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Supporting Information

A Renaissance of N,N-Dimethylacetamide-Based Electrolyte to Promote the

Cycling Stability of Li-O₂ Batteries

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Experimental Section

Materials: LiTFSI, LiNO₃, LiCF₃SO₃, N-Methyl pyrrolidone (NMP), Tetraethylene glycol dimethyl ether (TEGDME) and RuCl₃•xH₂O were purchased from Aladdin Reagent. N,N-Dimethylacetamide (DMA) was bought from J&K chemical. Lithium metal sheets were obtained from China Energy Lithium Co. Ltd. Super P was purchased from TIMCAL Graphite&Carbon. Carbon paper and Pluronic F127 were bought from Torray Japan and Sigma-Aldrich, respectively. CNTs were obtained from Cnano Technology Ltd.

Preparation of Air Cathode for Li-O₂ Battery: First, RuCl₃•xH₂O, CNTs and Pluronic F127 were mixed in water with a mass ratio of 1:1:5 and stirred for 24 hours. Then, the dried mixture was calcined at 300 °C for 3 hours under an atmosphere of 5% H₂/Ar. Finally, the obtained Ru/CNTs was cleaned with alcohol and dried under room temperature. In this manuscript, the Ru/CNTs was only used in the long-life cycling test of Li-O₂ batteries. For preparing air cathode, Super P or Ru/CNTs and PVDF binder with a mass ratio of 8:1 were dispersed in NMP to form uniform slurry and subsequently sprayed onto a carbon paper. The slurry coated carbon paper was then dried at 70 °C and stored in an Ar-filled glove box (<0.1 ppm O₂ and H₂O). All Li-O₂ batteries and Li-Li symmetrical batteries were assembled with 2025 coin-type cells (with or without holes) using an automatic crimping machine in an Ar-filled glove box (<0.1 ppm O₂ and H₂O).

Materials characterization: Power X-ray diffraction (XRD) was performed on a Bruker D8 Focus Powder X-ray diffractometer under 40 kV and 40 mA. For Scanning electron microscopy (SEM) characterization, Hitachi S4800 field emission scanning electron microanalyzer was used to evaluate the morphology of the synthesized materials. X-ray photoelectron spectroscopy (XPS) data was collected on ThermoFisher XPS Eacalab using a vacuum box. ⁷Li NMR and ¹⁹F NMR spectra were examined on a Bruker Avance II 400 spectrometer with an external standard of 1 M LiCl in D₂O or 1 M LiTFSI in D₂O, respectively. The viscosity of different kinds of electrolytes was obtained from the Viscosity 50 mm (with cone angle 1°) cone-and-plate geometry on the Anton Paar MCR302 rheometer at 30 °C. OLYMPUS GX71 optical microscope was employed for getting the in-situ optical microscope images. **Electrochemical measurements:** The electrochemical performances of Li/Li symmetrical batteries and Li-O₂ batteries were measured by Land CT2001A multichannel battery testing system. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests were conducted on BioLogic VMP3 electrochemical workstation. The Li⁺ conductivity of different kinds of electrolytes was measured by stainless-steel/electrolyte/stainless-steel batteries under different temperatures. The activation energy E_a was calculated by equation 1¹:

$$\sigma(T) = Aexp(-E_a/RT)$$
(1)

Where σ is the Li⁺ conductivity of electrolyte, A represents the pre-exponential factor and T is the absolute temperature.

The E_a of Li desolvation was obtained with equation 2^2 :

$$\frac{T}{R_{ct}} = Aexp(-\frac{E_a}{RT})$$
(2)

Where T, R_{ct} , A, E_a and R are the absolute temperature, charge transfer resistance, pre-exponential factor, activation energy and gas contant, respectively.

AIMD simulation: All DFT calculations and *ab initio* molecular dynamics (AIMD) were carried out by utilizing the Vienna *ab initio* simulation package (VASP).^{3, 4} In all simulation, the models were constructed strictly according to the measured results from experiments and the detailed information of simulated systems were shown in Table S1. In the course of AIMD, with plane-wave energy cutoff of 400 eV, four simulated systems were all large enough to utilize a Monkhorst-Pack k-point mesh grid scheme $(1 \times 1 \times 1)$.^{5, 6} A canonical (NVT) ensemble was performed by using a Nose-Hoover thermostat at 298 K.⁷⁻⁹ The total AIMD simulation time for each system was 10ps with a time step of 1 fs.

After the simulation, the average root mean square deviation (RMSD) was calculated by using Equation 3:

$$RMSD = \sqrt{\frac{\sum_{i=1}^{N_{atoms}} (r_i(t_1) - r_i(t_2))^2}{N_{atoms}}}$$
(3)

where the number of atoms whose positions are being compared is N_{atoms} , and $r_i(t)$ represents where the atom i is at time t. And the radial distribution function (RDF) was calculated by Equation 4:

$$g(r) = \frac{dN}{\rho 4\pi r^2 dr} \tag{4}$$

where g(r) is represented as the probability to find an atom in a shell dr at the distance r of another chosen reference atom, dN is the number of all atoms in a shell dr at the distance r of another chosen reference atom, and ρ is the bulk density of the system. The calculated data was analyzed by software, VMD.¹⁰ The use of VMD was from the reference of itself guide book and the website, <u>http://sobereva.com/</u>.



Fig. S1. Galvanostatic cycling performance of Li/Li symmetrical batteries with 1 M LiTFSI, 3 M LiTFSI, 4 M LiTFSI and 5 M LiTFSI electrolytes at a capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻².



Fig. S2. Galvanostatic cycling performance of Li/Li symmetrical batteries with 1 M LiNO₃, 4 M LiNO₃, 5 M LiNO₃ and 6 M LiNO₃ electrolytes at a capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻².



Fig. S3. Galvanostatic cycling performance of Li/Li symmetrical batteries with 3 M LiNO₃, 3 M LiTFSI, 1.5 M LiNO₃ 1.5 M LiTFSI, 1 M LiNO₃ 2 M LiTFSI and 0.5 M LiNO₃ 2.5 M LiTFSI electrolytes at a capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻².



Fig. S4. Galvanostatic cycling performance of Li/Li symmetrical batteries with 0.67 M LiTFSI 0.33 M LiNO₃, 1.33 M LiTFSI 0.67 M LiNO₃, 2 M LiTFSI 1 M LiNO₃ and 2.67 M LiTFSI 1.33 M LiNO₃ electrolytes at a capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻².



Fig. S5. Galvanostatic cycling performance of Li/Li symmetrical batteries with 1 M LiCF₃SO₃ in TEGDME electrolyte at a capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻².



Fig. S6. Calculated activation energy of 4 M LiTFSI, 5 M LiNO $_3$ and 2 M LiTFSI 1 M LiNO $_3$ electrolytes from the results in Fig. 2g.



Fig. S7. Viscosity of different kinds of electrolytes.



Fig. S8. Walden curves of 4 M LiTFSI, 5 M LiNO₃ and 2 M LiTFSI 1 M LiNO₃ electrolytes.



Fig. S9. Calculated activation energy of 4 M LiTFSI, 5 M LiNO₃ and 2 M LiTFSI 1 M LiNO₃ electrolytes from the results in Fig. 2h.



Fig. S10. SEM images of lithium deposition morphology in different kinds of electrolytes.



Fig. S11. a) N 1s and b) F 1s XPS curves of lithium after 40 cycles in 4 M LiTFSI electrolyte before and after etching for 5 minutes.



Fig. S12. N 1s XPS curves of lithium after 40 cycles in 5 M LiNO₃ electrolyte before and after etching for 5 minutes.



Fig. S13. a) F 1s and b) N 1s XPS curves of lithium after 40 cycles in 2 M LiTFSI 1 M LiNO₃ electrolyte before and after etching for 5 minutes.



Fig. S14. Details of snapshots of AIMD of different kinds of electrolyte.



Fig. S15. a) ⁷Li NMR spectra and b) ¹⁹F NMR spectra of 3 M LiTFSI and 2 M LiTFSI 1 M LiNO₃ electrolytes.



Fig. S16. Schematic of AGGs formed in 4 M LiTFSI electrolyte.



Fig. S17. Schematic of AGGs formed in 5 M LiNO₃ electrolyte.



Fig. S18. CV curves of $Li-O_2$ batteries with three different kinds of electrolytes.



Fig. S19. Full discharge curves of $Li-O_2$ batteries with different kinds of electrolytes at a current density of 1000 mA g⁻¹.



Fig. S20. Full discharge curves of $Li-O_2$ batteries with different kinds of electrolytes at a current density of 2000 mA g⁻¹.



Fig. S21. The discharge-charge curves of Li-O₂ battery with 4 M LiTFSI electrolyte and Ru catalyst.



Fig. S22. Discharge-charge curves of Li-O₂ battery with 5 M LiNO₃ electrolyte and Ru catalyst.



Fig. S23. Discharge-charge curves of $Li-O_2$ battery with 2 M LiTFSI 1 M LiNO₃ electrolyte and Ru catalyst.



Fig. S24. SEM images of the first cycle a) discharged and b) recharged cathodes.



Fig. S25. XRD curves of the first cycle discharged and recharged cathodes.



Fig. S26. a) SEM image b) and XRD patterns of lithium metal anode in Li-O₂ batteries after 50 cycles with 4 M LiTFSI electrolyte.

Systems	Molecular numbers of solvent(DMA)	Molecular numbers of LiTFSI	Molecular numbers of LiNO3	Total numbers of atom	Volume of computational supercell (^{Å³})	Density of solution ($g \cdot cm^{-3}$)
2 M LiTFSI 1 M LiNO ₃	43	8	4	793	20.601 × 20.601 × 20.60 1	1.20
5 M LiNO3	43		20	745	19.504 × 19.504 × 19.50 4	1.15
4 M LiTFSI	43	16		901	21.891 × 21.891 × 21.89 1	1.32
3M LiTFSI	43	12		837	21.086 × 21.086 × 21.08 6	1.27

 Table S1. Detailed information of four simulated electrolyte systems.

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