

## Methyl pivalate based electrolyte for non-aqueous lithium-oxygen battery

Taoran Li,<sup>a</sup> Zhiqun Wang,<sup>a</sup> Huanhuan Yuan,<sup>b</sup> Lei Li<sup>ab\*</sup> and Jun Yang<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Shanghai Key Lab of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 20024, China.

<sup>b</sup> Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

E-mail: lilei0323@sjtu.edu.cn

### 1. Experimental

#### 1.1 Preparation of methyl pivalate based electrolyte

Both Methyl pivalate (MP) and LiTFSI salt were purchased from Sigma-Aldrich. MP was first distilled and then dried with freshly activated 4 Å molecular sieves prior to use. LiTFSI was dried in vacuo at 150 °C for 24 h, then 1.0 M LiTFSI in MP used as electrolyte was prepared in argon-filled glove box.

#### 1.2 Electrochemical measurements

The cathodes were composed with multi-wall carbon nanotubes (Shenzhen Nanotech Port Co., Ltd., China) and poly(vinylidene fluoride) (PVDF). The weight ratio of MWCNTs: PVDF was 8: 2. The loading of MWCNTs in a cathode was about 1.0 mg·cm<sup>-2</sup>. A Li-O<sub>2</sub> battery was comprised of a modified 2032 coin-cell with six holes put in a glove box under high-purity oxygen (99.9%) atmosphere, a lithium metal anode (1.56 cm diameter and 0.45 mm thick), a Whatman glass filter separator (~28 mm diameter) impregnated with electrolyte and a prepared cathode. After assembling in an argon-filled glove box, the batteries were placed in a gastight box continuously saturated with 1.0 atm of high-purity oxygen and tested on Land CT2001A test system (Wuhan, China).

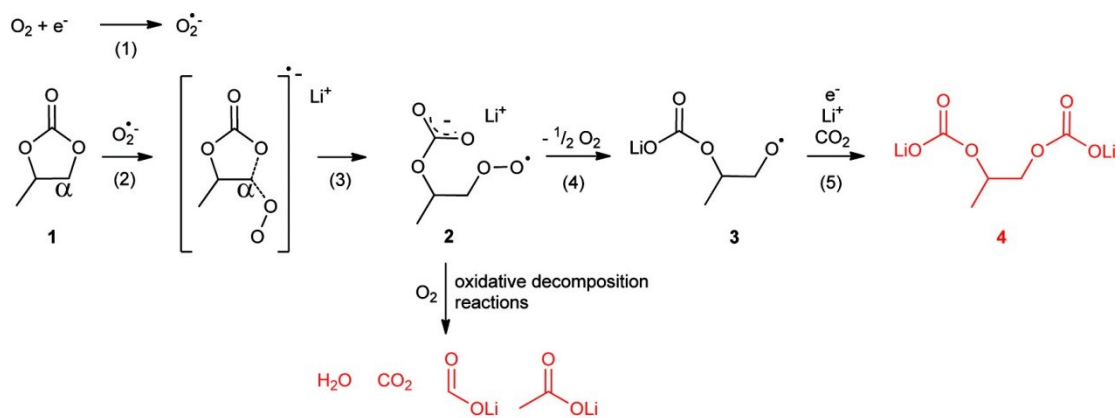
#### 1.3 Potassium superoxide (KO<sub>2</sub>) and lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) screening method

Potassium superoxide (KO<sub>2</sub>) screening method was employed to evaluate the chemical stability of MP based electrolyte in the presence of peroxy radical. Briefly, in a 5 ml vial, about 0.45 g of KO<sub>2</sub> powder was added in 5 ml of the based electrolyte (1.0 M LiTFSI in MP), and stirred throughout the experiments. Next 0.3 ml of the mixture of Electrolyte At the different time points, 0.3 ml of this mixed solution was transferred to a NMR tube containing 0.3 ml CDCl<sub>3</sub> and test for <sup>13</sup>C and <sup>1</sup>H Nuclear Magnetic

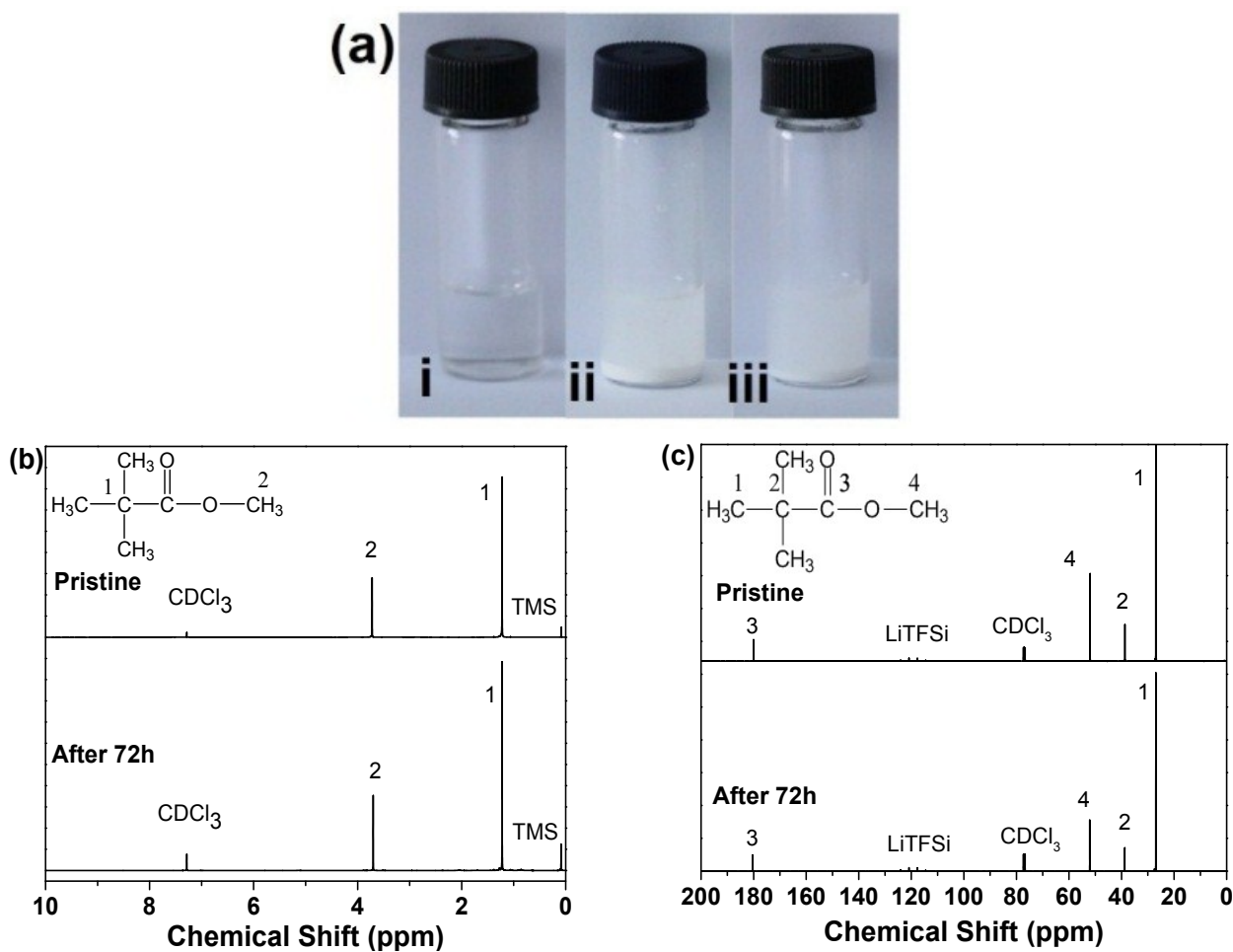
Resonance (NMR) analysis. All experiments (except  $^{13}\text{C}$  and  $^1\text{H}$  NMR) were performed in an argon-filled glove box. The NMR experiments were carried out on the AVANCE III HD 400 MHz Bruker (BioSpin Corp., Germany) instrument at room temperature. The  $^{13}\text{C}$  spectra in  $\text{CDCl}_3$  were referenced to the residual  $\text{CHCl}_3$  at 77.2 ppm. The  $^1\text{H}$  spectra in  $\text{CDCl}_3$  were referenced to the residual  $\text{CHCl}_3$  at 7.26 ppm. The lithium peroxide ( $\text{Li}_2\text{O}_2$ ) screening method is no different, but about 0.1 g of  $\text{Li}_2\text{O}_2$  was dissolved in 2 ml electrolyte in a 5 mL vial.

#### **1.4 Characterization**

The ionic conductivity was measured with a ZAHNER Zennium conductivity meter at room temperature. To evaluate the electrochemical window of the MP based electrolyte, Cyclic Voltammetry (CV) measurement was carried out in a three electrode glass cell on CHI 660D potentiostat. 1.0 M LiTFSI in MP was used as electrolyte. A glass carbon electrode, platinum wire and  $\text{Ag}^+/\text{Ag}$  non-aqueous reference electrode (10 mM  $\text{AgNO}_3$  in acetonitrile, from CHI, Inc.) were used as working, counter and reference electrodes, respectively. CV measurement was performed at a scan rate of  $1 \text{ mV s}^{-1}$  and room temperature. X-ray diffraction (XRD) measurements were applied on an X-ray diffractometer (D/max-2200/PC, Japan) with  $\text{CuK}\alpha$  radiation from  $10^\circ$  to  $80^\circ$  at a scanning rate of  $0.1^\circ \text{ sec}^{-1}$ . After the cycled test in Li- $\text{O}_2$  cells, the Whatman glass filter containing the MP based electrolyte was impregnated in  $\text{CDCl}_3$  for 24h, and then 0.6 ml of the mixed solution was transferred to a NMR tube for  $^{13}\text{C}$  and  $^1\text{H}$  NMR analysis.



**Fig. S1** Proposed mechanism for the decomposition of propylene carbonate (PC) by superoxide radicals ( $\text{O}_2^{\bullet -}$ ) attack.<sup>S1</sup>



**Fig. S2** (a) Photographic images of (i) MP solvent, MP based electrolyte before (ii) and (iii) after reacting with  $\text{Li}_2\text{O}_2$  for 72h.  $^1\text{H}$  NMR (b) and  $^{13}\text{C}$  NMR (c) spectrum of MP based electrolyte before (ii) and (iii) after reacting with  $\text{Li}_2\text{O}_2$  for 72h

## Reference

- S1. S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák and P. G. Bruce, *J. Am. Chem. Soc.*, 2011, **133**, 8040