

## **Supporting Information for**

# **Polyprotic Acid Catholyte for High Capacity Dual-electrolyte Li-air Batteries**

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## Experiment Section

All experiments were conducted with a layered battery structure described in our previous paper (See ref. 11 in the manuscript). 1 M  $\text{LiPF}_6$  in EC/DEC (1:1 v/v) was used as the electrolyte with the Li anode and 0.1 M  $\text{H}_3\text{PO}_4$ +1M  $\text{Li}_2\text{SO}_4$  was used as the catholyte. A LTAP membrane (0.15 mm thick,  $0.76 \times 0.76$  cm, OHARA Inc., Japan) was used as the separator between the two electrolytes. The air electrode was prepared by spraying the catalyst ink made with Pt/C (40 wt. %, Johnson Matthey),  $\text{IrO}_2$ , and Nafion (5 wt. %, EW1000, Dupont) onto a 10 BA gas diffusion layer (SGL). The Pt loading,  $\text{IrO}_2$  loading, and Nafion content in the air electrode were, respectively,  $1.2 \text{ mg cm}^{-2}$ ,  $1.2 \text{ mg cm}^{-2}$ , and 20 wt. %.  $\text{IrO}_2$  powder was prepared by the modified Adams fusion method.<sup>s1</sup> Two layers of Celgard<sup>®</sup> polypropylene separator were placed between lithium metal anode and the LTAP membrane. The anode side was assembled in an argon-filled glove box, and then combined with the cathode side outside the glove box by adding 0.2 mL catholyte containing 0.1 M  $\text{H}_3\text{PO}_4$  + 1 M  $\text{Li}_2\text{SO}_4$  (the pH measurement of the catholyte during the discharge process was conducted in a cell containing 1 mL catholyte). The cathode side of the cell was purged with water-saturated air during cycling test to suppress the evaporation of water from the catholyte.

An Arbin BT 2000 battery test system was used to conduct discharge-charge tests. Electrochemical impedance spectra (EIS) were recorded at open circuit voltage (OCV) with an impedance analyzer (Solartron 1260 A) in the frequency range of 2 MHz to 1 Hz. The ac voltage amplitude was 10 mV. All pH measurements were conducted with a HI 2223 pH benchtop meter controlled by HANNA HI92000 Windows<sup>®</sup> compatible software and a PerpHecT<sup>®</sup> ROSS<sup>®</sup> combination micro pH electrode. Before each test, the pH electrode was calibrated with three pH buffers: 1.68, 4.01, and 7.01. All tests were conducted at room temperature.

## Rate capability of phosphoric acid catholyte

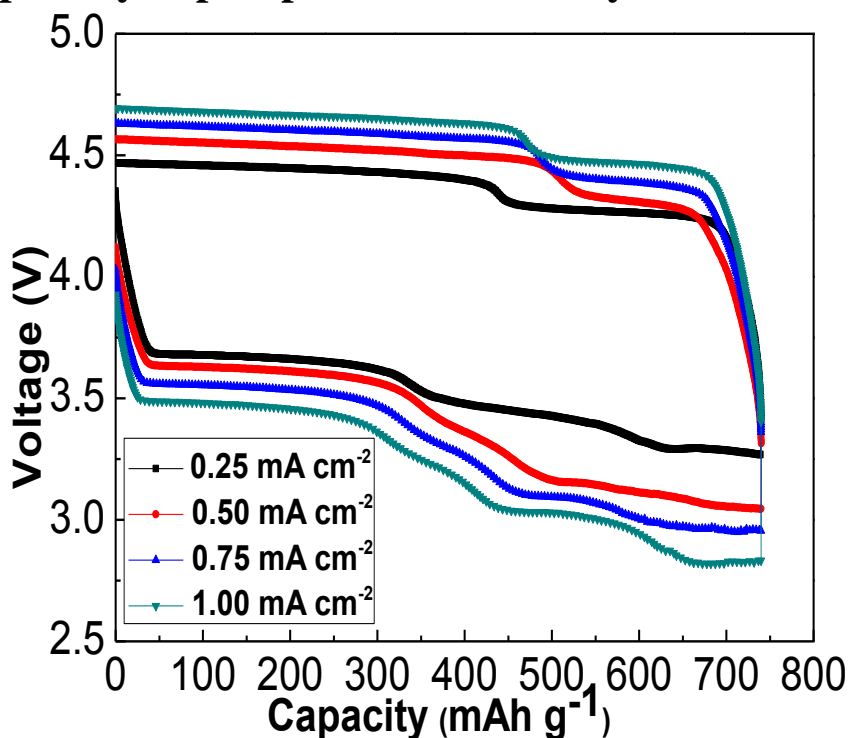


Figure S1. The discharge and charge cycles of the dual-electrolyte Li-air cell at various current densities from 0.25 to 1 mA cm<sup>-2</sup>.

Figure S1 shows the discharge-charge voltage profiles of the dual-electrolyte Li-air cell at various current densities of 0.25 to 1.0 mA cm<sup>-2</sup>. As we increased the current density, the discharge voltage decreased and charge voltage increased, corresponding to an increased overpotential. Although the overpotential increased with current densities, the shapes of the voltage profiles remained almost the same, indicating the distinct battery chemistry of the cell. Another feature of the voltage profiles is that every charge voltage profile has a sharp rise in the middle, which is due to the sharp decrease in pH, which also resembles the sharp increase in pH during the discharge process. Based on the discharge-charge voltage profiles at 0.25 mA cm<sup>-2</sup>,

the round-trip efficiency is > 80%, which is higher than most reported results for aprotic Li-air batteries.

## Reference

(S1)R. Adams and R. L. Shriner, *J. Am. Chem. Soc.*, 1923, **45**, 2171-2179.