

## Supporting Information

### A polymer lithium-oxygen battery based on semi-polymeric conducting ionomer as polymer electrolyte

Chaolumen Wu<sup>a</sup>, Chenbo Liao<sup>a</sup>, Taoran Li<sup>a</sup>, Yanqiong Shi<sup>a</sup>, Jiangshui Luo<sup>c</sup>, Lei Li<sup>a,b\*</sup>, Jun Yang<sup>a</sup>

<sup>a</sup>:Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China

<sup>b</sup>:Shanghai Key Laboratory of Electrical Insulation and Thermal Aging, School of Chemistry & Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China

<sup>c</sup>: Department of Materials Engineering, KU Leuven, Leuven 3001, Belgium

E-mai:lilei0323@sjtu.edu.cn

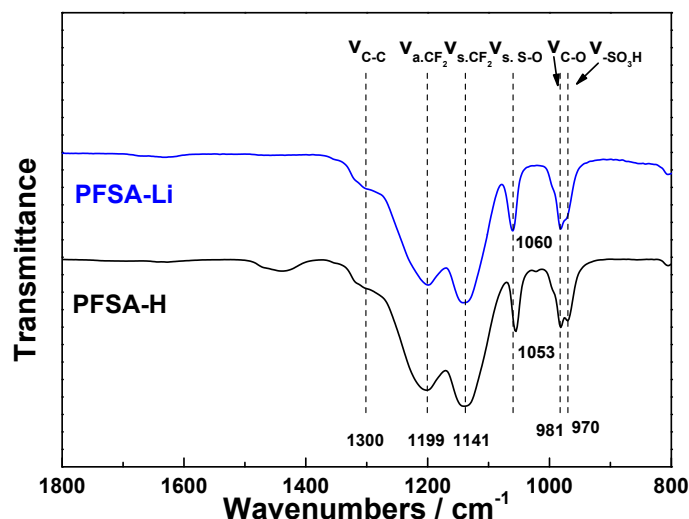
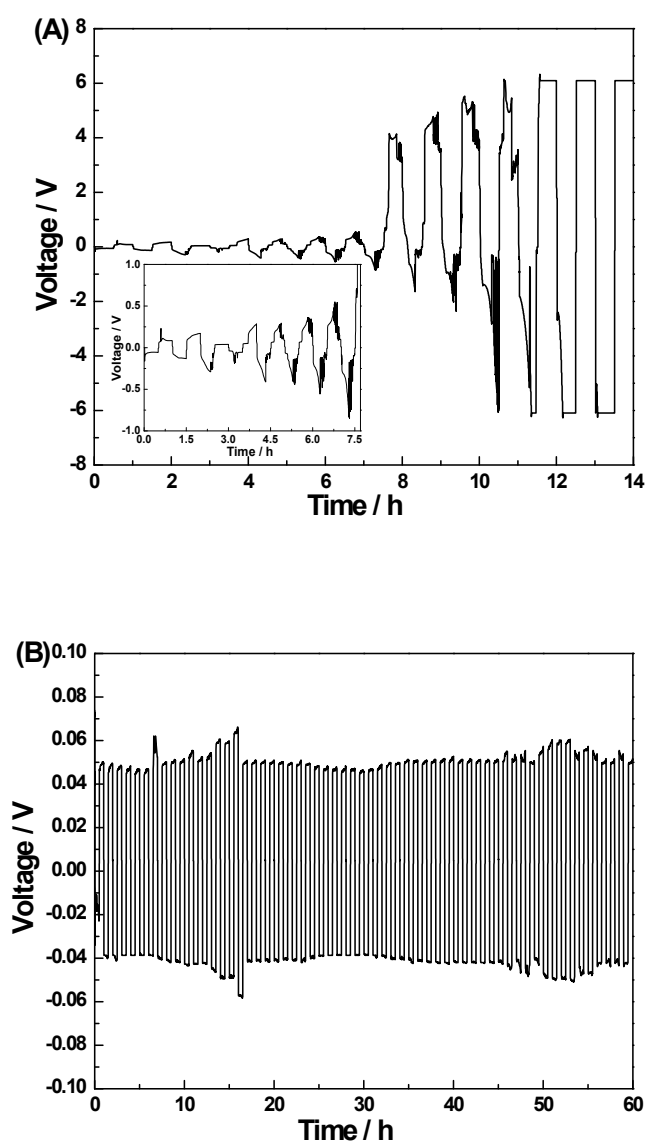


Figure S1 FT-IR spectra of PFSA membranes with H<sup>+</sup> and Li<sup>+</sup> forms.

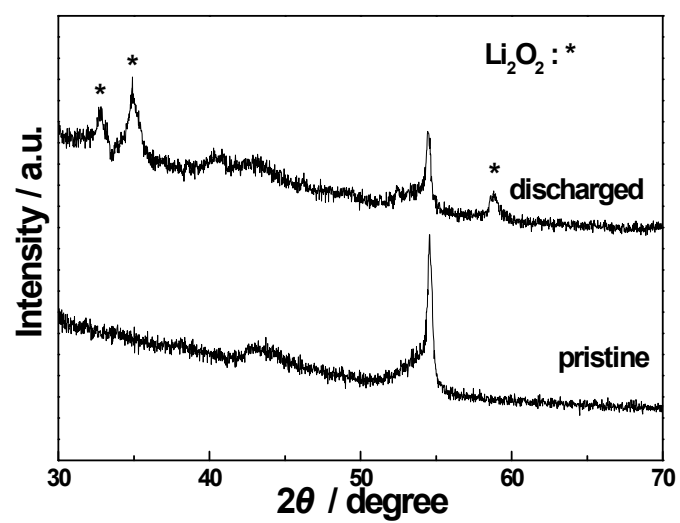
FT-IR spectra of PFSA membranes with the H<sup>+</sup> and Li<sup>+</sup> forms are showed in Figure S3. In the PFSA with the H<sup>+</sup> form, the band at 970 cm<sup>-1</sup> was assigned to -SO<sub>3</sub>H groups.<sup>[S1]</sup> This band disappeared when the H<sup>+</sup> ions of the membranes were exchanged with Li<sup>+</sup> ions. The band at 1053 cm<sup>-1</sup> of the PFSA with H<sup>+</sup> form was attributed to the -SO<sub>3</sub><sup>-</sup> symmetric stretch.<sup>[S2,S3]</sup> Due to the interaction between Li<sup>+</sup> and oxygen, this band shifted to 1060 cm<sup>-1</sup> of the PFSA-Li membrane. These results verify the conversion of the PFSA membranes from the H<sup>+</sup> form to the Li<sup>+</sup> form in our experiments.

\* Corresponding author. E-mail address: lilei0323@sjtu.edu.cn (L. Li).

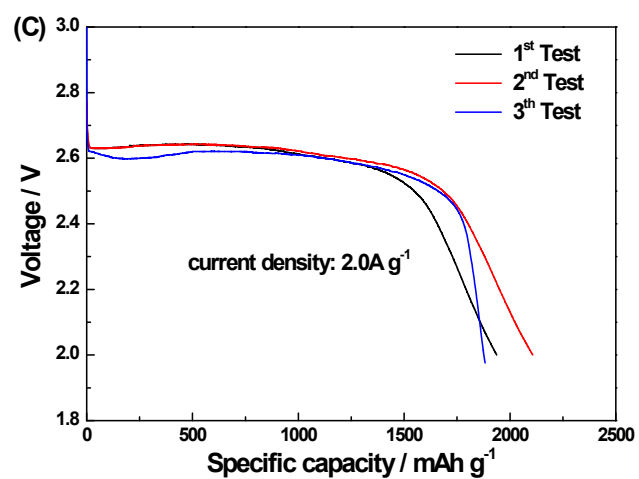
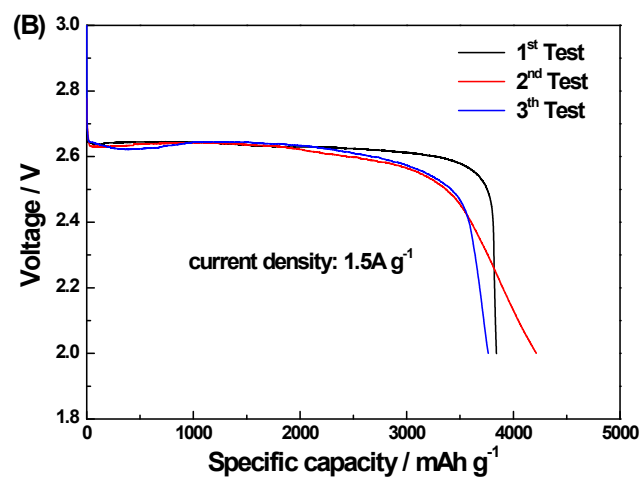
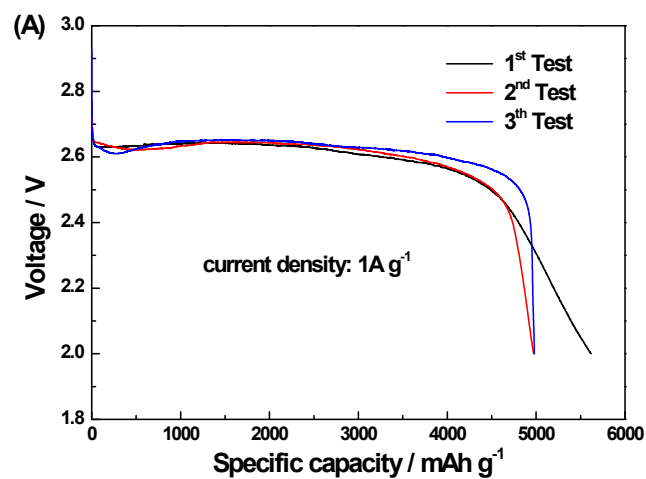


**Figure S2** Voltage-time plots of Li|electrolyte|Li symmetrical cell cycled at 0.25 mA cm<sup>-2</sup> at room temperature. (A) 1M LiTFSI in DMSO conventional liquid electrolyte, (B) PFSA-Li swollen with DMSO polymer electrolyte.

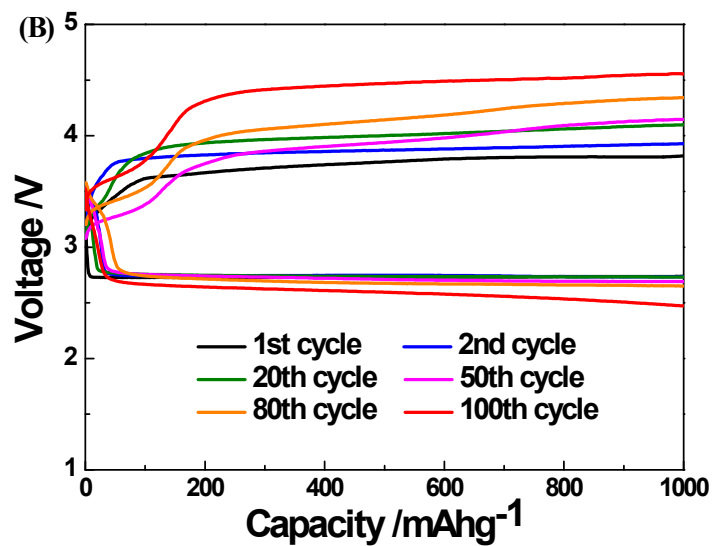
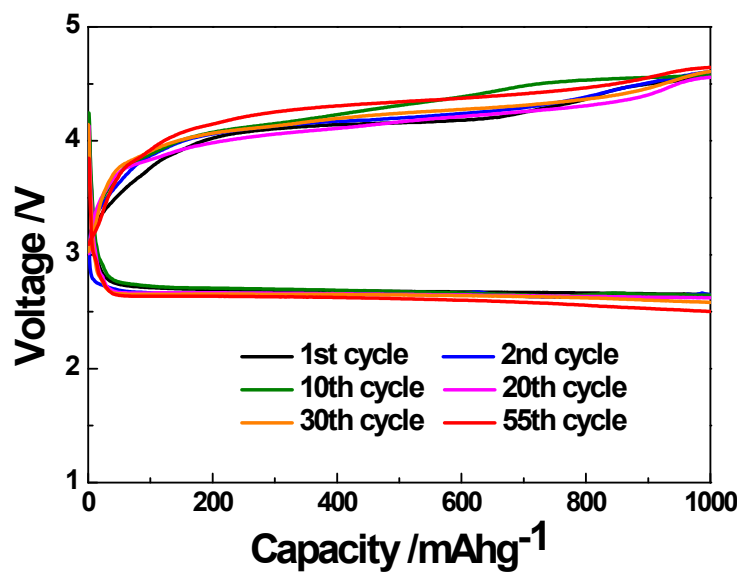
The LiTFSI in DMSO conventional liquid electrolyte shows an unstable and irreversible response from several cycles (less than 10 hours) with a tendency to diverge to high voltage limit. It could hardly tolerate the applied current density and thus exhibit very limited operating electrode lifetime. However, the cell with the PFSA-Li polymer electrolyte shows an improvement with a lower over potential of about 50 mV and a long cycle life of 60 hours.



**Figure S3** X-ray diffraction pattern of pristine MWCNTs cathode and MWCNTs electrode after discharged in Li-O<sub>2</sub> battery at 1.0 A g<sup>-1</sup>.



**Figure S4** Voltage profiles of the galvanostatic discharge of the lithium-oxygen polymer battery at different current densities and room temperature. The measurement has been repeated in order to determine the reproducibility of the test.



**Figure S5** Discharge-charge voltage profiles of the batteries using PFSA-Li/DMSO (A) and PFSA-Li/DMSO+LiI (B) as polymer electrolytes measured at a current density of  $1.0 \text{ A g}^{-1}$  and a fixed capacity of  $1000 \text{ mAh g}^{-1}_{\text{carbon}}$ . 50 mM LiI was added to DMSO.

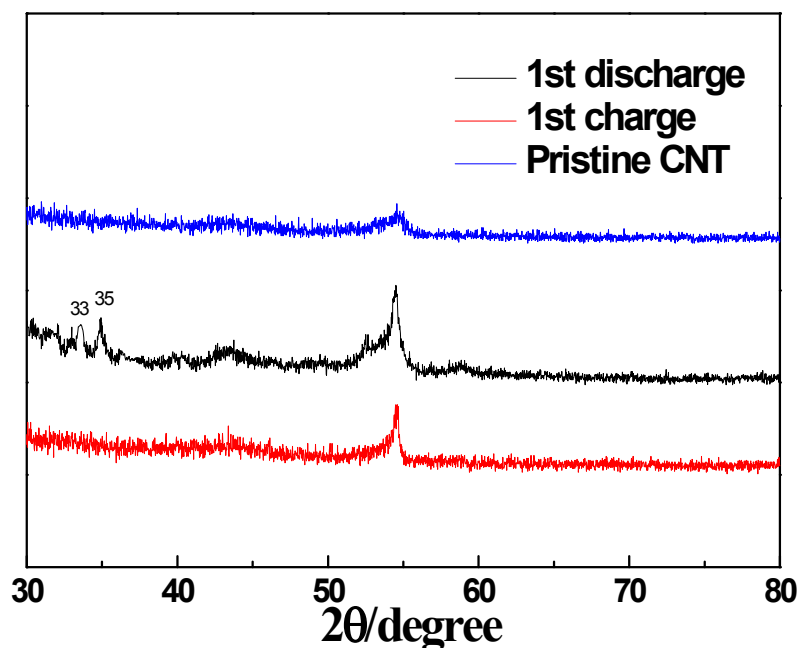


Figure S6 X-ray diffraction pattern of pristine MWCNTs cathode and MWCNTs electrode after discharged and charged in Li-O<sub>2</sub> battery with the PFSA-Li/DMSO+LiI polymer electrolyte.

We measured the discharge and charge products under the capacity of 1000mAhg<sup>-1</sup> with XRD, and the only discharge product is Li<sub>2</sub>O<sub>2</sub>, Which can clearly determine the I<sup>3-</sup> is the midterm product and not the final product. After charging, there is no remaining particles. Thus, Li-O<sub>2</sub> battery with polymer electrolyte added LiI can exhibited good cycling stability with low overpotential.

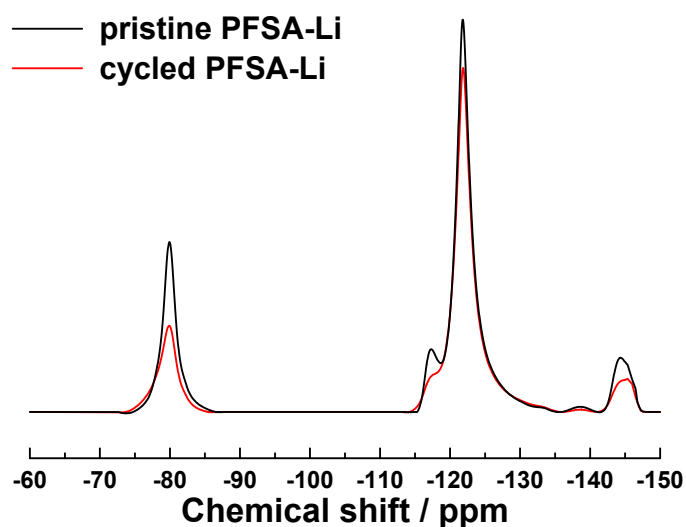


Figure S7 Solid state <sup>19</sup>F NMR spectrum of the PFSA-Li polymer before and after cycled (55 cycles at a current density of 1.0 A g<sup>-1</sup> and a fixed capacity of 1000 mAh g<sup>-1</sup><sub>carbon</sub> at room

temperature) in Li-O<sub>2</sub> battery.

### Reference

- S1. R. Buzzoni, S. Bordiga, G. Ricciardi, G. Spoto, A. Zecchina, *J. Phys. Chem.* **1995**, *99*, 11937.
- S2. M. Falk, *Can. J. Chem.* **1980**, *58*, 1495.
- S3. S. Zugmann, M. Fleischmann, M. Amereller, R. M. Gschwind, H. D. Wiemhöfer, H. J. Gores, *Electrochim. Acta* **2011**, *56*, 3926.