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Supporting Information

Ionic Activation via Hybrid IL-SSE Interfacial Layer for Li−O_2 Batteries with 99.5% Coulombic Efficiency

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1.0 Experimental Section

1.1 LAGP particles and surface layer

The LAGP solid-state electrolyte was synthesized by a high temperature solid-state reaction method. Stoichiometric amounts of Li_2CO_3, Al_2O_3, GeO_2 and $(NH_4)H_2PO_4$ were used as starting materials. The starting materials were mixed in a planetary ball mill and then heated at 700 ^oC for 6 h. The precursors were reground and heated at 800 ^oC for 6 h in air atmosphere to obtain the SSE powders. The SSE powders were homogeneously dispersed in a poly(vinylidene fluoride) and acetonitrile solution and then cast onto the surface of Li metal. The AN solvent was allowed to evaporate slowly at 40 ^oC in an Ar-filled dry box for 12 h and was then dried at 110 ^oC for 12 h under vacuum.

1.2 RuO_2 air cathode

RuO_2 nanoparticles were prepared in deionized water by a chemically precipitated method. 5 mg of Ru^{3+} in $RuCl_3$ was dissolved in deionized water solution and sonicated for 12 hours. 0.1 M $NaHCO_3$ solution was slowly added under vigorous stirring until the pH reaches $>$7.0. The obtained precipitate was washed with deionized water and dried by a controlled drying process. The dried precipitate was then treated at 150 ^oC for 3 h and 200 ^oC for 6 h, respectively. The RuO_2 nanoparticles were mixed with PTFE binder in the ratio 90:10 wt% using isopropanol, and then pressed onto a stainless steel mesh current collector. The loading area was 0.385 cm^2 (7 mm in diameter) and the loading weight of RuO_2 was $\approx$ 1.0 mg/cm^2. The cathode was vacuum dried at 100 ^oC for 24 hours.

1.3 Ionic liquid electrolyte

The ether-functionalized ammonium ion-based ionic liquid electrolyte consists of Li salt of 0.5 M $LiNTf_2$ in pure $[(C_1OC_2)C_2C_2C_1N][NTf_2]$. The imidazolium ion-based ionic liquid electrolyte consists of Li salt of 0.5 M $LiNTf_2$ in pure $[C_2C_1im][NTf_2]$. Water content in both the ionic liquid electrolytes is lower than 5 ppm.

1.4 Li anode

The Li foil of thickness 0.2 mm was cut into a disc of 10 mm in diameter, and then pressed onto a stainless steel spacer in Li-O_2 coin cells.

1.6 Assembling Li-O_2 coin cell

All the manipulations of cell assembling were carried out in an argon-filled high-integrity glovebox. CR2032-type coin cells with holes for O_2 access were used as the holder. The amount of the ionic liquid electrolyte was 60 μL, immersed in a Waterman GF/C glass fiber separator. After assembling, the coin cells were put into a glass chamber with complete gas tightness and gas valves for the entrance and exit of oxygen, and then taken out from the argon-filled glovebox.

2.0 Electrochemical analysis and material characterization

2.1 Electrochemical measurement

Pure O_2 was passed through the glass chamber to replace the argon gas completely, and then the gas valves were closed to prevent the exchange of outside air and inside pure O_2. All the tests were carried out in the O_2-tight glass chamber with an initial pressure of 1 atm. The glass chamber was placed in an incubator to control the measured temperature at 60 ^oC. The current density was constant at 360 mA/g, and the capacity was normalized by the weight of the RuO_2. The electrochemical tests were performed at 60 ^oC using Land charge/discharge machine and Autolab instruments.

2.2 XRD Analysis

X-ray powder diffraction (Rigaku) was used to analysis the crystalline structure of RuO_2 nanoparticles.

2.3 SEM observation and EDX analysis

The Li anodes after cycling at 60 ^oC were washed by pure dimethoxyethane (DME) and then dried before SEM observation. The Nova Nano field emission and S-3400 SEM instruments were used for micrograph observation and energy dispersive X-ray (EDX) mapping analysis.

2.4 FTIR analysis

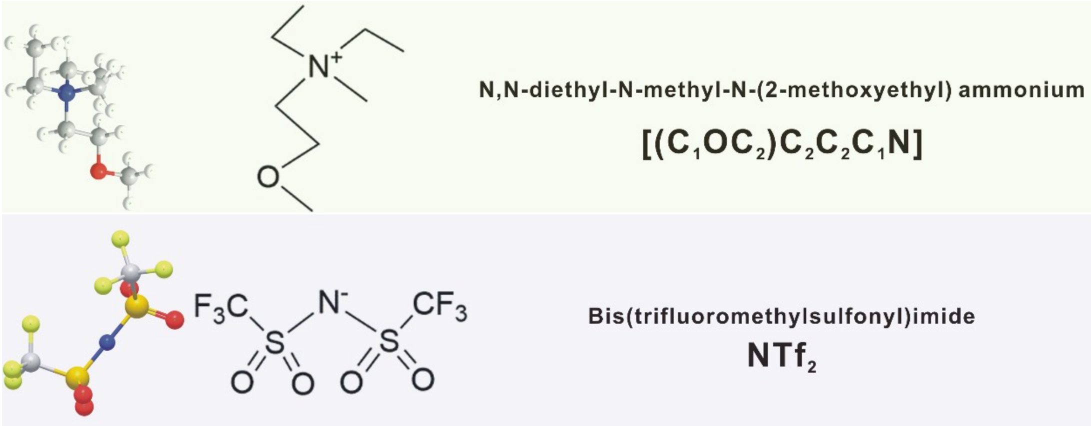
The ionic liquid was ground together with KBr and pressed into pellets under high pressure for Fourier transform infrared (FTIR) analysis. FTIR was obtained on a JASCO instrument of FT/IR-6200 from 1300 to 900 cm^{-1} with a resolution of 2 cm^{-1}.

2.5 XPS analysis

The discharge products were analyzed by the X-ray photoelectron spectroscopy (Thermo Fisher Scientific ESCALAB 250). The samples for X-ray photoelectron spectroscopy (XPS) measurements were prepared in the argon-filled glove box. The cells were disassembled after cycling and cycled anode sample were washed with 1,2-dimethoxyethane (anhydrous, Sigma) and then dried for 2h. A special transfer system was employed to transfer cycled cathode samples from the glove box to XPS system without being exposed to air.

2.6 N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide molecular structural formula

N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide



3.0 Supplementary Fig.S

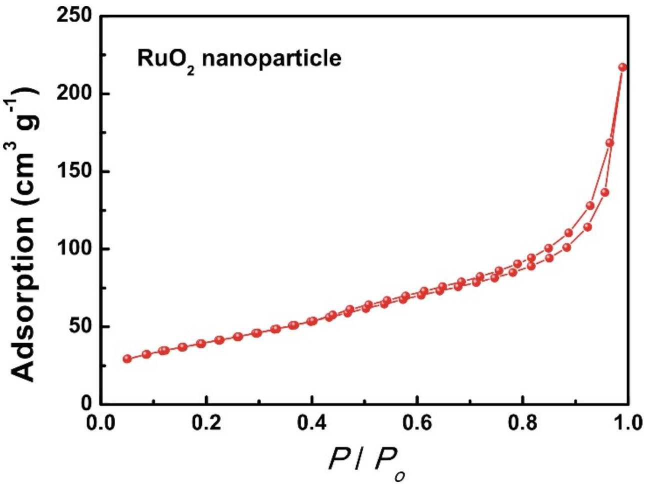


Fig. S1 I Nitrogen-adsorption-desorption isotherms of the RuO$_2$ nanoparticle.

The Brunauer-Emmett-Teller (BET) surface area of the RuO$_2$ nanoparticles is as high as 145 m^2 g^{-1}.

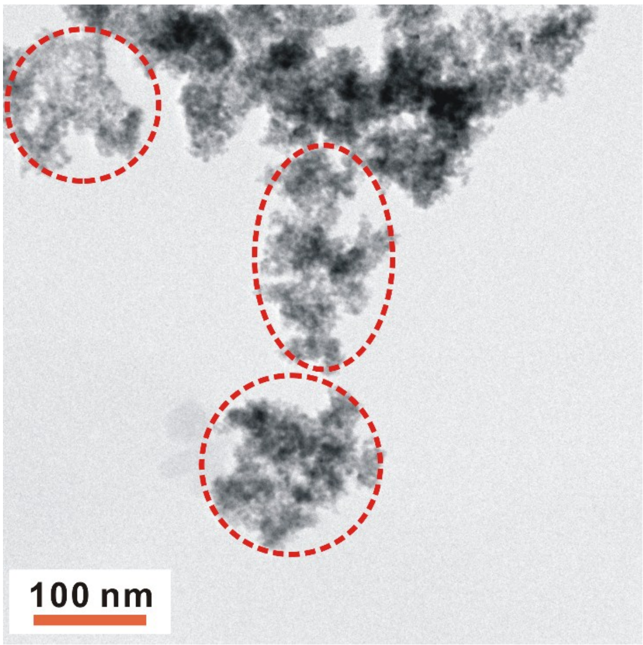


Fig. S2 | TEM image of the RuO_2 nanoparticles. The average size of quadric particle is ~100 nm.

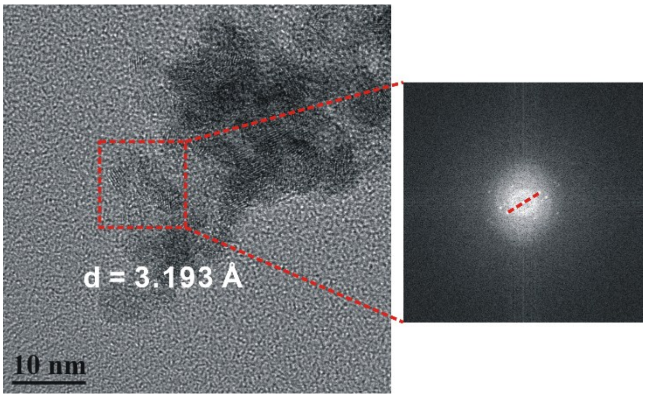
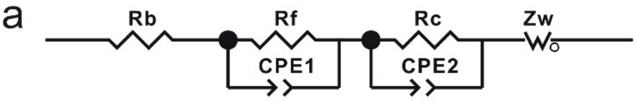


Fig. S3 | HRTEM image and the corresponding analysis of the (110) interplanar spacing through the reciprocal space. The calculated interplanar spacing within the red square is 3.193 Å, agreement with the indexed value of 3.183 Å.



	R_b Ω cm^2	R_f Ω cm^2	R_c Ω cm^2
Pristine	4.25	2.12	6.87
After 100 cycles	9.16	23.49	40.89
Reassemble after 100 cycles	5.38	10.74	24.35

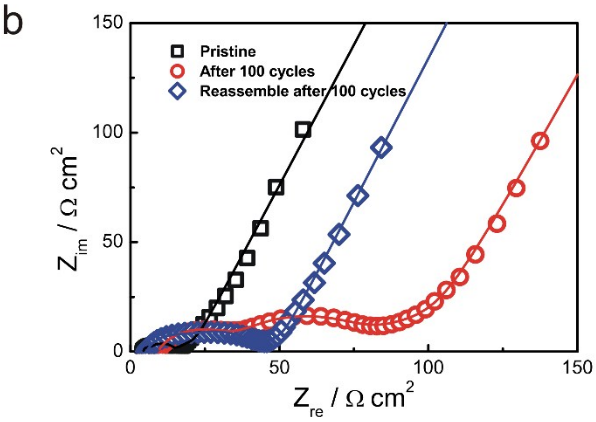


Fig. S4 | EIS analysis corresponding to *Fig. 2d*. EIS analysis with (a) equivalent circuit model and fitting parameters, (b) Nyquist plots of experimental (symbols) and fitted results (lines). R_b: equivalent series resistance for the electrolyte, current collectors and electrode materials. R_f: resistance derived from the interfacial contact and interface layers at the electrode surface. R_c: charge transfer resistance at the interface of electrolyte and active materials.

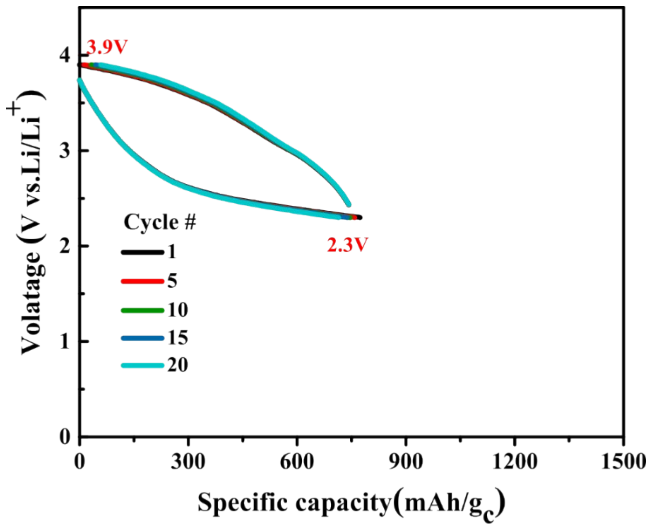


Fig. S5 | Discharge/charge curves of the Li−O_2 cell at a potential-controlled model of 2.3-3.9 V for 20 cycles. The Li anode of the Li−O_2 cells after 100 cycles was replaced with a fresh Li metal.

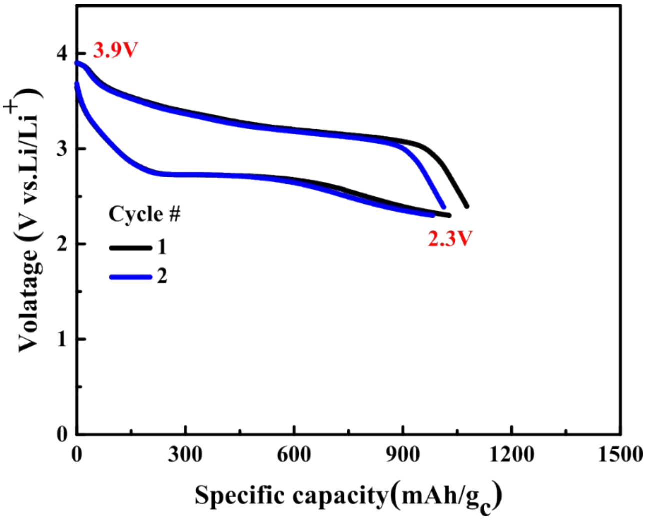


Fig. S6 | Discharge/charge curves of the Li−O_2 cell at a potential-controlled model of 2.3-3.9 V for 2 cycles. The Li−O_2 cells was assembled with the washed RuO_2 air cathode.

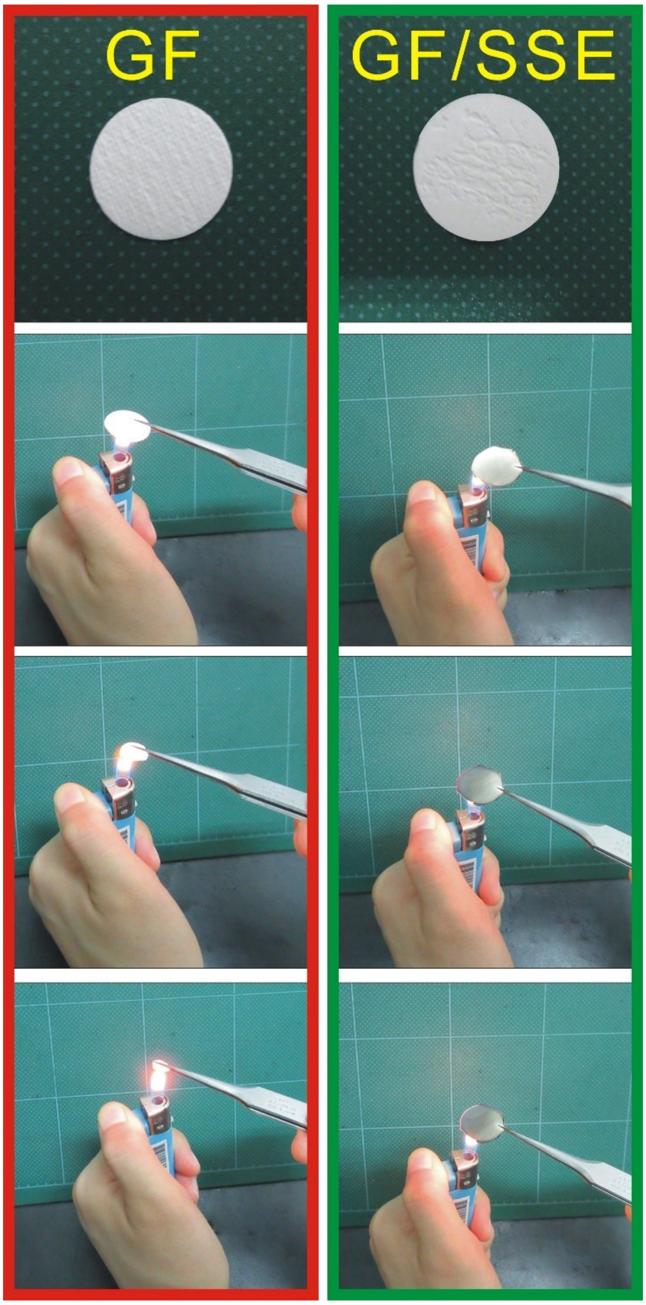
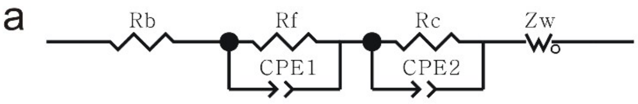


Fig. S7 | Safety experimental of IL-SSE-based Li-O_2 cell. When the separator of glass fiber (GF) was heated, it became shrunk and finally fired. In stark contrast, the GF with SSE film was inflammable, exhibiting much higher thermal stability of the IL-SSE-based Li-O_2 cell.



	R_b $\Omega\ cm^2$	R_f $\Omega\ cm^2$	R_c $\Omega\ cm^2$
Pristine	11.15	3.60	47.20
After 100 cycles	7.67	38.65	13.27

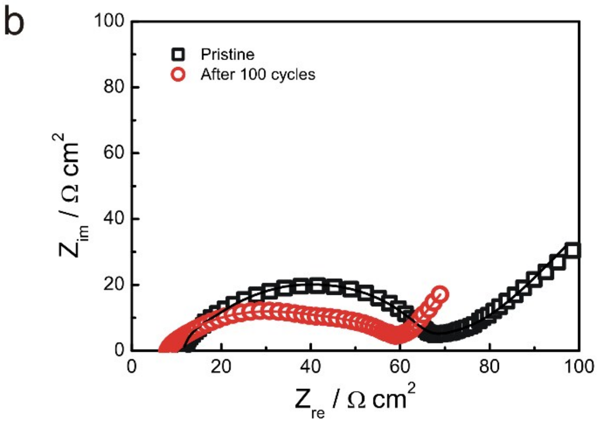


Fig. S8 l EIS analysis corresponding to *Fig. 4a*. EIS analysis with (a) equivalent circuit model and fitting parameters, (b) Nyquist plots of experimental (symbols) and fitted results (lines). R_b: equivalent series resistance for the electrolyte, current collectors and electrode materials. R_f: resistance derived from the interfacial contact and interface layers at the electrode surface. R_c: charge transfer resistance at the interface of electrolyte and active materials.

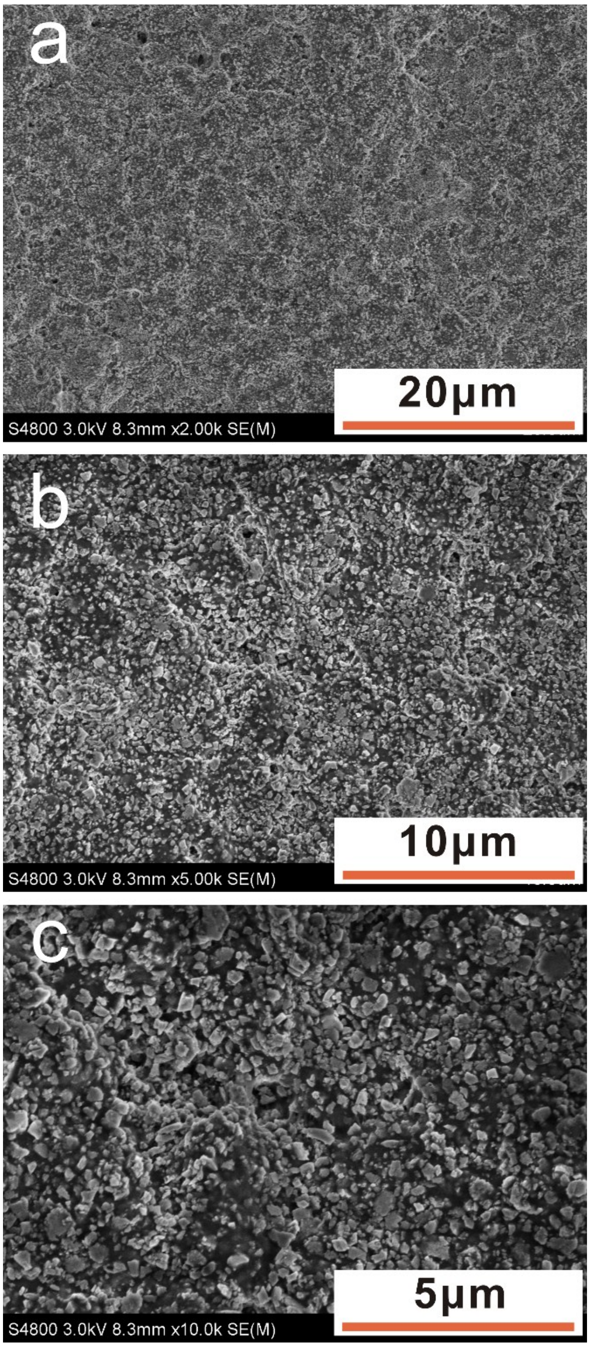


Fig. S9 | Broader SEM images corresponding to the inset in *Fig. 4a*. (a), (b) and (c) are obtained from the observation for the same area, representing different magnification of SEM images, which are obtained from the observations for the same area.

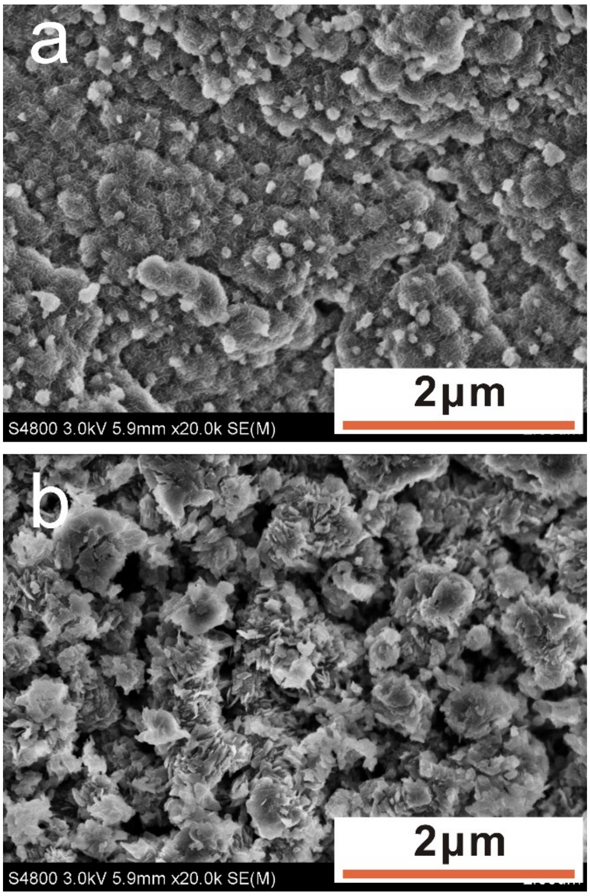


Fig. S10 | Magnification of surface SEM images. (a) and (b) are corresponding to *Fig. 4b* and *4c*, respectively.

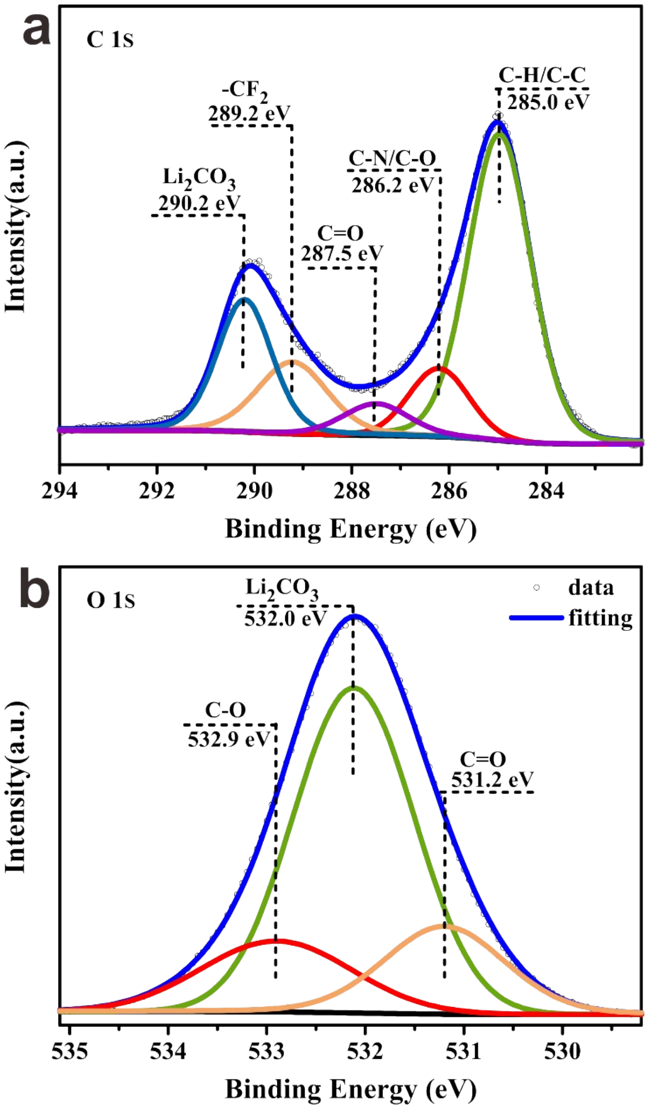


Fig. S11 | XPS spectra of the Li anode surface after 100 cycles for IL-SSE-based Li-O_2 cell. (a) C 1s XPS spectra of the of the Li anode surface; (b) O 1s XPS spectra of the of the Li anode surface.

As can be seen in Fig. S9 ,The C 1s signal of the Li anode surface in Fig. S9a consists of five different peaks centered at 285.0, 286.2, 287.5, 289.2 and 290.2 eV, corresponding to the C-H/C-C, C-N/C-O,C=O, -CF_2, Li_2CO_3 functional groups, respectively. The O1s spectrum of the Li anode surface in Fig. S9b can be divided into three peaks, centering at 531.2, 532.0 and 532.9 eV and corresponding to C=O, Li_2CO_3, C-O respectively.

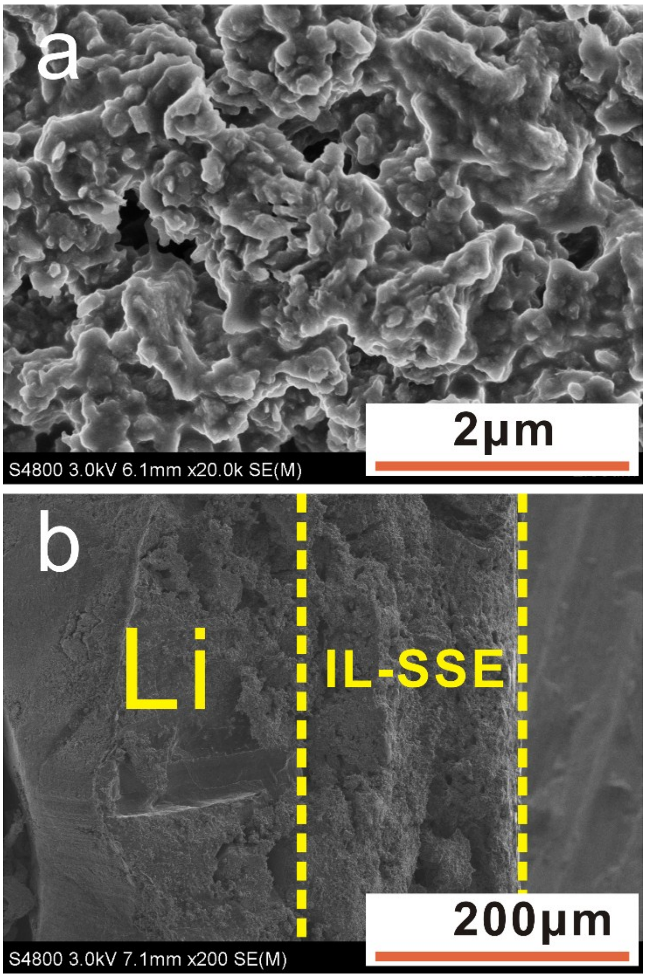


Fig.S12 l Magnification of interface and cross section SEM images. (a) and (b) are corresponding to *Fig. 5b* and *6a*, respectively.