Supporting Information

**Dual redox catalysts for oxygen reduction and evolution reactions: towards a redox flow Li-O$_2$ battery**

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**Materials and Methods**

**Materials**

Tetraethyleneglycol dimethylether (TEGDME, 99%, Sigma-Aldrich) and lithium bis(trifluoromethane)sulfonimide (LiTFSI, Sigma-Aldrich) were used as solvent and lithium salt for electrolyte preparation. Ethyl viologen diperchlorate (EV, 98%, Sigma-Aldrich) and LiI (99%, Sigma-Aldrich) were employed as redox mediators for oxygen reduction and evolution reactions, respectively. Vinylene carbonate (VC, 97%, Sigma-Aldrich) was used to passivate Li metal and promote the formation of solid electrolyte interface (SEI) film on lithium surface. Prior to use, all the above chemicals were stored in an argon-filled glove box without exposure to air.

**RFLOB Cell assembly**

Lithium foil was pretreated by immersing in 1 M LiTFSI-TEGDME electrolyte containing 5 vol.% VC for 24 h and used as anode. Carbon felt was used as cathode current collector. The electrochemical cell was fabricated by sandwiching the lithium foil and carbon felt in a cell stack made of stainless steel, in which the two electrodes are separated by a Celgard 2300 separator. The size of the electrode is 2 cm $\times$ 2 cm. The gas diffusion tank (GDT) is made of a glass vial loaded with nickel foam to construct gas diffusion layers and provide deposition site
for Li$_2$O$_2$. 8 ml electrolyte consisting of 10 mM LiI and 10 mM EV in 1 M LiTFSI-TEGDME was prepared and transferred into the GDT tank. The GDT tank has an inlet and an outlet for the electrolyte fluid and oxygen, respectively, and is connected with the electrochemical cell. Electrolyte fluid is circulated between the cell and tank by a peristaltic pump. The cell used for cycling test was fabricated with PVDF-Nafion membrane in place of Celgard separator. To speed up the testing, 4 ml electrolyte consisting of 10 mM LiI and 10 mM EV in 1 M LiTFSI-TEGDME was used. The preparation and evaluation of the PVDF-Nafion membrane will be reported elsewhere since it is beyond the scope of this study.

**Electrochemical measurements**

Cyclic voltammograms of the two redox molecules were measured with a three-electrode system at different scan rates (0.01, 0.02, 0.05, 0.1, 0.2 V/s). Lithium metal was used as counter and reference electrodes, and a Pt disk was used as the working electrode. The battery was tested at galvanostatic mode at different current densities. All the above electrochemical measurements were performed on an Autolab electrochemical workstation (Metrohm Autolab, PGSTAT302N).

**Characterizations**

Field emission scanning electron microscopy (FESEM) images were obtained on a Zeiss Supra 40 field-effect scanning electron microscope. Prior to the FESEM measurement, the Ni foam was taken out of the GDT tank and washed by acetonitrile for three times before drying in a vacuum oven at 80 °C for 24 h. High-resolution transmission electron microscopy (HRTEM) images were recorded with JEOL 3010F. The Ni foam sample was washed in acetonitrile for three times and sonicated for 20 min. The suspension was collected and dropped onto copper mesh for TEM measurement. The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos Analytical Axis Ultra DLD Spectrometer. All the
samples were protected by argon during the preparation and transfer processes. Powder X-ray diffraction (XRD) pattern was measured by a powder diffractometer (Bruker D8 Advanced Diffractometer System) with Cu Kα (1.5418 Å) source. The samples were sealed by Kapton film in the glove box with argon and then transferred outside to take XRD measurement.

Computation Method

A two-dimensional slab model was adopted to simulate the stable Li$_2$O$_2$ (0 0 0 1) surface. First-principles calculations were performed by using the plane-wave technique implemented in Vienna ab initio simulation package (VASP). The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional has been employed to describe the exchange-correction potential in all calculations. Projector-augmented wave potentials were employed to describe the electron-ion interaction and a cutoff energy is set to 400 eV.
In general, one should note that these two molecules would not chemically react with each other upon operation. During discharging, both of the molecules will subsequently be reduced to I⁻ and EV⁺ in the cell. Similarly during charging, both of molecules will subsequently be oxidized to EV²⁺ and I₂. So it is unlikely that both I₂ and EV⁺ co-exist in the catholyte causing reaction between the two.

As a preliminary proof-of-concept study, we do not attempt to study the influences of the flow rate and other operation parameters on the overall device performance before the following factors are optimized: firstly, the PVDF–Nafion membrane is resistive, which makes up a big IR drop. Secondly, the sluggish reaction between I₂ and Li₂O₂ and those of I⁻ on the electrode account for a major loss of overpotential during charging. As a result, the discharging/charging current density is relatively low.

**Figure S1.** CV curves of 5 mM EV (a) and 5 mM LiI (b) in 1 M LiTFSI-TEGDME electrolyte at various scan rates (0.2, 0.1, 0.05, 0.02, 0.01 V/s). (c) Charge/discharge curves of 5 mM EV and 5 mM LiI in static cells with PVDF-Nafion membrane. The current density is 0.05 mA/cm².
Figure S2. Electron density difference maps associated with the interactions in Li$_2$O$_2$/I$_2$ (a) and Li$_2$O$_2$/I$_3^-$ system (b). Isovalues: |0.0012 a.u.|. I$_2$ and I$_3^-$ are adsorbed on the (0001) surface of Li$_2$O$_2$ in parallel adsorption geometry. The blue and yellow zones correspond to electron density deduction and enhancement regions, respectively.

Figure S3. Charge and discharge curves of RFLOB in the absence of redox mediators in the electrolyte. The current density was 0.05 mA/cm$^2$. 
Figure S4. XRD pattern of the discharging products deposited on Ni foam in the GDT tank. Diffraction peaks from Li$_2$O$_2$ are clearly identified (JCPDS File No. 01-074-0115) besides those from Ni foam.

Figure S5. SEM photos show the morphology of pristine nickel foam before (a) and after (b) fully discharging the cell as indicated in Fig.2c.
Reference