Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A long life solid-state lithium-oxygen battery enabled by durable oxygen deficient flowerlike CeO_2 microspheres based solid electrolyte

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EXPERIMENTAL SECTION

Synthesis of LLZO nanoparticles

$Li_7La_3Zr_2O_{12}$ (LLZO) was prepared by sol-gel method using $C_6H_8O_7\cdot H_2O$ (AR, Sinopharm Chemical Reagent Co., Ltd.), $C_{10}H_{16}N_2O_8$ (99%, Aladdin), $LiNO_3$ (99.9%, Aladdin), $La(NO_3)_3\cdot 6H_2O$ (99.9%, Aladdin), $ZrO(NO_3)_2\cdot xH_2O$ (99.5%, Aladdin), $Al(NO_3)_3\cdot 9H_2O$ (99.0%, Aladdin) and C_2NbO_4 (AR, Alfa) as starting materials. They were weighed according to the molar mass ratio of 0.0248 mol: 0.01224 mol: 0.007 mol: 0.003 mol: 0.00175 mol: 0.00024 mol: 0.00025 mol and mixed in 40 ml deionized water. Then the pH of the above solution was adjusted with concentrated nitric acid and ammonia to approximately 8. Finally, a homogeneous solution was obtained and then it was heated at 80^{o}C for 7 h to evaporate solvent under magnetic stirring. The obtained sol was carbonized at 250^{o}C for 5 hours and then eventually became gel. After the above product was grinded, it was calcined in a muffle furnace at 850^{o}C for 2 h in air atmosphere, and the calcined product was ball-milled for 12 h to obtain the final LLZO powder.

Preparation of flowerlike CeO_2

All chemicals were purchased from Beijing Chemical Reagents Company and used without further purification. In a typical experiment, glucose (0.01 mol) was dissolved into deionized water (80 mL) with magnetic stirring, which was followed by addition of acrylamide (0.015 mol) and hydrated cerium (III) nitrate (0.005 mol) to form a transparent solution. After that, ammonia solution (3.2 mL, 25 wt %) was added to the solution dropwise with stirring. Upon the addition of ammonia solution, the solution became stiff gel. The color of the gelatinous mixture finally became deep brown with continuous stirring. The pH value of the resultant gelatinous mixture is about 10. This solution mixture was stirred for 5 h before being transferred into a 100 mL Teflon-lined autoclave. Then the autoclave was sealed and kept at 180 ℃ for 72 h in an electric oven. After that, the autoclave was cooled to room temperature naturally. The orange suspension and precipitate were separated by centrifugation, and the suspension was washed with water and alcohol three times and then dried at 80 ℃ for more than 10 h. The flowerlike $CeOHCO_3$ microspheres were finally obtained.

The flowerlike CeO_2 microspheres were obtained from the as prepared $CeOHCO_3$ microspheres via a two-step calcination procedure. First, the as-prepared products were calcined under Ar with a flow rate of 10 mL min^{-1} in a tube furnace at 600 ℃ for 6 h. Then, the obtained products were calcined in air in a tube furnace at 400 ℃ for 4h.

Preparation of Ru-CNTs

30 mg of $RuCl_3$ (99.8%, Macklin) was dissolved in 60 mL of ethylene glycol (99.9%, Acros) and vigorously stirred. After stirring for 3 hours, 48 mg of the multi-walled carbon nanotube (96%, DoDoChem) solution was added and the stirring was maintained for 1 hour. The stirred solution was placed to a 100mL stainless steel reactor lined with PTFE and stored in an oven at 170℃ for 4 hours. After the reaction kettle was completely cooled, the precipitated black powder was filtered and washed with ethanol for many times. The product was first dried in a vacuum oven for 4 hours to remove the solvent at 80 ℃, then heated to 180 ℃ for 10 hours before being used.

Preparation of $LiFePO_4$ positive electrode

Active cathode material (LFP, AR, PULEAD Technology Co., Ltd.), conductive additives (Super-P carbon black, Alfa, 99%+), poly(vinyl difluoride) (AR, HF-Kejing Technology Co., Ltd.) binder were mixed at a weight ratio of 8:1:1 and were added into N-1-methyl-2-pyrolidone (NMP, Alfa, 99%+) to form homogeneous cathode slurry. The slurry was then applied onto aluminum foil (15 μm, HF-Kejing Technology Co., Ltd.) and was dried at 120^{o}C for 12 h at vacuum oven and following by punching it into round discs with a diameter of 12 mm.

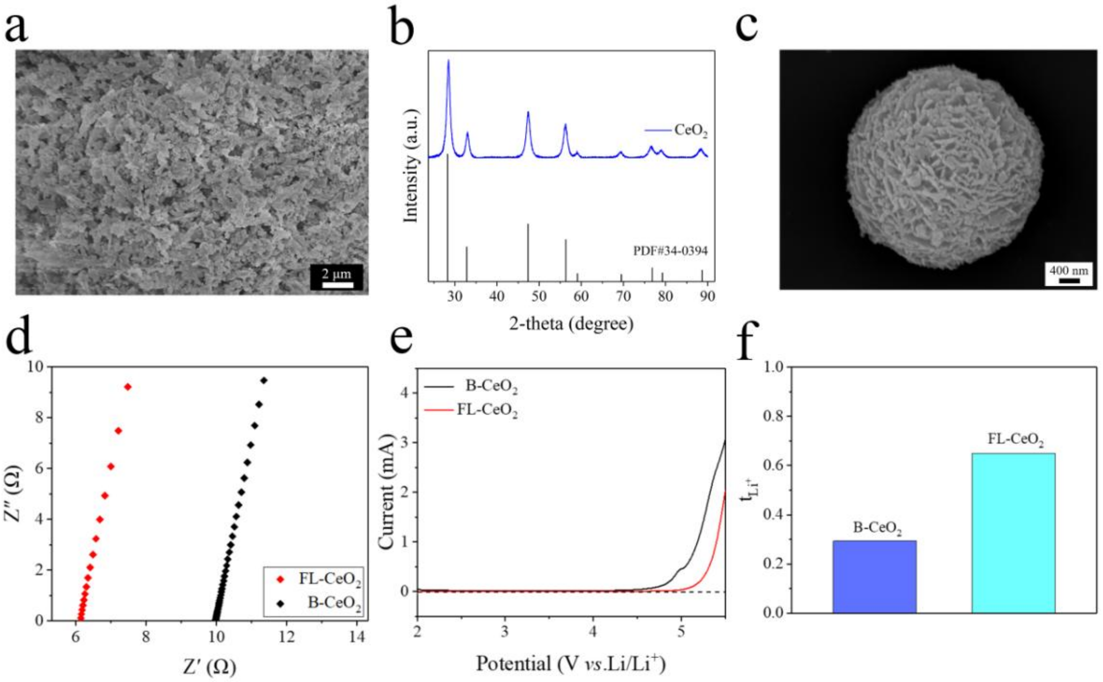

Fig. S1 (a) SEM image of the LLZO powder. (b) XRD pattern of the as-prepared FL-CeO$_2$ powder. (c) SEM image of the FL-CeO$_2$. (d) Nyquist plots, (e) Linear sweep voltammograms (LSV) curves and (f) The histogram of Li$^+$ transfer number (t_{Li^+}) of various electrolyte membranes with commercial bulk ceria (B-CeO$_2$) and FL-CeO$_2$.

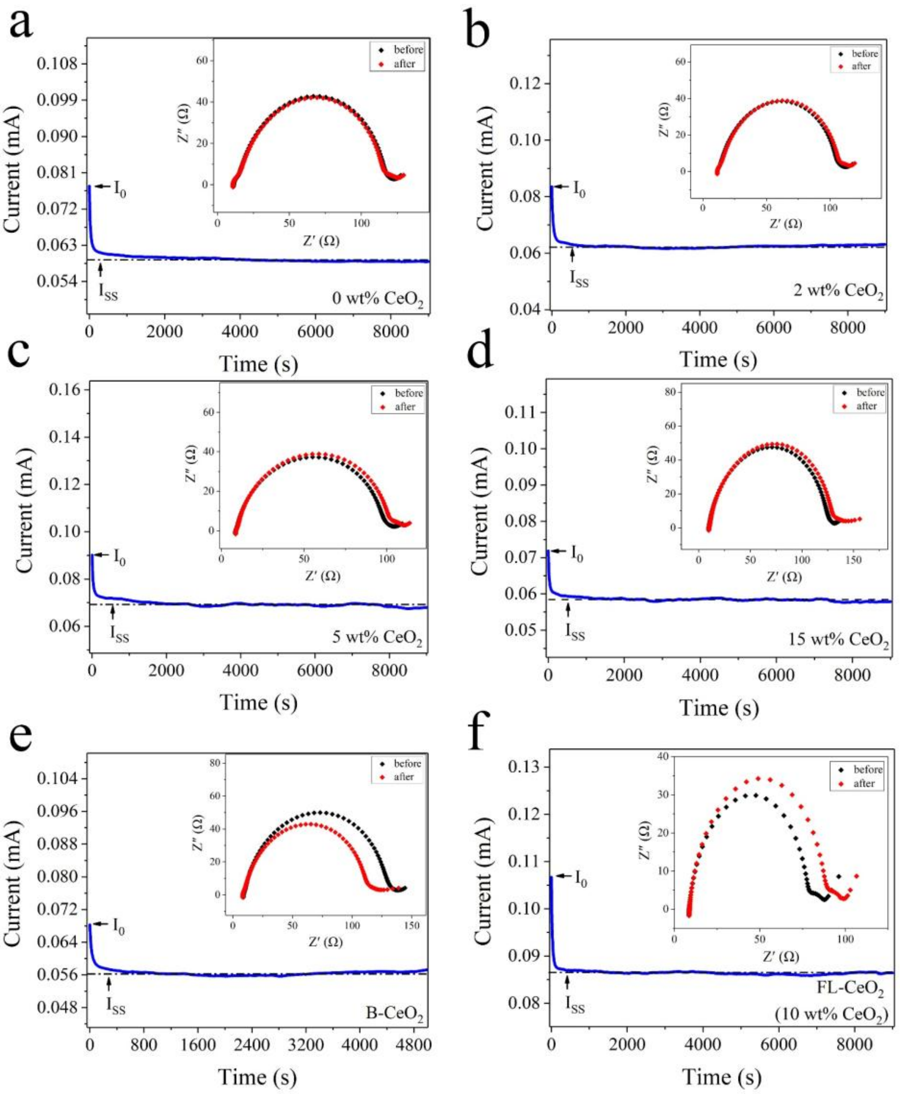

Fig. S2 Current-time profile of a symmetrical Li|PVDF-HFP/LiTFSI/LLZO/x-CeO_2|Li cell under a polarization voltage of 10 mV, used for determining transfer number of lithium ion. The inset shows the Nyquist plots of the cell before and after polarization.

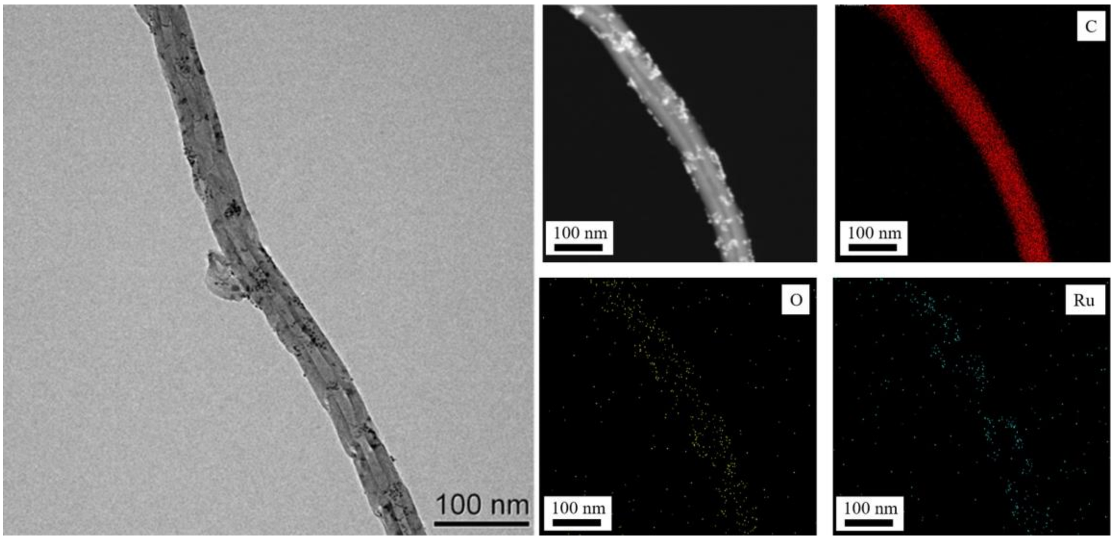

Fig. S3 TEM image and elemental mappings of Ru-CNT.

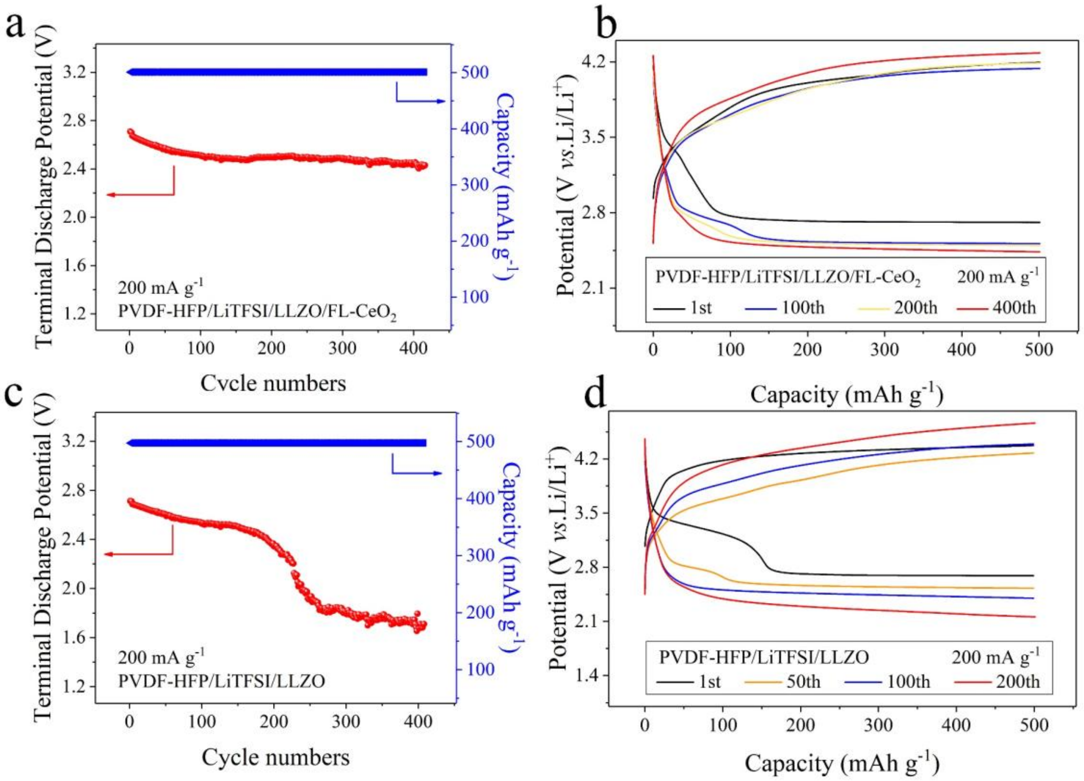

Fig. S4 (a) Discharge-charge profiles of the solid-state Li-O_2 cell with PVDF-HFP/LiTFSI/LLZO/FL-CeO_2 electrolyte membrane. (b) Cycle performances of the solid-state Li-O_2 cell with the PVDF-HFP/LiTFSI/LLZO/FL-CeO_2 electrolyte membrane. (c) Discharge-charge profiles of the solid-state Li-O_2 cell with the PVDF-HFP/LiTFSI/LLZO electrolyte membrane. (d) Cycle performances of the solid-state Li-O_2 cell with the PVDF-HFP/LiTFSI/LLZO electrolyte membrane. All the tests were performed at a current density of 200 mA g^{-1} with a limited capacity of 500 mAh g^{-1}.

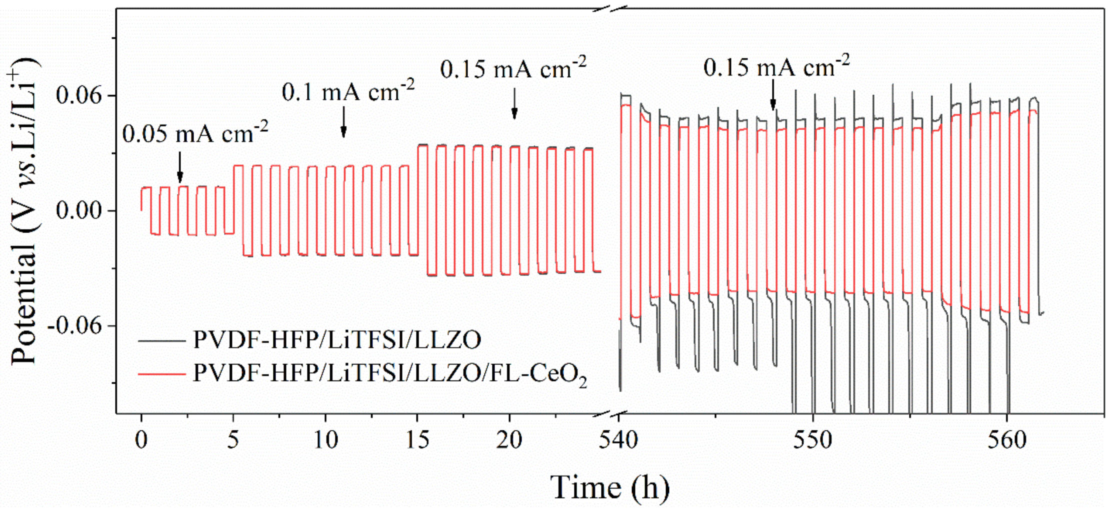

Fig. S5 Voltage profile of the lithium plating/stripping cycling in the symmetrical Li|CSEs|Li cells with different current densities of 0.05, 0.1 and 0.15 mA cm^{-2}, respectively.

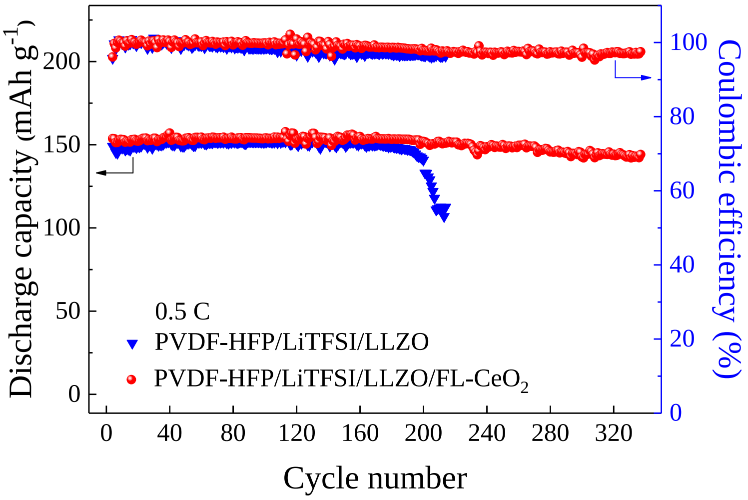

Fig. S6 Long-term cycling performance of $LiFePO_4$|CSEs|Li at 0.5 C.

Table S1. Comparison of ionic conductivity of the PVDF-HFP/LiTFSI/LLZO/FL-CeO_2 with those electrolytes reported in the literature.

Electrolyte	Solvents/Liquid electrolyte used	Ionic conductivity at room temperature	References
PVDF-HFP/PAN/ Al-doped LLZO	DMF	1.12×10^{-4} S cm^{-1}	1
PVDF-HFP/ $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$	LiTFSI in DOL/DME	3.3×10^{-4} S cm^{-1}	2
PVDF-HFP/ LATP/FL-CeO_2	DMF	1.4×10^{-4} S cm^{-1}	3
PVDF-HFP/ ($Li_7La_3Zr_2O_{12}$	LiTFSI in DOL/DME	1.1×10^{-4} S cm^{-1}	4
PVDF/ $LiClO_4$ /$(Mg,Al)_2Si_4O_{10}(OH)$	DMF	1.2×10^{-4} S cm^{-1}	5
PVDF-HFP/ LiTFSI/LLZO/ FL-CeO_2	DMAc+ Acetone	4.86×10^{-4} S cm^{-1}	This work

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