Supporting Information

Elucidation and Comparison of the Effect of LiTFSI and $LiNO_3$ Salts on Discharge Chemistry in Nonaqueous Li-O_2 Batteries

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Experimental

Materials- Cell building

For the electrochemical tests, ECC-air test cells (EL-Cell GmbH) were assembled in an argon-filled glove box with lithium metal (diameter: 14 mm, thickness: 0.3 mm, Rockwood Lithium GmbH) as anode. The oxygen and water contents of the gloveboxes were below 1 ppm. On the lithium metal a glass microfiber filter separator (diameter: 17 mm, thickness: 0.26 mm Whatman) was placed, followed by a Celgard 2400 separator (diameter: 17 mm, thickness: 25 μm). Toray carbon paper without catalysts (TGP- H-60, diameter: 16 mm, thickness: 0.19 mm) was used as cathode material. It was dried overnight in a vacuum drier at 95 ˚C before cell assembly. Electrolytes were prepared in argon atmosphere glove box by mixing and dissolving lithium nitrate ($LiNO_3$, 99.99 %, trace metal basis, Sigma-Aldrich) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95 %, trace metal basis, Sigma-Aldrich) in tetraethylene glycol dimethyl ether (TEGDME, ≥99 %, Sigma-Aldrich). The concentration of Li^+ ions in the electrolytes was kept constant at 1 M in order to exclude any cationic effect. We focused especially on the range where the concentration of $LiNO_3$ varied from 0 M to 1 M. All the electrolytes, salts, and solvents were stored in the glovebox. During the cell assembly, 180 μL electrolyte was injected to each cell. After cell assembly, the cells were transferred to electrochemical test station and flushed with 1.5 atm pure oxygen continuously.

Electrochemical testing:

The galvanostatic discharge measurement was carried out with BaSyTec battery test systems (BaSyTec GmbH). The cells were discharged to 2 V with a constant current density of 0.05 mA/cm^2 at 25 °C.

Post-mortem analysis:

After discharge measurement, the cells were opened and the cathodes were analyzed using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and Raman spectroscopy in an argon-filled glove box. Moreover, the morphology of the cathodes was analyzed using scanning electron microscopy (SEM).

ATR-FTIR analysis was carried out on the cathodes using a Bruker, Vertex 70 FTIR Spectrometer equipped with an ATR internal reflection system (Bruker Corporation) in the wave number region of 350-5000 cm^{-1}. The resolution of spectra was 4 cm^{-1}, and data were collected in the transmittance mode.

Raman spectra of the cathodes were obtained with a RamanScope III (Bruker Corporation) in the wavenumber region of 60-3700 cm^{-1}. The excitation wavelength of the applied laser was 532 nm and the laser intensity was 10 mW. Collection time constant was 70 s and coadditon was 3.

A high-resolution field emission scanning electron microscope (Leo Supra 35VP) was employed to analyze the morphology of the discharge products on the cathode surface. Samples were prepared in the glovebox and transferred to SEM as fast as possible.

All the measurements were performed at the 298.15 K.

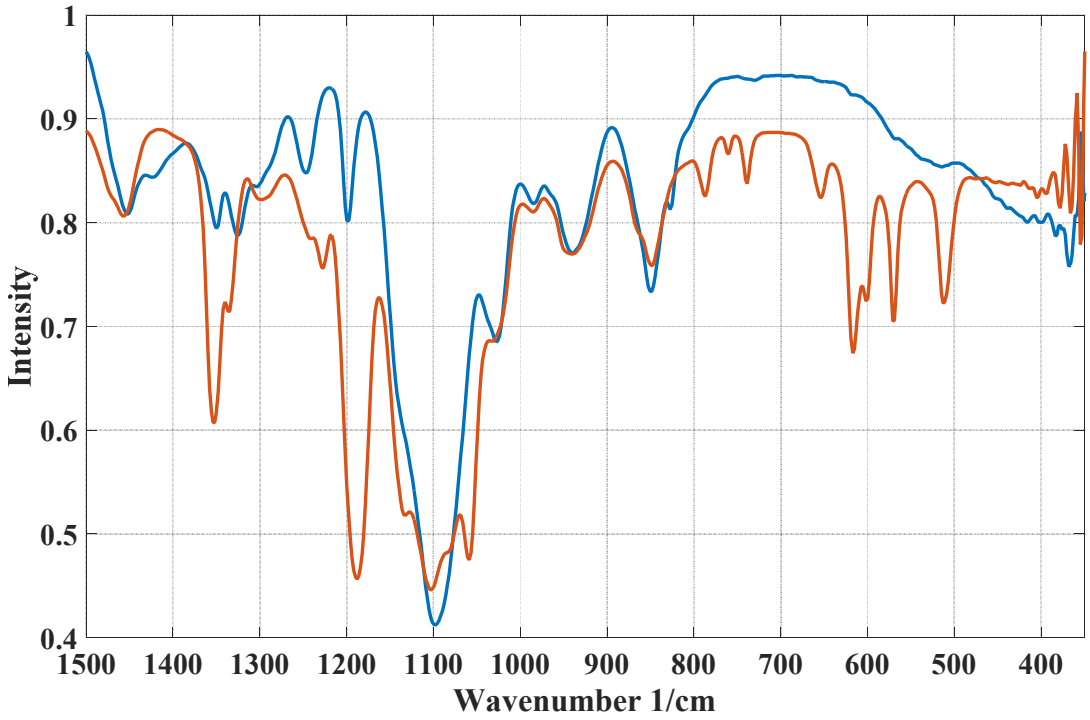

Figure S1. FT-IR spectra of 1 M LiTFSI in TEGDME (red) and 1 M $LiNO_3$ in TEGDME (blue) electrolytes

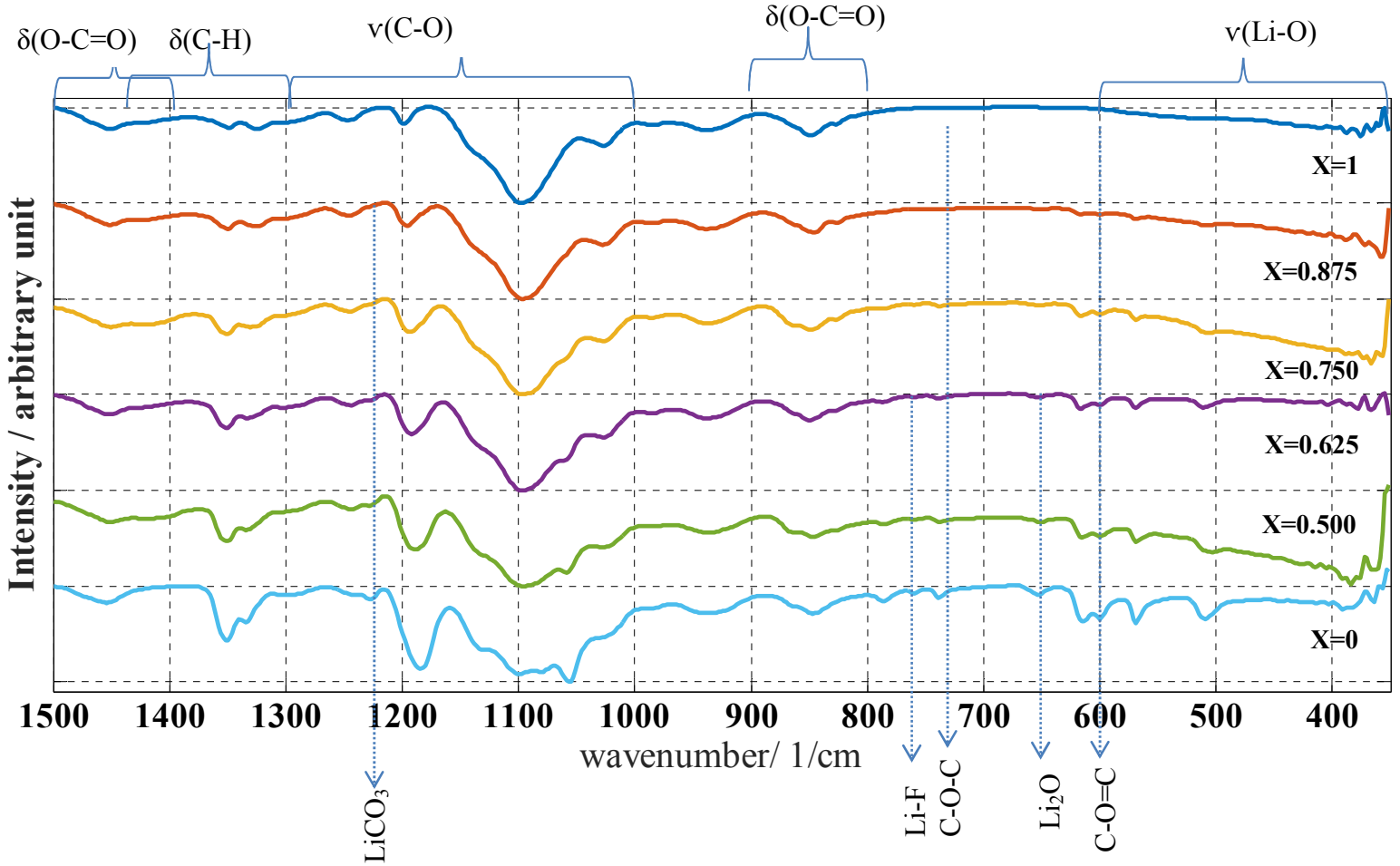

Figure S2. ATR-FTIR spectrums of after the first discharge performance of Li-O_2 cells with different electrolyte compositions $LiNO_3$ [(x) M]+ LiTFSI [(1-x) M].