Sodium-ion battery based on ion exchange membranes as electrolyte and separator

Chengying Cao, Weiwei Liu, Lei Tan, Xiaozhen Liao and 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

1. Experimental

1.1 Membrane preparation and characterization

Perfluorinated sulfonic ion exchange membranes with ion exchange capacity (1.18 mmol g^{-1}) were prepared according to our previous reports.[S1] The thickness of our PFSA membranes was about 90±3 μm. Both Nafion 115 and our PFSA membranes were converted to their Na-form by using 1M NaOH aqueous solution at 80 ^oC for 12 h. After that, both membranes were washed by de-ionized water at room temperature. Since the water content directly affect the membrane properties, the dehydration process of the membranes was carried out in the glove-box under argon atmosphere. The membrane sample was first weighed (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. Ionic conductivity was determined with two electrodes AC impedance method by using Autolab PGSTAT302 electrochemical test system (Eco Chemie, the Netherlands) over a frequency range of 10 to 10^6 Hz. 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 ^oC. Before each experiment, the cell was left about 1 h to reach thermal equilibrium. The ionic conductivity (σ) was calculated as follows:

$$\sigma = \frac{L}{R \cdot A} \qquad (1)$$

where L and A are the distance between the two electrodes and the cross-sectional area of the sample, respectively, R is the resistance of the membrane. The typical AC

impedance spectra of the membranes were shown in Fig. S1. The value of the intersection with Z' axis was considered as the resistance of the membranes.

1.2 Preparation and characterization of $Na_{0.44}MnO_2$

$Na_{0.44}MnO_2$ powder was prepared through a classic solid-state reaction method.[S2] Na_2CO_3 was ball milled with Mn_2O_3 in a 0.55:1 M ratio in agate mortar to obtain homogeneous mixture. The mixture was successively heated from room temperature to 300 ^{o}C at the rate of 20 ^{o}C min^{-1}, stayed for 2 h at 300 ^{o}C , then rised to 800 ^{o}C at the same rate and kept for 12 h at 800 ∘C under air with intermediate grinding. The morphology of the obtained $Na_{0.44}MnO_2$ powder was carried out with a Tecnai G220S-Twin equipment operating at 200 kV (see in Fig. S2). It can be found that the rod-like $Na_{0.44}MnO_2$ powder with about 400 nm in diameter and 5-10 μm in length was obtained in our experiments. These results are in agreement with the literature.[S2]

1.3 Electrochemical measurements

Cyclic voltammetry was carried out on Autolab PGSTAT302 electrochemical test system (Eco Chemie, the Netherlands) with sodium 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. $Na_{0.44}MnO_2$ electrodes were prepared by mixing 80 wt% $Na_{0.44}MnO_2$ powder,10 wt% carbon black and 10 wt% poly (vinylidene fluoride) (PVDF) in N-methylpyrrolidone (NMP) solvent. The blended slurry was then coated onto an aluminum foil collector and dried in vacuum at 80 ^{o}C for 12 h. Then the electrode disks (1.5386 cm^{2}) were punched out of the coated foil sheets and weighted. $Na_{0.44}MnO_2$/Na half cells were fabricated with 2016-coin type cells in the argon-filled glove box using both PFSA-Na and Nafion-Na ion-exchange membranes 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 2.0-4.0 V.

Reference

S1 L. Li, F. Shang, L. Wang, S. Pei and Y. Zhang, *Energy Environ. Sci.,* 2010, 3, 114

S2 F. Sauvage, L. Laffont, J.-M. Tarascon, E. Baudrin, *Inorg. Chem.,* 2007, 46, 3289.
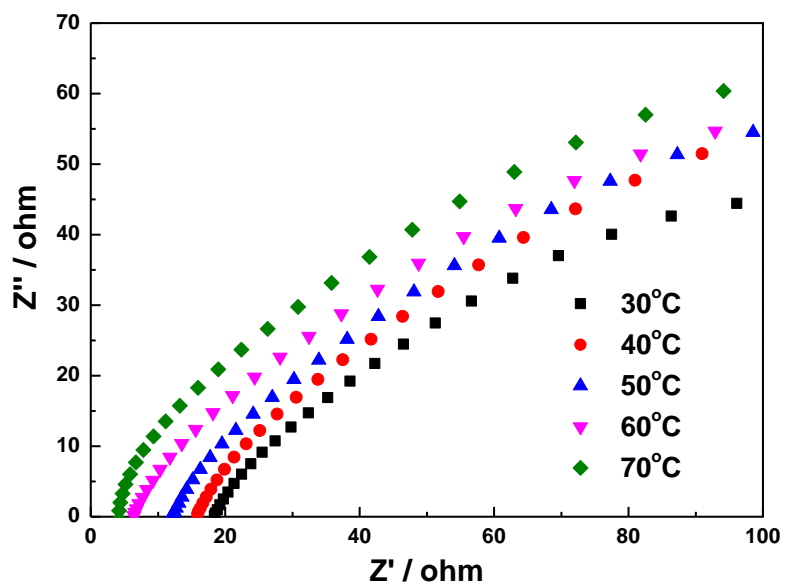
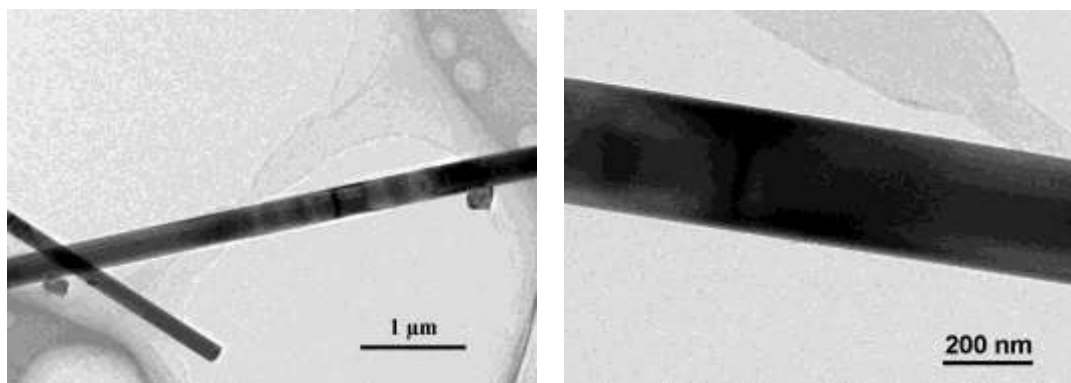**Fig. S1** Typical AC impedance spectra of membranes (PFSA-Na) at different temperature.

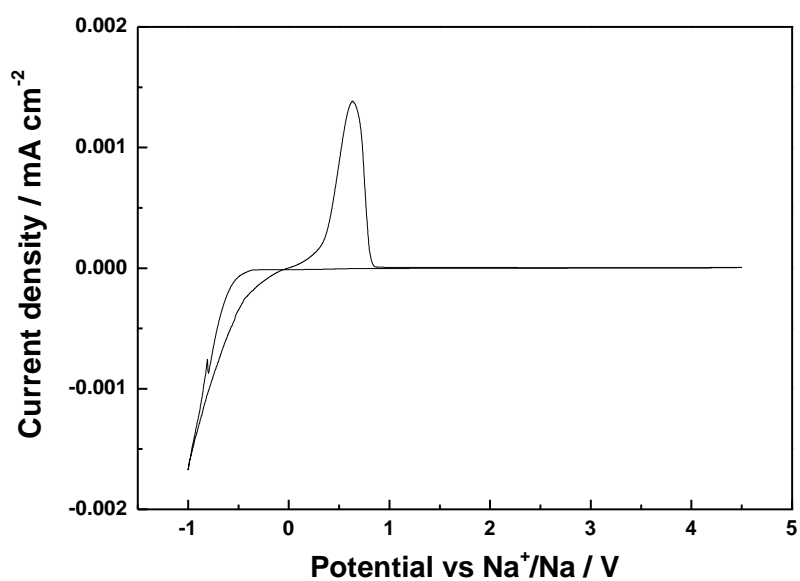**Fig. S2** TEM images of the rod-like $Na_{0.44}MnO_2$ powder.

Fig. S3 Cyclic voltammetry curve of the perfIuorianted slufonic membrane in the Na-form with stainless steel as working electrode, sodium foil as reference and counter electrodes (scan rate: 10 mV sec^{-1}) at room temperature.
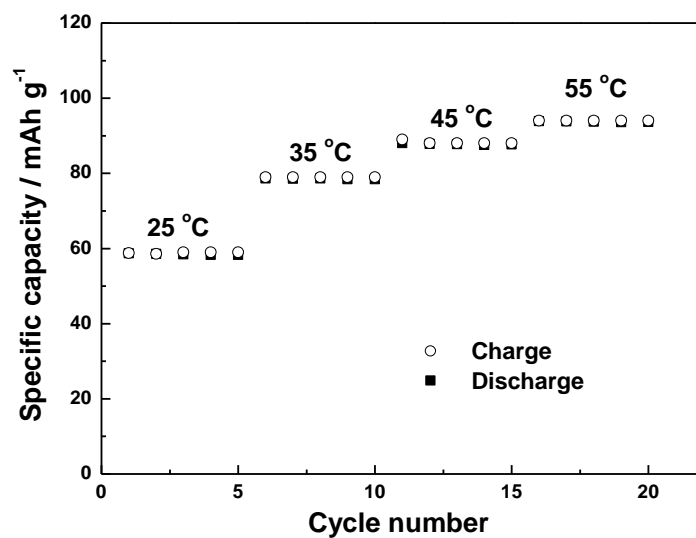
Fig. S4 Specific capacity values vs. cycle number of battery using PFSA-Na membrane as electrolyte at different temperature. Charge and discharge rates at 0.1 C (12 mA g^{-1}).
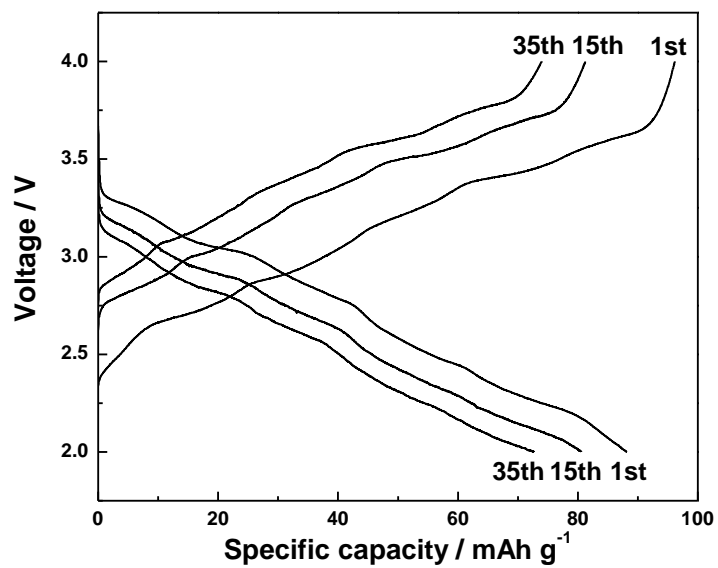
Fig. S5 Charge-discharge curves of battery using liquid electrolyte (1 mol L^{-1} NaClO$_4$ in EC : PC = 1 :1, v : v) at different cycle numbers. Rate: 0.1 C (12 mA g^{-1}).