Electronic Supplementary Information

Enhanced electrochemical performance and thermal stability of

LiNi_{0.5}Mn_{1.5}O₄ using the electrolyte with sulfolane

Qian Zhang, Jia-Jia Chen, Xue-Yin Wang, Cheng Yang, Ming-Sen Zheng^{*} and Quan-Feng Dong^{*}

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian, 361005, China *E-mail: <u>qfdong@xmu.edu.cn</u>, <u>mszheng@xmu.edu</u>

1. Experimental

1.1. Material Preparation

The micro-sized LiNi_{0.5}Mn_{1.5}O₄ was prepared by ordinary solid state reaction. Stoichiometric proportions of LiOH, Ni(OH)₂ and γ -MnOOH were mixed by high-energy ball-milling for 30 min. The precursor was sintered at 900°C for 5h in the muffle furnace and cooled to room temperature. Then the powder was grinded and secondary calcined at 700°C for 48 h. The heating rate of calcination process was 5°C/min.

The solvents for electrolytes were all purchased, sulfolane (SL, Tokyo Chemical Industry), propylene carbonate (PC, Zhuhai Saiwei) and ethyl methyl carbonate (EMC, Zhuhai Saiwei). Before use they were dried over 4A molecular sieve. The two electrolytes tested were prepared inside the Ar-filled glove box. $LiPF_6$ (Zhuhai Saiwei) with 1.0 mol/L concentration was dissolved in propylene carbonate- ethyl methyl carbonate (PC-EMC, 1:1 by volume) solvent and propylene carbonate- ethyl methyl carbonate (PC-EMC-SL, 1:1:1 by volume) solvent, respectively, which were named as E0 and E1 electrolyte.

1.2. Electrochemical Tests

Positive electrodes were made of 80 wt% $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material, 10 wt% acetylene black, and 10 wt% water soluble polymer n-lauryl acrylate (Chengdu, China). The cathode slurry was prepared by ball milling for 6h and then coated onto the Al foil current collectors. The active material on the Al foil was about 1mg/cm². The cathodes were dried at 60°C under vacuum for 24h. The CR2016-type coin cells were assembled in the Ar-filled glovebox, which consisted of cathodes, separators (Celgard Inc.), lithium plates as the negative electrodes and the electrolytes above-mentioned. With the same area of cathodes (2.01cm²), the injection volume of both electrolyte added in the cells was 50 µL.

Charge and discharge performances of the LiNi_{0.5}Mn_{1.5}O₄/Li half cells were investigated by Neware BT5-5 Tester (Neware Co., Ltd, Shenzhen, China) at room temperature in galvanostatic and potentiostatic modes (< 0.05 C) between 3.5 and 4.9V. Electrochemical impedance spectroscopy (EIS) was performed by a Zahner electrochemical workstation (model Im6) with a frequency range of 10⁵ Hz to 10⁻² Hz and an AC perturbation of ±5 mV. Data were fitted by using the Zview software package.

1.3. Characterization of Material and Cathodes

The morphology of $LiNi_{0.5}Mn_{1.5}O_4$ material was observed by scanning electron microscopy (SEM, HITACHI S-4800) at 15 kV accelerating voltage. The product was characterized by X-ray diffraction (XRD) on a Panalytical X'pert PRO instrument with Cu-K α as X-ray source. Raman

spectra were analyzed using Xplora at 532 nm excitation.

Before the characterization, the cathodes taken from the cells were washed and soaked in ethyl methyl carbonate (EMC) for 12h in the glovebox to remove the remanent electrolyte from the surface, till the tests were they transferred from the glovebox.

The transmission electron microscopy (TEM) was performed on F30 (Hitachi, 200 kV). X-ray photoelectron spectroscopy (XPS) of cathodes was carried out by using a Qtac-100 LEISS XPS instrument. The binding energy was calibrated from contaminations using the C1s peak at 284.6 eV. The spectra obtained were analyzed by XPSPEAK4.1 software. The peak positions and areas were optimized by a weighted least square fitting method using Gaussian-Lorentzian (80:20) line shapes with Shirley-type background subtraction.

1.4. Thermostability test

In order to evaluate the thermal behavior of the two electrolytes, a technique called Accelerating Rate Calorimetry (North House, Bletchley, U.K.) was used. The temperature of the sample is raised successively and adiabatically to high temperature until a spontaneous thermal reaction between the elements of the battery produces additional heat. ARC can acquire thermodynamic and kinetic information for runaway reactions of overheated or overcharged batteries. After exothermal process, the instrument will terminate automatically. The main operation indexes of the ARC are temperature range 50~400 °C, slope sensitivity 0.02 °C /min. Tested samples were 1.0 g E0 or E1 electrolyte with 50 mg delithiated LiNi_{0.5}Mn_{1.5}O₄ material, named as Sample0 and Sample1. To prepare the samples for ARC test, first the cells were charged to 4.9V in galvanostatic -potentiostatic mode until the current density decreased to 0.05C. Then the delithiated LiNi_{0.5}Mn_{1.5}O₄ material was scraped from the Al foil and washed by EMC solvent in the Ar-filled glovebox. After weighing, the dry material with the corresponding electrolyte were transferred into a sealed bomb and taken out of glovebox for ARC test.

(a) ¹⁵⁰⁰ ¹⁰⁰⁰

2. Supplementary Results

Fig. S1: (a) The Raman spectra of $LiNi_{0.5}Mn_{1.5}O_4$ material, which is characteristic of a typical disordered *Fd*-3*m* spinel, (b) the SEM and TEM images of fresh cathode



Fig. S2: The electrochemical windows of E0 and E1 electrolyte, work electrode: Pt, counter electrode: Li, reference electrode: Li, scan rate: 0.1mV/s.



Fig. S3: The first three charge/discharge curves of spinel cathode at 0.1C in E0 (a) and E1 electrolyte (b).



Fig. S4: The cyclic voltammograms of $LiNi_{0.5}Mn_{1.5}O_4/Li$ half cells at different scan rates of 0.1 mV/s (a) and 0.5 mV/s (b) in the two electrolytes.



Fig. S5: The charge and discharge curves of $LiNi_{0.5}Mn_{1.5}O_4$ at different current densities in E0 electrolyte (a) and E1 electrolyte (b).

Table S1 Fitting results of Nyquist plots using the equivalent circuit of pristine EIS in Fig. 2c



Fig. S6: EIS of LiNi_{0.5}Mn_{1.5}O₄/Li cells after 1, 20 and 50 cycles at 1C in E0 electrolyte (a) and E1 electrolyte (b).

Table S2 The speculated SEI substances on the surface of the LiNi_{0.5}Mn_{1.5}O₄ cathodes by XPS spectra in Fig. 3cCycling in E0 electrolyteROCO₂Li, LiF, LiPF_y, Li_xPO_yF_zCycling in E1 electrolyteROCO₂Li, LiF, LiPF_y, Li_xPO_yF_z, HCO₂Li, RSO₃⁻, R₁SSO_xR₂



Fig. S7: The ARC results of E0 electrolyte (a) and E1 electrolytes (b).

Table 55 The mential decomposition characteristic data of two samples by Fice in Fig. 4 and Fig. 56					
	Exothermal	Max heating	Max heating rate	Max	Quantity of
	onset	rate (°C/min)	temperature (°C	pressure	heat release
_	temperature (°C)		/min)	(bar)	(J)
Sample0	178.31	3.258	226.61	85.20	861.12
Sample1	178.41	0.144	186.55	52.58	1408.58
E0 electrolyte	158.68	3.398	206.23	99.92	935.86
E1 electrolyte	154.47	0.958	206.05	84.31	1208.61

Table S3 The thermal decomposition characteristic data of two samples by ARC in Fig. 4 and Fig. S6