Ion exchange membranes as electrolyte to improve high temperature capacity retention of LiMn$_2$O$_4$ cathode lithium-ion battery

Yanbo Liu, Lei Tan, Lei Li*

School of Chemical and Chemistry Engineering, Shanghai Jiaotong University, No. 800 Dongchuan Road, Shanghai 200240, P. R. China
*E-mail:lilei0323@sjtu.edu.cn

Experimental

Perfluorinated sulfonic ionomer with 1.18 mmol g^{-1} was used in our experiments. PFSA membranes with H-type were prepared according to the literature.[S1] The thickness of the membranes was about 90±3 μm in our experiments. After that, the membrane was dipped into 500 ml of lithium hydroxide aqueous solution (40 g LiOH·H$_2$O in 500 ml of de-ionized water) at 80 ^{o}C for 8 h. Then, the obtained PFSA-Li membranes were washed by de-ionized water at room temperature until neutrality of the washing water was obtained. Finally, the membranes were kept in de-ionized water ready to use.

Since the sensitivity of the membrane properties to water content, the dehydration process of the PFSA-Li membranes was carried out in the glove-box under argon atmosphere. The membrane sample was first weighted (W_d) after the surface water wiped with filter paper. Then it was left in contact with 20 ml mixed EC-PC (1:1 *v:v*) nonaqueous solvents in the presence of 20 g activated 4A molecular sieves in a sealed container for 48 h at room temperature. This process was repeated in order to remove most of water absorbed into membranes. Then the membranes were reweighed (W_w) after the surface solvents were blotted out. Solvent uptake at room temperature $W_{solvent}$ was determined by the following equation:

$$W_{solvent} = \frac{W_w - W_d}{W_d} \times 100\%$$

Ionic conductivity was determined with two electrodes AC impedance method by using Autolab PGSTAT302 electrochemical test system (Eco Chemie, the Netherlands). The conductivity measurement cell containing two stainless steel electrodes was employed. The sample was removed from nonaqueous solvents and blotted dry with filter paper prior to assembly into the cell in the glove-box under argon atmosphere. AC impedance experiments were carried out in the temperature range of room temperature to 70 ^{o}C. Before each experiment, the cell was left about 1

h to reach thermal equilibrium. The ionic conductivity was calculated from the bulk sample impedance at a zero-phase angle.

Cyclic voltammetry was carried out on Autolab PGSTAT302 electrochemical test system (Eco Chemie, the Netherlands) with lithium foil as both the counter and reference electrodes and stainless steel as the working electrode. The experiments were performed with sweep rate of 10 mV sec^{-1}. All the test cells were assembled and sealed in the glove box. The manganese concentration in the Li anode was determined by using inductively coupled plasma atomic emission spectrometry (iCAP 6000 Radial, THERMO).

$LiMn_2O_4$ electrode materials with carbon treatment were purchased from Hunan Reshine New Material Co., Ltd., China. The $LiMn_2O_4$ electrodes were prepared by mixing 90 wt% $LiMn_2O_4$ powder, 5 wt% carbon black and 5 wt% poly(vinylidene fluoride) in N-methylpyrrolidone solvent. The blended slurry was coated onto aluminum foil and dried at 80 ^{o}C for 0.5 h, then dried at 125 ^{o}C at 1.5 h. The dried electrode was compressed by a roller to make a smooth and compact film structure at room temperature. Then the electrode disks (1.5386 cm^2) were punched out of the coated foil sheets and weighted. $LiMn_2O_4$/Li half cells were fabricated with 2016-coin type cells in the argon-filled glove box using the PFSA-Li ion-exchange membrane as both electrolyte and separator. The charge-discharge performance of the cells was tested on Land CT2001A tester (Wuhan, China) at the constant current mode over the range of 3.0-4.5 V after a procedure of activation (charge at 0.1 C for 5 h, then discharge at 0.1 C to 3.0 V).

Reference

S1. Y. Luan, H. Zhang, Y. Zhang, L. Li, H. Li and Y. Liu, Y. *J. Membr. Sci.*, 2008, **319**, 91.
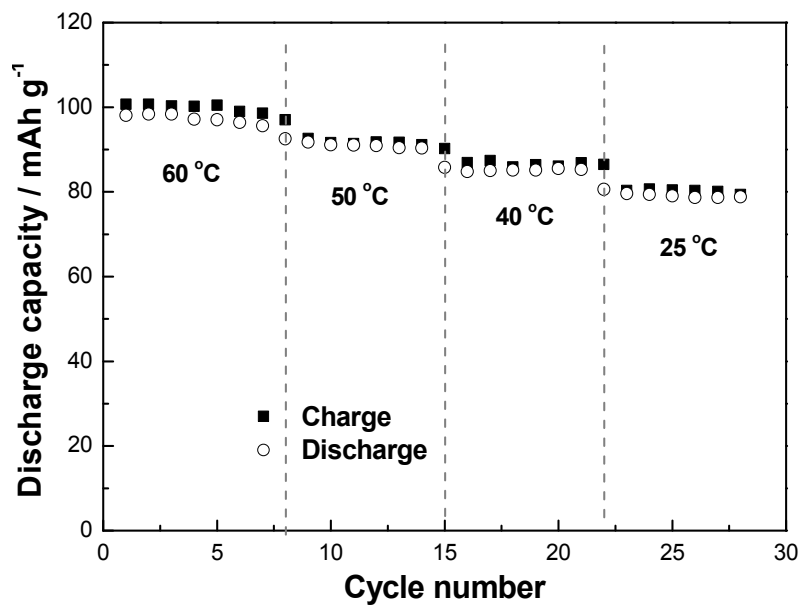
Fig. S1 Cycling stability of the Li/EP-PFSA-Li/LiMn$_2$O$_4$ battery at various temperatures. Rate: 0.5 C, corresponding to current density of 0.40 mA cm^{-2}.
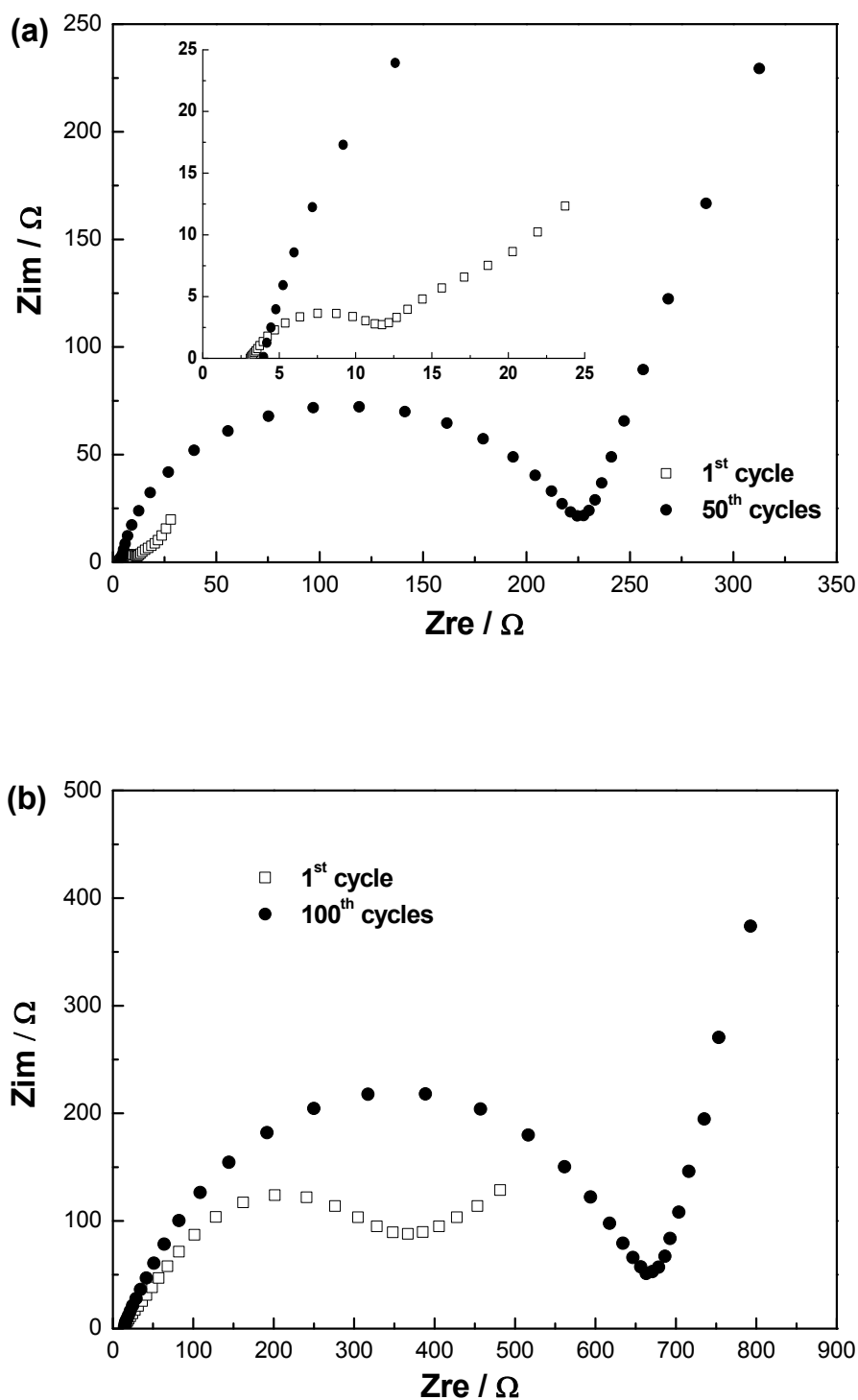
Fig. S2 Impedance spectra of batteries: (a) the $Li/LiPF_6$-EC-DMC/$LiMn_2O_4$ (1 mol L^{-1} $LiPF_6$ in EC:DMC = 1:1 *v:v*) battery after 50 cycles 1 C charged-discharged; (b) the Li/EP-PFSA-Li/$LiMn_2O_4$ battery after 100 cycles 1 C charged-discharged. Temperature: $60^{\circ}C$. Frequency range: 0.1-10^6 Hz.
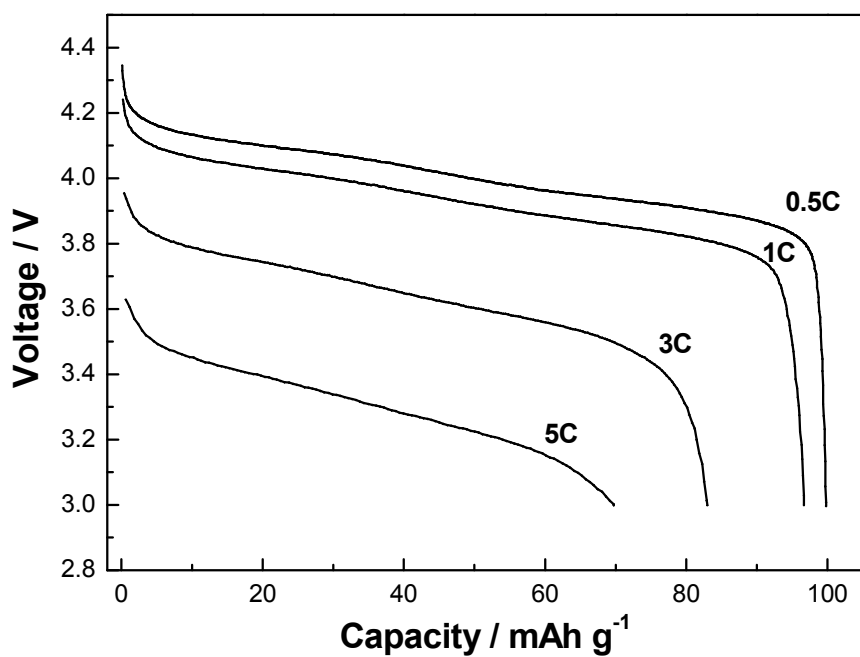
Fig. S3 Discharge voltage profiles of the Li/LiPF$_6$-EC-DMC/LiMn$_2$O$_4$ (1 mol L^{-1} LiPF$_6$ in EC:DMC = 1:1 *v:v*) battery at various rates. Temperature: 60 $^{\circ}$C. Charge rate: 0.5 C.