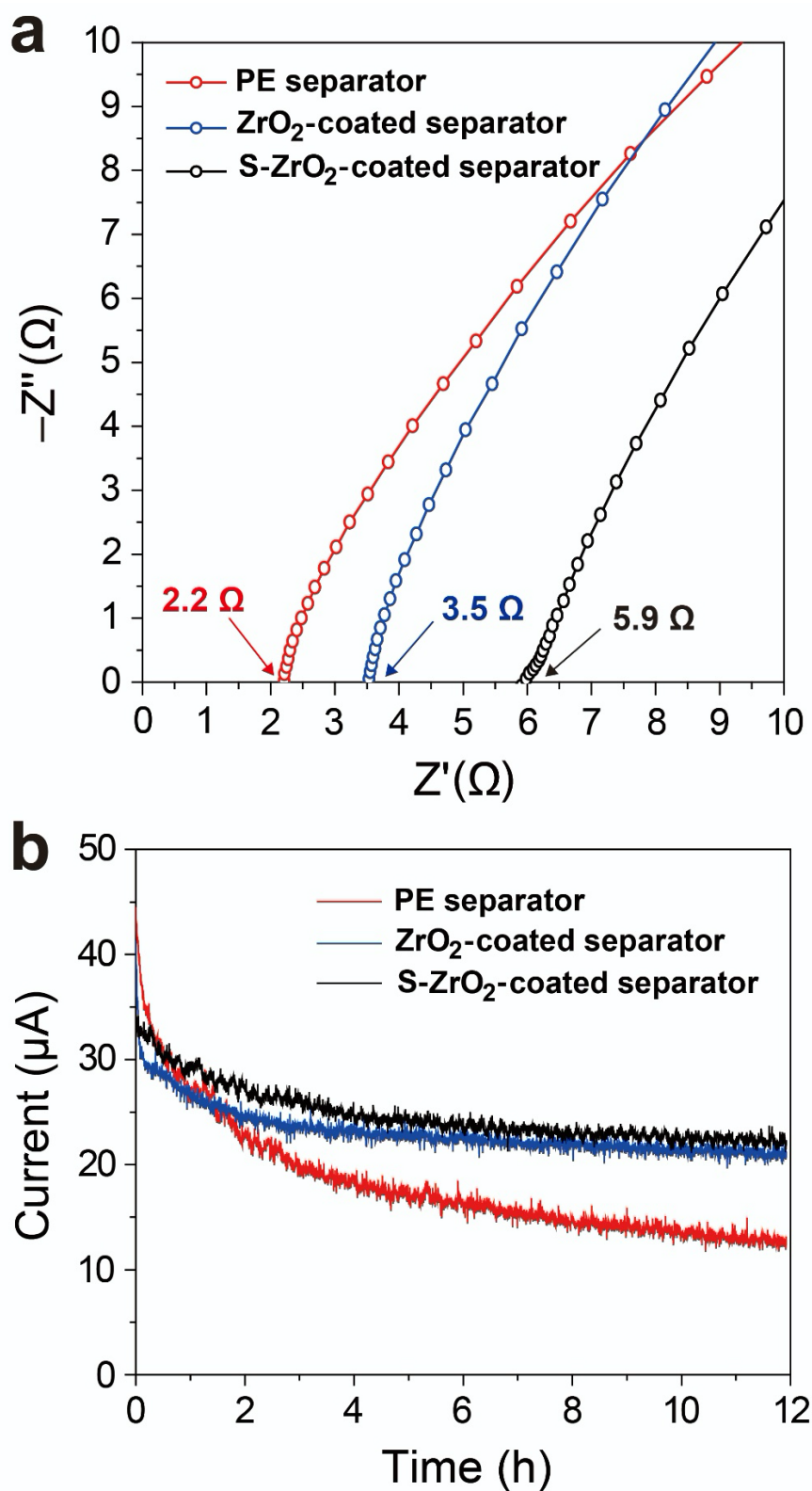


Fig. S6 (a) EIS profiles and (b) polarization curves of the three separators. See the Methods section for detailed experimental conditions.

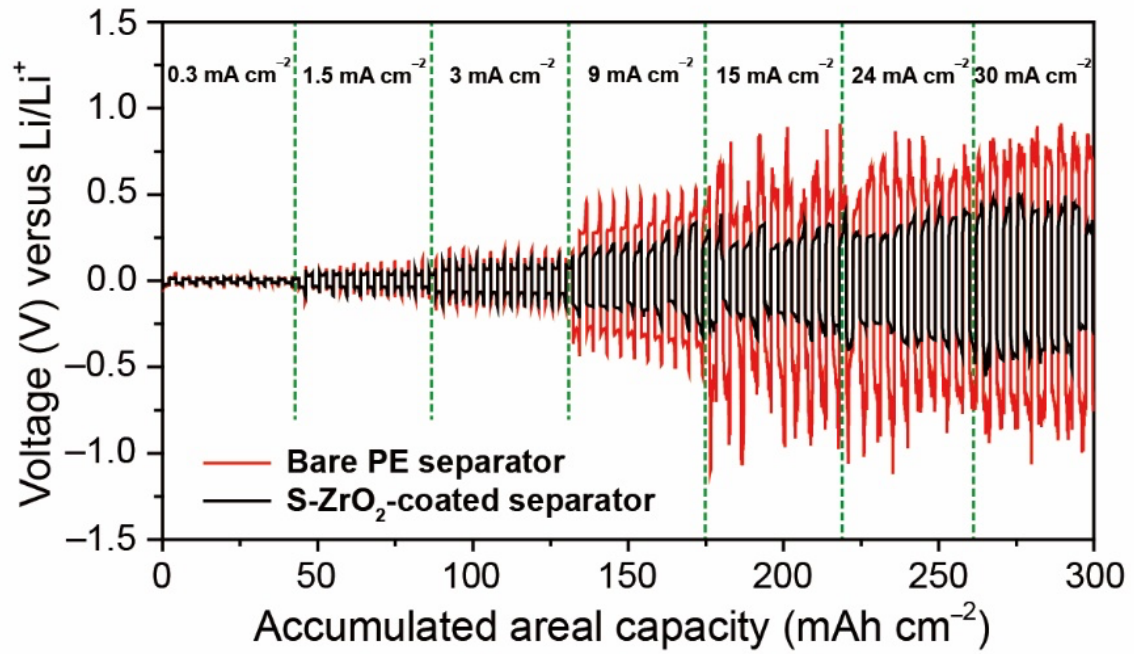


Fig. S7 Potential profiles of the bare PE and ZrO_2 -coated cells when tested under the Li-Li symmetric cell configuration at various current densities. The capacity in each cycle of Li plating and stripping is 2.2 mAh cm^{-2} .

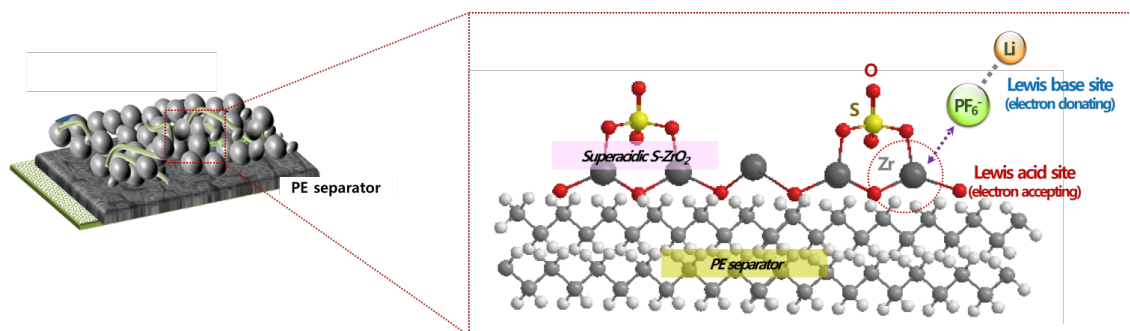


Fig. S8 Role of superacidity of S-ZrO₂ in attracting the PF₆⁻ anion.

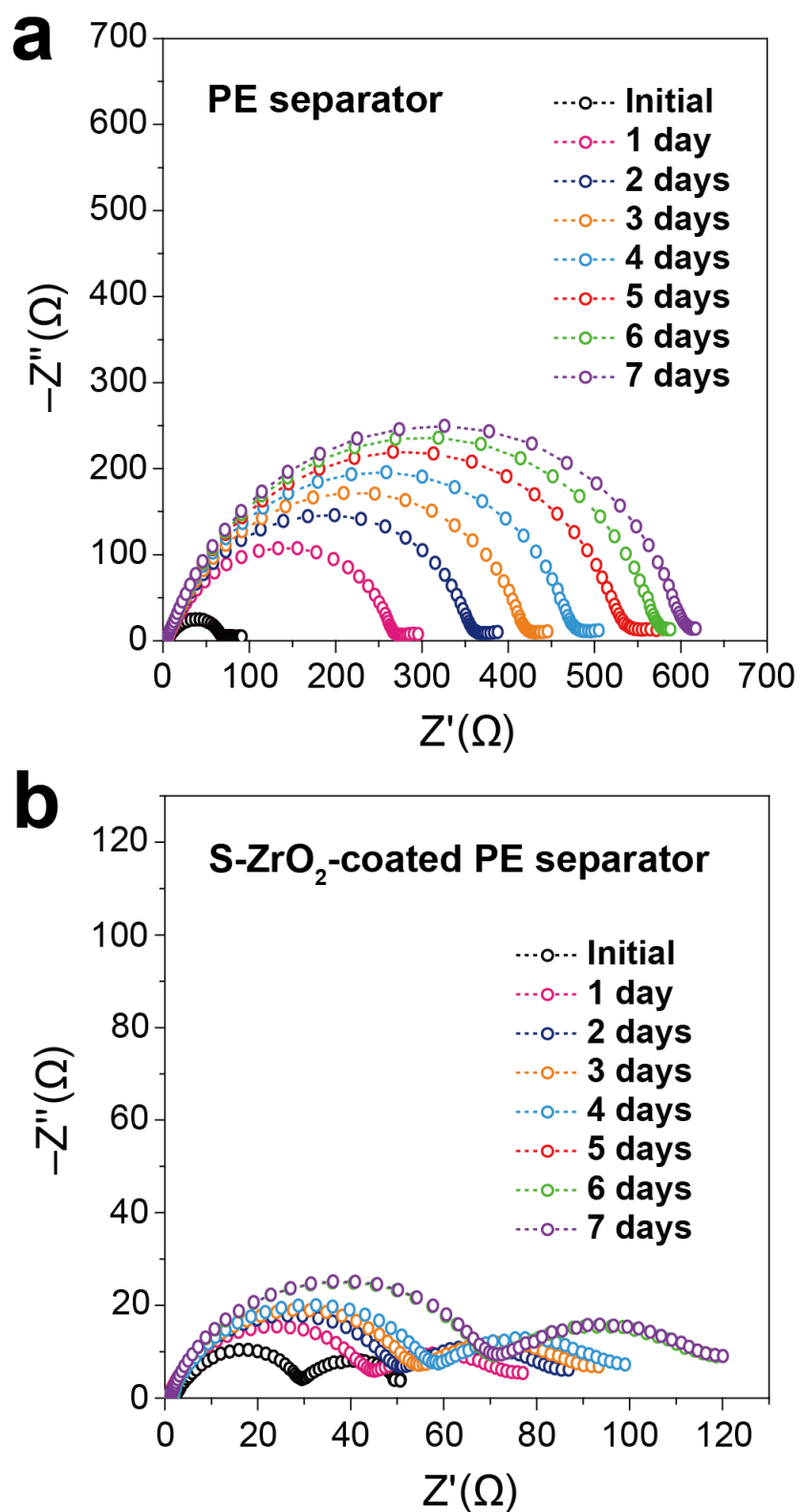


Fig. S9 EIS spectra after different periods of soaking in the carbonate electrolyte (1 M LiPF₆ in EC:DEC=3:7=v:v with 10 vol% FEC). (a) Bare PE separator. (b) S-ZrO₂-coated separator.

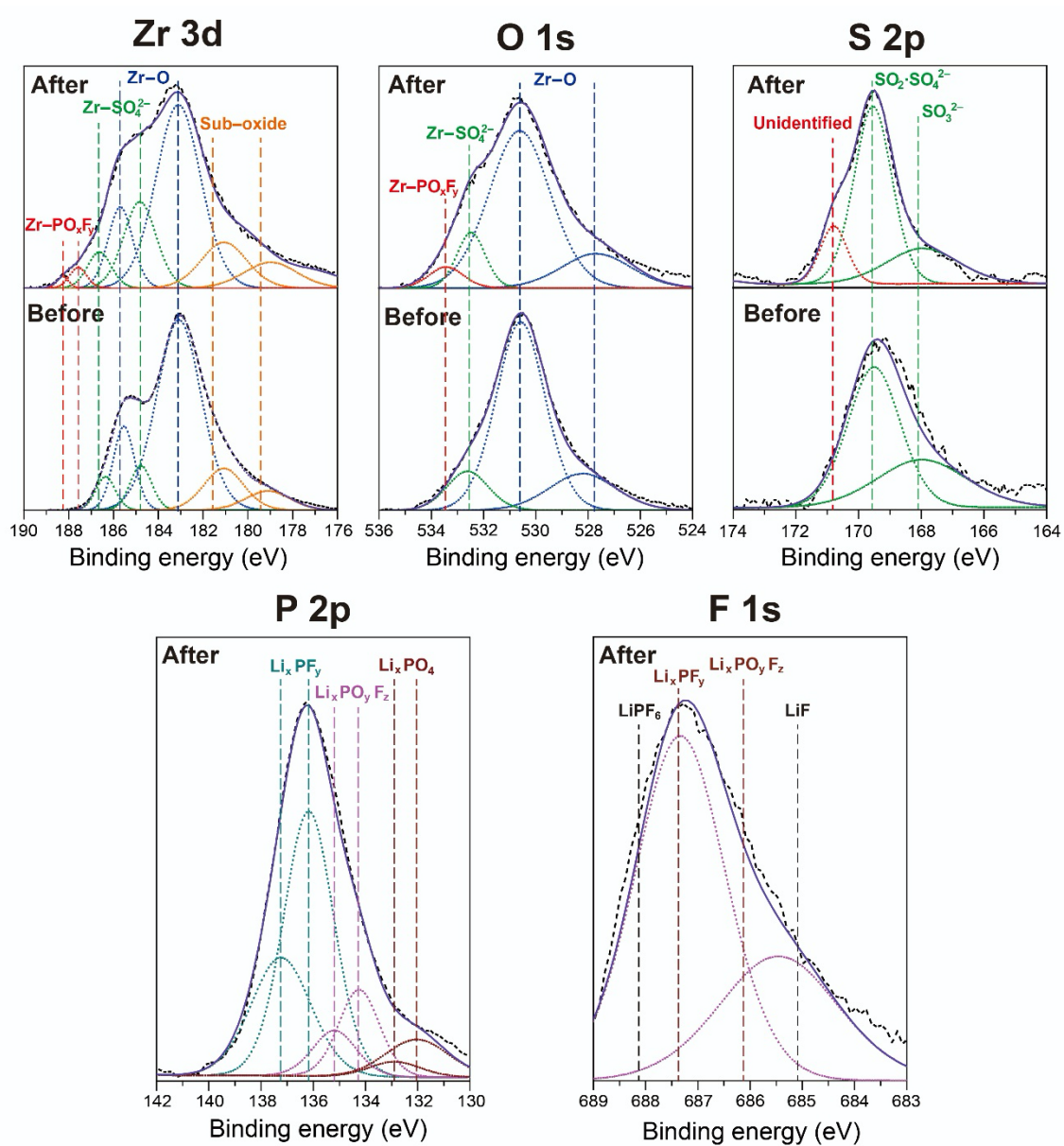


Fig. S10 XPS profiles of S-ZrO₂ powder before and after immersion in the electrolyte for 24 hours. The electrolyte was 1 M LiPF₆ in EC/DEC (3/7=v/v) with 10% FEC.

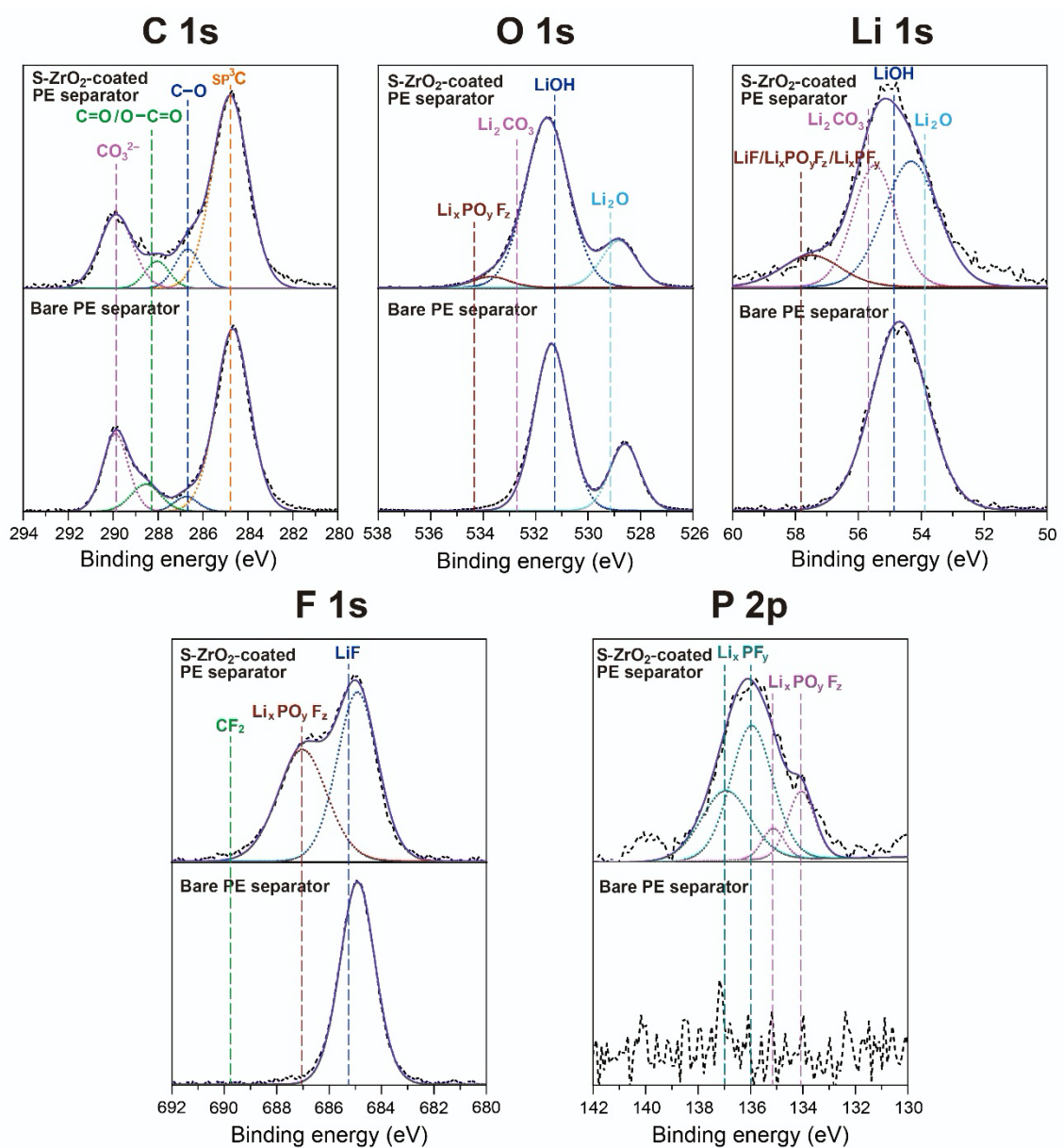


Fig. S11 XPS profiles of the Li metal electrode before and after the 1st Li plating. The electrodes were etched for 300 seconds before analysis using an Ar beam.

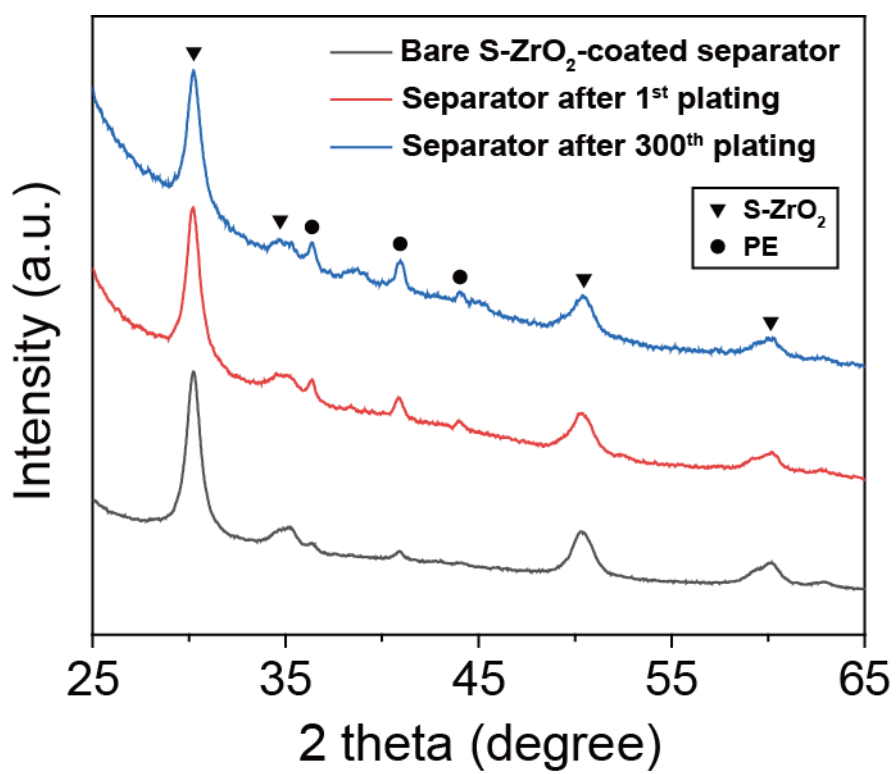


Fig. S12 XRD patterns of the S-ZrO₂-coated separator before and after the 1st and 300th Li plating.

Reference

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- S4. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133-A1138.