Supporting Information

A Stable Sulfone Based Electrolyte for High Performance Rechargeable Li-O$_2$ Batteries

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Experiment section

Reagents. Tetramethylene sulfone (TMS), dimethyl sulfoxide (DMSO), propylene carbonate (PC), tetraethylene glycol dimethyl ether (TEGDME), dimethoxy ethane (DMF), and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) were purchased from Aladdin. All electrolytes were prepared in argon-filled glove box.

Li-O$_2$ batteries. Slurry with 90 wt% commercial KB carbon (Ketjen Black EC600JD) and 10 wt% polyvinylidenefluoride (PVDF) in N-methyl-2-pyrrolidinone was brushed onto Ni foam (110 PPI, 420 g m^{-2}) and dried as O$_2$ electrode. The as-prepared carbon electrode with loading of 1 mg$_{carbon}$/cm^2 was used as cathode, glass fiber membrane (Whatman) as separator and lithium metal as anode to assemble Li-O$_2$ batteries. All procedures were carried out in argon-filled glove box with oxygen and water contents below 1 ppm. All batteries were assembled with Swagelok and gas tightness except for the stainless steel mesh window exposed to the porous cathode to O$_2$ atmosphere.

Characterization. Li-O$_2$ batteries run under 1 atm O$_2$ pressure at 25 ^{o}C and electrochemical performances were recorded on Land Battery Testing System within a voltage range of 2.2-4.5 V at constant current density. Other electrochemical measurements were investigated using VMP3 Biologic electrochemical workstation. Electrochemical window of electrolytes was examined from 0 to 6 V at scan rate of 0.5 mV/s under Ar atmosphere. The cyclic voltammetry (CV) was carried out in both an airtight three-electrode cell (50 mV/s) and a two-electrode Li-O$_2$ cell (0.1 mV/s) containing 1 M lithium electrolyte saturated with O$_2$. The morphologies of O$_2$

electrode were observed using a Hitachi S-4800 filed emission scanning electron microscope (SEM). Powder X-ray diffraction (XRD) was performed on Bruker D8 Focus Powder X-ray diffractometer using Cu $K\alpha$ ($\lambda = 0.15405$ nm) radiation.

Table **S1.** Comparison of physical/chemical properties of DMSO and TMS.

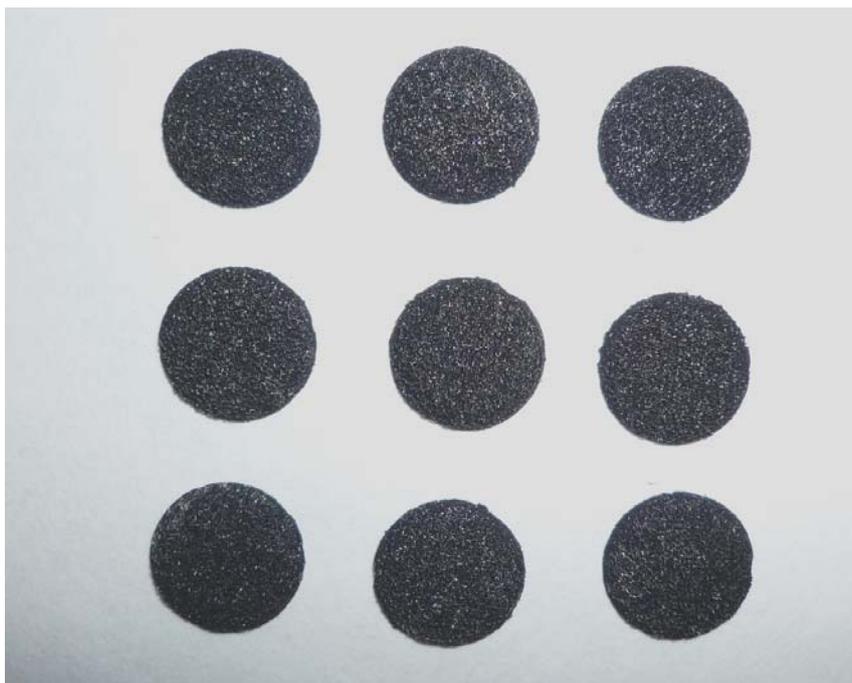|	DMSO	TMS
Formula		
Boiling point (B.P.)	189 °C	285 °C
Melting point (M.P.)	18 °C	28 °C
Vapor pressure (20 °C)	0.42 mm Hg	0.01 mm Hg
Oxidation potential	4.8 V	5.6 V

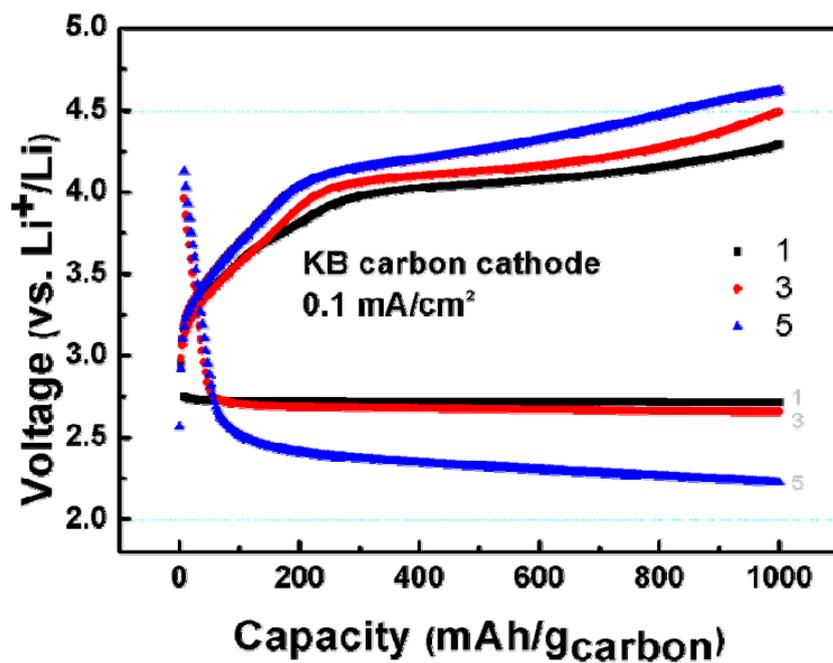**Fig. S1** Optical images of as-prepared O_2 electrodes.

Fig. S2 Cycle performance of Li-O_2 battery with TMS based electrolyte using
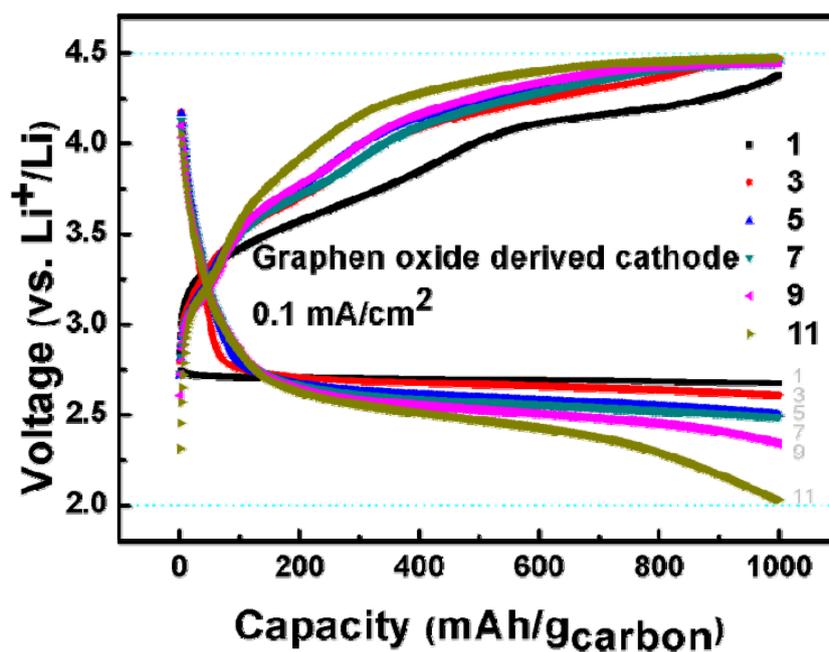
KB carbon cathode.

Fig. S3 Cycle performance of Li-O$_2$ battery with TMS based electrolyte using advanced graphene oxide derived cathode.
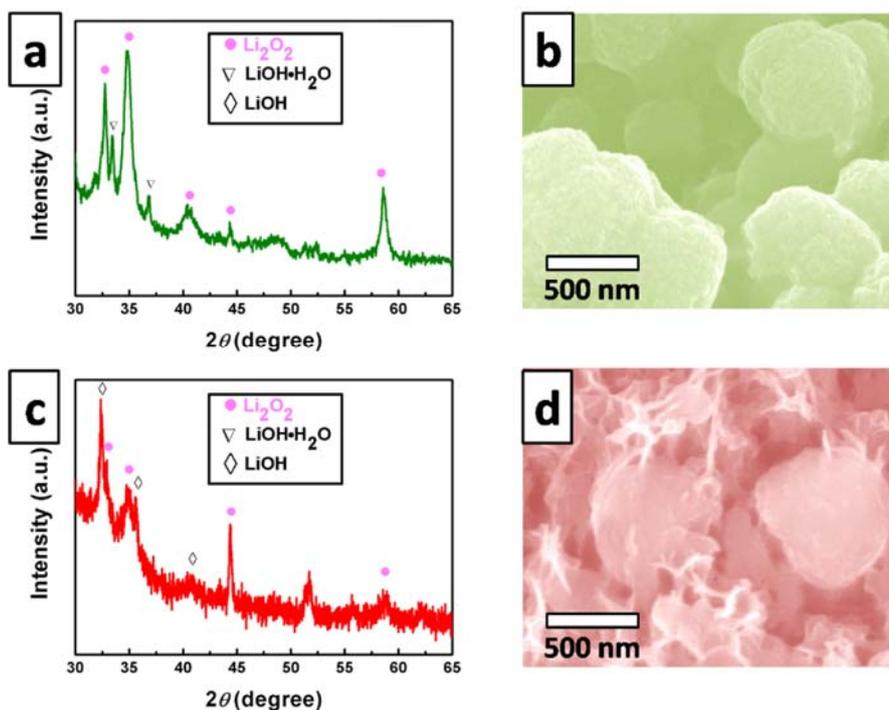
Fig. S4 XRD profiles and SEM images of discharged products in O_2 electrode in TMS

(a, b) and DMSO (c, d) based electrolyte.

Fig. S4 compares the XRD profiles and SEM images of discharged product of Li-O_2 battery with DMSO or TMS based electrolyte. Interestingly, when carbon is employed as the cathode material, the dominance of Li_2O_2 can be clearly found in the discharged product of Li-O_2 battery with TMS based electrolyte (Fig. S4a), but not with DMSO based electrolyte (Fig. S4c). In addition, the morphology of Li_2O_2 in TMS and DMSO and found to be quite different. Only pure Li_2O_2 spheres is found in the discharged electrode with TMS (Fig. S4b). But with DMSO, Li_2O_2 is shown to be broken and accompanied with LiOH and LiOH.H_2O nanosheets (Fig. S4d).
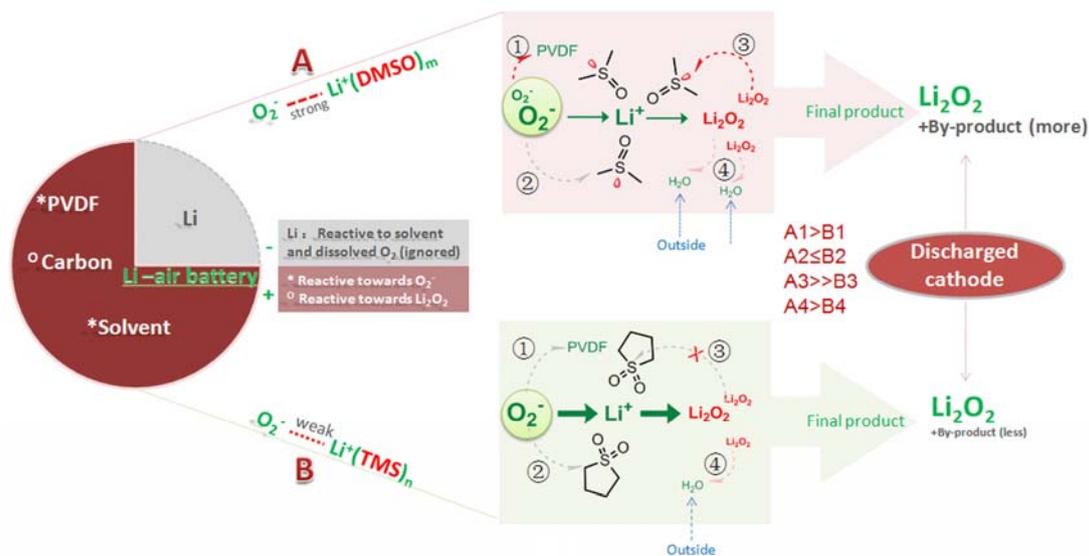
Fig. S5 Proposed mechanism of reactions in Li-O$_2$ battery with (a) DMSO and (b) TMS based electrolyte.

In a Li-air battery, many side reactions could happen in cathode due to the very active O$_2^-$ and/or Li$_2$O$_2$ induced degradation and/or decomposition of solvent and binder (PVDF) into organic lithium salts and H$_2$O, wherein solvent could play an important role on the extent of such side reaction. For our experiment, the underlying mechanism might be summarized in Fig. S5. For DMSO, due to its strong solvation with Li$^+$, the reaction of O$_2^-$ with Li$^+$ could be hindered and thus the O$_2^-$ could has more chance to decompose electrode components, such as solvent and PVDF. On the other hand, sulphur (S) atom in DMSO is at moderato oxidation state (+4) and could be further oxidized by peroxide oxidant (here Li$_2$O$_2$). In addtions, DMSO extremely trends to capture the water (even in trace amount) due to their high dipolarity comparing to other solvents, which leads to a further degradation of Li$_2$O$_2$. On the contrary, TMS holds weaker solvation to Li$^+$ and thus would not impede the reaction

of Li^+ with O_2^-, which could decrease the probability of the side reactions between O_2^- and electrode components. On the other hand, S atom in TMS is already at its highest oxidation state and is hardly to be oxidized further by peroxide oxidant. In addition, TMS possesses more hydrophobic alkyl ($-(CH_2)_4-$) groups than DMSO in its structure, which could decrease the hydrophicility and less Li_2O_2 will be degraded by H_2O. Taken together, TMS can thus support more robust Li_2O_2 than DMSO.

References

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