Supporting Information

# A long life solid-state lithium-oxygen battery enabled by durable oxygen deficient flowerlike CeO<sub>2</sub> microspheres based solid electrolyte

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# **EXPERIMENTAL SECTION**

## Synthesis of LLZO nanoparticles

Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) was prepared by sol-gel method using C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> H<sub>2</sub>O (AR, Sinopharm Chemical Reagent Co., Ltd.), C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub> (99%, Aladdin), LiNO<sub>3</sub> (99.9%, Aladdin), La(NO<sub>3</sub>)<sub>3</sub>  $_{5}$ H<sub>2</sub>O (99.9%, Aladdin), ZrO(NO<sub>3</sub>)<sub>2</sub> xH<sub>2</sub>O (99.5%, Aladdin), Al(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O (99.0%, Aladdin) and C<sub>2</sub>NbO<sub>4</sub> (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°C for 7 h to evaporate solvent under magnetic stirring. The obtained sol was carbonized at 250°C for 5 hours and then eventually became gel. After the above product was grinded, it was calcined in a muffle furnace at 850°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<sub>2</sub>**

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 °C 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  $\,^{\circ}$ C for more than 10 h. The flowerlike CeOHCO<sub>3</sub> microspheres were finally obtained.

The flowerlike CeO<sub>2</sub> microspheres were obtained from the as prepared CeOHCO<sub>3</sub> microspheres via a two-step calcination procedure. First, the as-prepared products were calcined under Ar with a flow rate of 10 mL min<sup>-1</sup> in a tube furnace at 600  $^{\circ}$ C for 6 h. Then, the obtained products were calcined in air in a tube furnace at 400  $^{\circ}$ C for 4h.

# **Preparation of Ru-CNTs**

30 mg of RuCl<sub>3</sub> (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 °C 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 °C, then heated to 180 °C for 10 hours before being used.

## **Preparation of LiFePO<sub>4</sub> 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  $\mu$ m, HF-Kejing Technology Co., Ltd.) and was dried at 120°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<sub>2</sub> powder. (c) SEM image of the FL-CeO<sub>2</sub>. (d) Nyquist plots, (e) Linear sweep voltammograms (LSV) curves and (f) The histogram of Li<sup>+</sup> transfer number ( $t_{Li^+}$ ) of various electrolyte membranes with commercial bulk ceria (B-CeO<sub>2</sub>) and FL-CeO<sub>2</sub>.



**Fig. S2** Current-time profile of a symmetrical Li|PVDF-HFP/LiTFSI/LLZO/x-CeO<sub>2</sub>|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<sub>2</sub> cell with  $PVDF-HFP/LiTFSI/LLZO/FL-CeO_2$  electrolyte membrane. (b) Cycle performances of the solid-state Li-O2 cell with the PVDF-HFP/LiTFSI/LLZO/FL-CeO2 electrolyte membrane. (c) Discharge-charge profiles of the solid-state Li-O2 cell with the PVDF-HFP/LiTFSI/LLZO electrolyte membrane. (d) Cycle performances of the solid-state Li-O2 cell with the PVDF-HFP/LiTFSI/LLZO electrolyte membrane. All the tests were performed at a current density of 200 mA  $\rm g^{\text{-1}}$  with a limited capacity of 500 mAh  $\rm g^{\text{-1}}.$ 



**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<sup>-2</sup>, respectively.



Fig. S6 Long-term cycling performance of LiFePO<sub>4</sub>|CSEs|Li at 0.5 C.

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

**Table S1.** Comparison of ionic conductivity of the PVDF-HFP/LiTFSI/LLZO/FL-CeO<sub>2</sub> with those electrolytes reported in the literature.

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