Supporting Information

A Bi-functional Redox Mediator Promoting ORR and OER for Non-

Aqueous Li-O₂ Batteries

Experimental details

Preparation of positive electrode and electrolyte. The positive electrode was prepared by mixing Ketjen black (KB) and polyvinylidene difluoride (PVDF) in n-methyl pyrrolidone (NMP, Aladdin) with the weight ratio of 2:1. Then the mixture was casted on a nickel foam (Φ 15 mm, 1mm thick). The areal loading of the active material is 1mg cm⁻². The capacities of the batteries were calculated based on the weight of active material. The electrodes were dried at 110 °C in a vacuum oven for 24 h before use. The electrolyte is prepared by dissolving 0.5 M LiTFSI (Aladdin), 0.5 M LiNO₃ (Aladdin) and 5 mM HeptVBr₂ (TCI) in anhydrous diglyme (Aladdin). The HeptV(OTf)₂ was synthesized by dissolving 1g silver trifluoromethanesulfonate (Aladdin) and 1g HeptVBr₂ in 30 ml deionized water. Then the solution was stirred at room temperature for 1h. After removing the pale yellow precipitate (AgBr) by centrifugation, the clear solution was dried in a rotary evaporator at 50 °C in order to obtain the final product.

Electrochemical measurements. The testing cells were assembled and tested in CR2032 coin cells with punched cathode shells (as shown in **Figure S7**). Polished Li metal foil (China Energy Lithium) was used as anode and Whatman glassfibre was used as separator. In total 200 μ L of the electrolyte was added into the cell. The cells were assembled in an Ar-filled glovebox with water and oxygen level less than 0.1ppm. The cyclic voltammetry (0.2 mV s⁻¹) data were collected with a CHI600E electrochemical workstation basing on a three-electrode system. The charge and discharge performances were tested in an O₂-saturated box and no more O₂ was added into the box during testing.

Characterization methods. The scanning electron microscopy was carried out using ZEISS Supra 55 scanning electron microscopy. Raman spectroscopy was carried out using Olympus BX41 Raman spectrometry.

Additional Tables and Figures.

Table S1. Representative works and rate performances of Li-O ₂ batteries in recent year
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	Cathode	Electrolyte	Highest i/ mA cm ⁻²	Capacity/ mAh g ⁻¹	Areal Loadin g/ mg cm ⁻²	Ref
Heterogeneous catalyst	CeO_2 : Super P = 1:1	1M LiNO ₃ in DMAc	0.32	1000	0.16	1
	Cobalt in nickel form	0.5 M LiClO ₄ in DMSO	0.132	1000	0.33	2
	NiMn ₂ O ₄ : Super P: PVDF= 3:6:1	1M LiTFSI in TEGDME	0.176	900	0.44	3
	Co ₉ S ₈ @C: Super P: PTFE 6:3:1	1M LiTFSI in TEGDME	0.15	500	0.5	4
	Doped CNT/graphe ne frameworks : KB: PTFE= 6:3:1	1M LiTFSI in TEGDME	0.5	1500	0.62	5
Homogeneous redox mediator	Carbon fiber or graphene	0.1 M LiTFSI+ 2 mM FePc in TEGDME / DMSO	0.5	3500 (Complete discharge)	0.25	6
	Carbon-fibre gas diffusion layer	1 M LiTFSI + 10 mM DBBQ in TEGDME or DME	2	90 (mAh m ⁻² Complete discharge)	N/A	7
	Nanoporous gold electrode	1 M LiClO ₄ + 10 mM TTF in DMSO	1	300	0.15 - 5	8
	Ketjen black	0.1 M LiTFSI + 10 mM TEMPO in diglyme	1	1000	0.225- 0.375	9
	CNT fibrils	1 M LiTFSI + 0.05 M LiI in TEGDME	0.048	1000	0.008	10
	Ketjen black: PVDF= 2:1	0.5 M LiTFSI + 0.5 M LiNO ₃ + 5 mM HeptVBr ₂	4	1200 1800 (Complete discharge)	1	This work



Figure S1. The molecular structure of HeptVBr₂.



Figure S2. Discharge profile of the cell with HeptVBr₂ at the current density of 4 mA cm⁻².



Figure S3. The cycling performance for Li-O_2 cells (a) without and (b) with HeptVBr₂ at the current density of 2 mA cm⁻².



Figure S4. Raman spectra of discharged cathode for different batteries.



Figure S5. SEM images of discharged cathode at the current density of 0.02 mA cm⁻².



Figure S6. Charging profiles for $Li-O_2$ cells (a) without and (b) with HeptVBr₂ at various current densities.



Figure S7. The punched cathode shell.

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