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Supporting Information

Redox Flow Lithium Battery Based on the Redox Targeting Reactions between $LiFePO_4$ and Iodide

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Experimental Section

Materials: Lithium bis(trifluoromethane)sulfonimide (LiTFSI, Sigma-Aldrich), Tetraethyleneglycol dimethylether (TEGDME, 99%, Sigma-Aldrich), $LiFePO_4$ (Li-Cell, China), lithium iodide (LiI, 99.9%, Sigma-Aldrich), Polyvinylidene fluoride (PVDF, Alfar aesar), Dimethylformamide (DMF, 99%, Sigma-Aldrich), Lithium hydroxide (LiOH, 98%, Sigma-Aldrich), fluorine-doped tin oxide (FTO, Pilkington TEC-15) glass and Nafion 212 membrane (Ion Power. Inc) were used as received.

Preparation of the lithiated Nafion/PVDF membrane: The detailed preparation procedures of the lithiated Nafion/PVDF membrane were described elsewhere[1]. 250 mg dry Nafion 212 membrane and 125 mg dried PVDF powder were added into 5 mL DMF solvent. The mixture was vigorously stirred at room temperature for 4 h and then placed in an ultrasonic bath for 20 minutes to dissolve the Nafion membrane and the PVDF powder. Afterwards, the solution obtained was poured into a petri dish with a diameter of 7 cm and dried in an oven at 80 ^{O}C for 3 h, followed by heating to 140 ^{O}C for 16 h to remove the solvent. The cast membrane cooled to room temperature naturally. The cast membrane was first boiled in 0.5 M H_2SO_4 at 80 ^{O}C for 2 h, followed by 1 M LiOH solution at 80 ^{O}C for 2 h. After rinsing in deionized water and drying in oven at 80 ^{O}C overnight, the lithiated Nafion/PVDF polymeric membrane is ready for use.

Cross-diffusion of I_2 was investigated by ultraviolet-visible spectrophotometry (UV-Vis) using a Shimadzu UV-vis-NIR spectrophotometer (Solidspec-3700). Both catholyte and anolyte contain 1 M LiTFSI/TEGDME. 0.1 M of I_2 was added to the catholyte. The catholyte and anolyte were separated by the lithiated Nafion/PVDF membrane as shown in **Fig. S1**. The anolyte was extracted after 3 days and 1 week respectively for the UV-Vis test. Any I_2 species that came from the catholyte by diffusion across the membrane would be detected by the UV-Vis spectra. The samples were diluted 200 times before the test and freshly prepared 1 M LiTFSI/TEGDME was used as the reference. No sign of crossover of the I_2 species across the membrane was detected after 1 week.

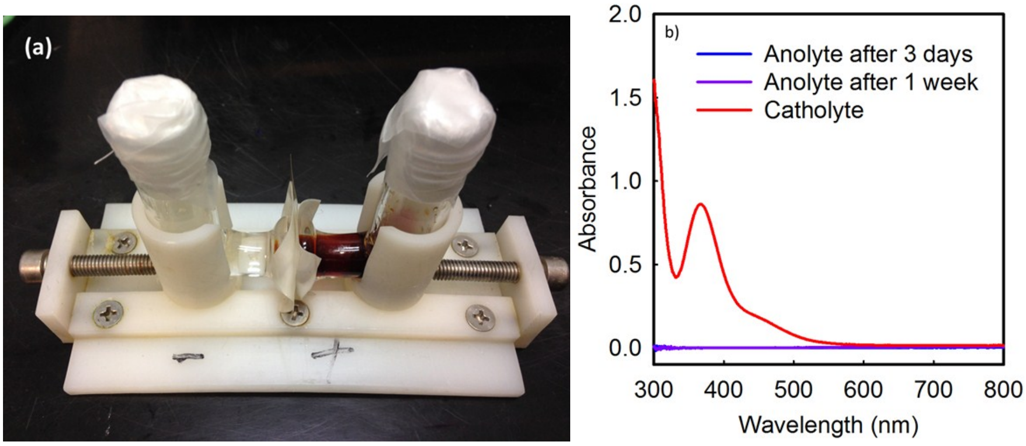

Fig. S1. (a) glass cell setup for crossover test. The compartment on the right contains catholyte which consists of 0.1 M I2 in 1 M LiTFSI/TEGDME. The compartment on the left contains anolyte which consists of 1 M LiTFSI/TEGDME. (b) UV-Vis spectra of the 200 times diluted catholyte and anolyte.

Voltammetric and chronopotentiometric measurements were performed with a potentiostat (Autolab PGSTAT 302N/FRA2, Ecochemie) controlled by the Nova 1.9 software package. All the electrochemical measurements were conducted in an argon-filled glove-box at room temperature.

The structure of the half cell is illustrated in **Figure 1**. The anode was lithium foil and a stainless steel plate was the current collector. The separator used was the PVDF polymeric membrane. The gasket material is nitrile rubber. On top of the cathodic titanium end plate, a layer of carbon felt functions as the current collector. The effective area of the membrane is 4.0 cm^2. In the anodic compartment, lithium foil is secured on the stainless steel plate. Both the anodic and cathodic compartments share a common electrolyte (1 M LiTFSI in TEGDME). In the cathodic compartment, various concentration of LiI is added to the electrolyte and a piece of carbon felt serves as the cathode. $LiFePO_4$ remains in the cathodic reservoir throughout the reaction. The cathodic electrolyte was circulated between the cathodic reservoir and the cathodic compartment by a peristaltic pump. The flow rate was set at constant 90 ml min^{-1}.

Powder X-ray diffraction (XRD) measurements of $LiFePO_4$ and $FePO_4$ particles (porous granule around 1 mm in diameter with BET surface area 20~30 m^2 g^{-1}) after chemical delithiation/lithiation was carried out on a Bruker D8 with Cu Kα1 radiation (λ = 0.154059 nm). $FePO_4$ powder was oxidized from $LiFePO_4$ by adding excess amount of nitrosoniumtetrafluoroborate ($NOBF_4$, Sigma Aldrich, 95%) in the electrolyte under Ar atmosphere. The mixtures were stirred rigorously for 24 hours to ensure complete reaction. $FePO_4$ powder was then separated from the solution by repeated centrifuging and rinsing in ethanol. The collected $FePO_4$ powder was further dried at 120 °C in vacuum for 2 days. I_2 solution was obtained by the oxidation of LiI similarly by $NOBF_4$. To study the process of chemical delithiation, 6.3 mg of $LiFePO_4$ was added into 10 ml of 20 mM I_2 solution and vigorously stirred for 2 minutes. The powder was then separated from the solution by repeated centrifuging and rinsing in ethanol. After drying at 120 °C in vacuum for 2 days, the powder underwent XRD and FTIR characterization. The same procedure was repeated for 20 minutes reaction time. To study the process of chemical lithiation, 6.0 mg of $FePO_4$ reacted with 10 ml of 20 mM LiI solution in a similar way. The reaction time varied from 1 hour to 2 hours.

$LiFePO_4$ samples were extracted after charge and discharge and sent for XRD measurement (**Fig. S2**). The results are consistent with those obtained from the chemical lithiation/delithiation tests.

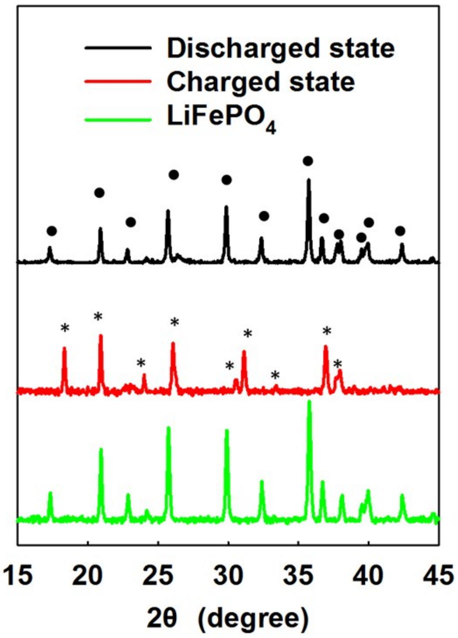

Fig. S2. XRD patterns of $LiFePO_4$ after charge and discharge in the half cell. * represents the peaks of $FePO_4$ and ● represents the peaks of $LiFePO_4$.

Voltage profile of Li-I RFLB half cell: The charge/discharge profile of the 1st, 10th, 20th and 40th cycles of the half cell is shown in **Fig. S3**.

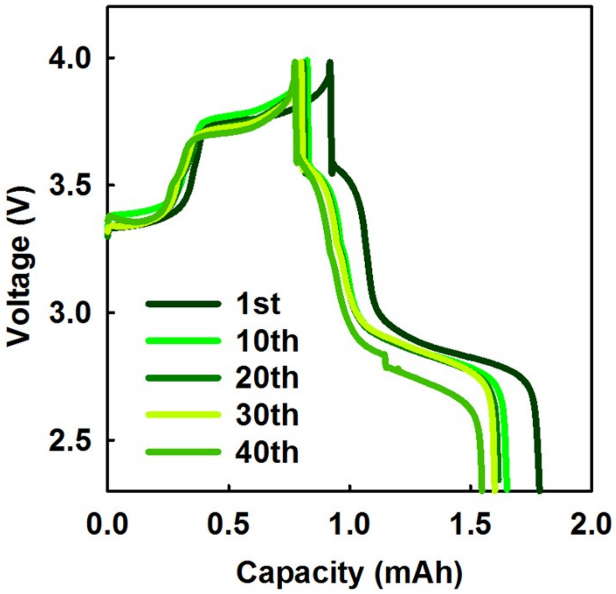

Fig. S3. Charge/discharge profile of the Li-I RFLB cell containing 10 mM LiI with 6.4 mg $LiFePO_4$ (20 mM equivalent concentration) loaded in the cathodic reservoir in 2 ml catholyte.

Computational details: First-principles calculations were applied to study the interaction of redox molecule and the electrode ($I_2/LiFePO_4$ and $I^-/FePO_4$). All calculations were performed within the Vienna Ab-initio Simulation Package (VASP).[2-5] To overcome the failures in density functional theory (DFT) descriptions of transition metal oxides result from the over delocalization of electrons, the spin-polarized, DFT+U approach of Dudarev et al. was employed to ameliorate these errors.[6] A U−J correction of 4.3 eV was added via the Dudarev functional in combination with the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional.[7] Such a value has been successfully applied to describe the F3-3*d* electron in $LiFePO_4$ and $FePO_4$.[8-11] We used an energy cutoff of 500 eV for the plane wave basis set for all systems to ensure equal footing. The energy relaxation for each strain step is continued until the forces on all the atoms are converged to less than 1×10^{-2} eV·Å. A two-dimensional slab model was adopted to simulate the stable $LiFePO_4$ (010) and $FePO_4$ (010) surface. The charge density difference is defined as the charge density difference before and after the interaction between the redox molecule and the electrode as shown in **Equation S1**:

$$\Delta\rho = \rho_{Redox/electrode} - \rho_{redox} - \rho_{electrode} \quad \textbf{(S1)}$$

Estimation of energy density: Density of pure $LiFePO_4$ is 3.6 g cm^{-3}. Assuming 50% porosity of $LiFePO_4$, the volumetric energy density (VED) could be estimated with the **Equation (S2)**:

$$VED = Q_{LiFePO_4} \cdot \rho \cdot 0.5 \cdot E \quad \textbf{(S2)}$$

where VED is the volumetric energy density (Wh L^{-1}), Q_{LiFePO_4} is the specific capacity of $LiFePO_4$, (0.12 Ah g^{-1}) ρ is the density of $LiFePO_4$ (3600 g L^{-1}) and E is the average discharge voltage of the cell (3.1 V). The volume in the pores will be occupied by the electrolyte. Therefore, the LiI electrolyte will not affect the volumetric energy density.

The gravimetric energy density (GED) could be estimated with the **Equation S3**:

$$GED = Q_{LiFePO_4} \cdot E \quad \textbf{(S3)}$$

where GED is the gravimetric energy density (Wh g^{-1}), Q_{LiFePO_4} is the specific capacity of $LiFePO_4$, (120 Ah kg^{-1}) and E is the average discharge voltage of the cell (3.1 V).

We believe that these values are theoretic ones under ideal conditions and based on $LiFePO_4$ alone. When system components such as pumps, containers and cells are taken into consideration, these values would certainly be lower in practical devices. However, it is possible to increase the volumetric energy density close to the 670 Wh L^{-1} if the tank size is large enough so that the most space occupied by the Li-RFLB system is filled by the 50% porous active solid material.

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