Supporting Information

Novel DMSO-based Electrolyte for High Performance Rechargeable Li-O₂ Batteries

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1M LiTFSI/DMSO electrolyte. Dimethyl sulfoxide (DMSO) (>99.5%) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (>99.9%) were purchased from Aladdin. DMSO was distilled before use and LiTFSI was dried under vacuum oven to remove moisture. 1 M LiTFSI/DMSO electrolyte was prepared under in argon-filled glove box.

Oxygen electrode. A slurry with 90 wt % commercial KB carbon (EC600JD) and 10 wt % polyvinylidenefluoride (PVDF) in 5 mL of N-methyl-2-pyrroli-dinone (NMP) is brushed onto Ni foam (110 PPI, 420 g m^{-2}) and dried at 80°C for 24 h as cathode.

Li- O_2 batteries. Use the as-prepared O_2 electrode as cathode, glass fiber membrane (Whatman) as separator and Lithium metal as anode to assemble Li- O_2 batteries. All procedures are carried out in a argon- filled glove box with oxygen and water contents below 1 ppm. The electrochemical characterizations were carried out using 2025-type Coin cell and Swagelok cell (Fig. S2). The cell was gas tightness excepting for the stainless steel mesh window that is exposed the porous cathode to O_2 atmosphere.

Characterization. Li-O₂ batteries run under 1 atm O₂ pressure at 25 $^{\circ}$ C and electrochemical performances were recorded on Land batteries system in a voltage range of 2.2-4.3 V at constant current density. The cyclic voltammetry was carried out in a conventional airtight three-electrode cell containing 1 M LiTFSI in pure PC electrolyte at room temperature. The electrochemical cell designed and built in-house consisted of a traditional three-electrode system utilizing Ag/AgCl as the reference electrode and platinum wire as the counter electrode. This reference electrode was

used instead of the Li foil electrode typically used in Li⁺ conducting electrolytes because of its instability as a reference electrode in this electrolyte. The Ag/AgCl gives a voltage of 3.72 V versus Li⁺/Li, as measured using a Li foil reference electrode in a LiTFSI solution in DMSO. The cathode morphologies of the samples were observed using a Hitachi S-4800 filed emission scanning electron microscope (SEM). Powder X-ray diffraction (XRD) was carried out using a Rigaku-Dmax 2500 diffractometer with a Cu K α X-ray radiation at the angle range of 30–70°.

Novel graphene oxide-derived carbon cathode: The porous graphene oxide-derived carbon electrodes were prepared using traditional organic sol-gel method. In a typical preparation process, GO (4.5 mL, 1 wt%) solution was dispersed by sonication for 4 h and then resorcinol (110 mg), formaldehyde solution (36 wt%, 160 mg), and sodium carbonate catalyst (1 mg) were added in the GO solution. The amount of resorcinol and formaldehyde (RF solids) was 4 wt%. After stirring for 2 h, the sol-gel mixture was dropped into the nickel foam disks and then transferred to glass molds, sealed and cured in an oven at 85 °C for 48 h. The water in the resulting gels was removed from the pores of gel network by a frozen-dry technology. The dry gels embedded in the nickel foam were carbonized in N₂ at 800 °C for 2 h and the obtained products were FHPC electrodes that could be directly used as cathode of Li-O₂ batteries. The mass of carbon in the nickel foam was measured by sonication of FHPC electrode and etching Ni particles with HCl solution. In average, each electrode has 0.8 mg carbon.



Fig. S1 (a) Electrochemical window (versus Li^+/Li) of 1 M LiTFSI/DMSO electrolyte under Ar atmosphere, and (b) Cyclic voltammogram of 0.1 M LiTFSI/DMSO under O_2 atmosphere.

Solvent	Boiling point(°C)	O ₂ solubility (mM/cm ⁻³)	O ₂ diffusion coefficent	Conductivity (mS/cm)	Viscosity (cP)	ε (25°C)
TEGDME	275	4.43	2.17×10 ⁻⁶	0.3	4.05	7.8
DMSO	18 9	2.10	1.67×10 ⁻⁵	2.11	1.95	48.0

Fig. S2 Properties of DMSO based electrolyte.



Fig. S3 Charge curve of DMSO based electrolyte under 1 atm O₂ pressure.



Fig. S4 Digital pictures of real Li-O₂ batteries.



Fig. S5 SEM images of fresh O_2 electrode with KB carbon on Ni foam.



Fig. S6 SEM images of O_2 electrode after discharge on KB carbon based cathode.



Fig. S7 XRD spectrums of discharged and charged cathode.



Fig. S8 Discharge and charge curve of Li-O₂ battery with PC based electrolyte.



Fig. S9 Discharge and charge curve of Li-O₂ battery with TEGDME based electrolyte