

Supporting information

A new electrolyte with good compatibility to a lithium anode for non-aqueous Li-O₂ batteries

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Experimental

Preparation of the electrolyte solution

Lithium battery grade LiTFSI and LiFSI were obtained from Capchem. Co., Ltd. and Suzhou Fluolyte. Co., Ltd., respectively, and were heated at 100 °C under vacuum prior to the electrolytes preparation. TEGDME (≥ 99.5%, aladdin) and DX (≥ 99.5%, aladdin) were dried with an activated molecular sieve before use. DX, as a co-solvent, was mixed with the TEGDME at a 1:4 volume ratio, and then, 1 M LiFSI was dissolved in the obtained solvent and further stirred for 12 h at room temperature to form the electrolyte solution. A 1 M LiTFSI/TEGDME solution was also prepared for comparison. All of the experiments were performed in an Ar-filled dry glove box (MB-10 compact, MBRAUN) with oxygen and water contents of less than 1 ppm.

Cells assembly and electrochemical tests

A pure lithium foil (Φ16 mm) was employed as an electrode to assemble the CR2016-type of symmetrical Li|Li cells, with ENTEK ET 20-26 (PE, thickness: 20 μm) as the separator. Li-O₂ cells were also assembled using CR2032-type coin cells with several even holes on the cathode side and glass fibre separator. The oxygen cathode was prepared by casting a 4:1 (w/w) mixture of multi-wall carbon nanotubes (>97%, Shenzhen Nanotech Port. Co., Ltd.) and a poly(vinylidene difluoride) binder onto a carbon paper. The as-obtained Li-O₂ cells were placed in a glove box and then tested in high purity oxygen atmosphere.

Galvanostatic discharge/charge tests at room temperature were performed using a LAND CT2001A battery test system (Wuhan, China) by using symmetrical Li|Li cells at a fixed current density of 0.25 mA cm⁻² for 8 h during each cycle. Li-stainless steel (SS) cells were also assembled to determine the coulombic efficiency, with the experiment performed as described in the literature. In briefly, an initial amount of lithium (several coulombs per cm²) was galvanostatically plated on the SS electrode followed by galvanostatic cycling of a fraction of the initial amount (10%-30% of this amount). The number of cycles required to consume the initial amount (indicating by a sharp increasing of the dissolution potential) was used to calculate the average efficiency. Cyclic voltammogram was generated with a three-electrode cell system, Pt disc as working electrode (area: 0.0314 cm²) and lithium slice as counter and reference electrode using a CHI604A electrochemical workstation (Shanghai, China) at the scanning rate of 10 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) data were collected over a frequency range of 0.1 Hz to 100 kHz, with a potential amplitude of 10 mV on an AUTOLAB PGSTAT302N (Metrohm). The surface morphologies of the lithium metal electrodes after cycling were observed by a JEOL JSM-7401F field emission scanning electron microscope (FE-SEM). X-ray powder diffraction (XRD, D/max-2200/PC, Japan) patterns were recorded by continuous scanning in the 2θ range of 10–80.

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Figures

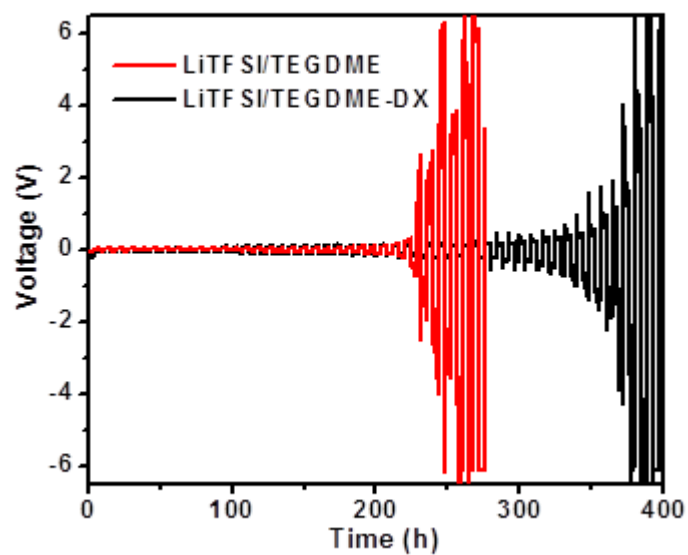


Figure S1. Voltage–time plots of Li|Li symmetrical cells in LiTFSI-based electrolytes with and without DX, at constant current density of 0.25 mA cm^{-2} and 8 h for each cycle.

Fig. S1 shows that using DX as co-solvent in the LiTFSI/TEGDME solution can prolong the life span of Li|Li symmetrical cells to some extent. However, the cell with LiTFSI/TEGDME-DX electrolyte fails the cycling operation at about 360 h, which is far less than the performance in LiFSI/TEGDME-DX electrolyte system. The synergistic effects of DX solvent with LiFSI is well above that with LiTFSI.

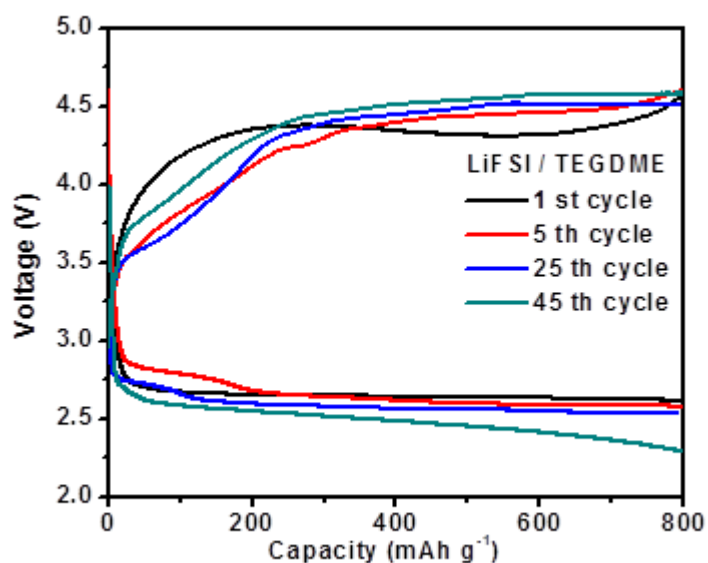


Figure S2. Galvanostatic charge-discharge profiles of Li-O₂ cells in LiFSI-based electrolyte without DX, at a current density of 200 mA g⁻¹ to the fixed capacity of 800 mAh g⁻¹.

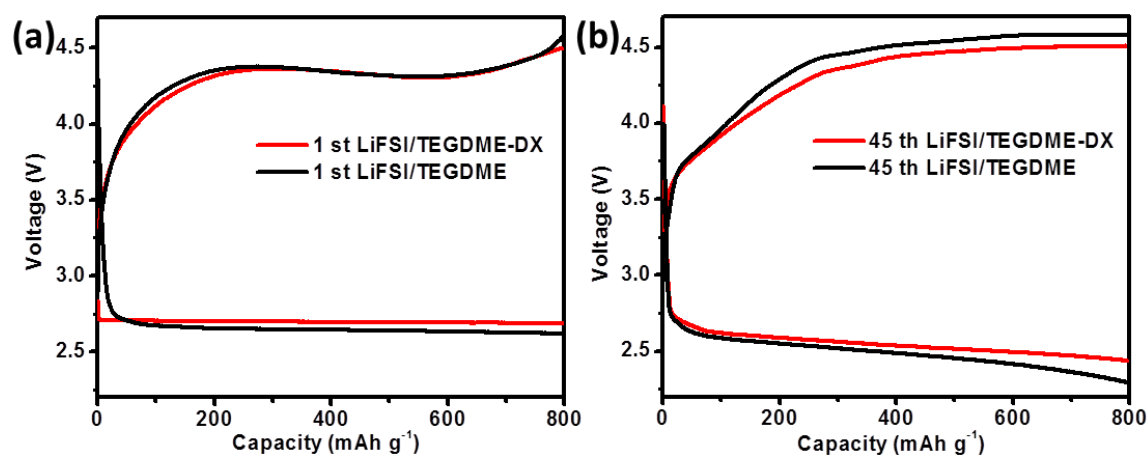


Figure S3. Galvanostatic charge-discharge profiles of Li-O₂ cells in LiFSI-based electrolytes with and without DX, at a current density of 200 mA g⁻¹ to the fixed capacity of 800 mAh g⁻¹.

As is shown in Fig. S2 a reversible cycle operation can be observed in the non-aqueous Li-O₂ batteries with LiFSI/TEGDME electrolyte, accompanying an obvious discharge voltage drop at 45th cycle. When comparing with the electrolyte containing DX as co-solvent, the polarizing voltage of the first cycle between the two kinds of electrolytes is negligible. However, the value is getting widening with the increasing of cycling number. And a lower polarizing voltage was obtained when DX was used as co-solvent (Fig. S3), which is in accordance with the EIS results mentioned in the article.