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High performance of lithium-ion polymer battery based on nonaqueous lithiated perfluorinated sulfonic ion-exchange membranes

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Experimental procedures

Perfluorinated sulfonic ionomer with $–SO_2F$ form shown in Figure S-1 (1.18 mol g^{-1}, Shandong Dongyue Group, China) was converted to $–SO_3H$ form by using 6M NaOH and 2M H_2SO_4 aqueous solution, respectively [1]. Then, the ionomer was dissolved into *N*,*N*-dimethyl formamide in an autoclave at 230 ^oC to obtain a 5 wt% solution. The solution was subsequently condensed to 40 wt%, cast onto a glass plate using a stainless steel scraper, put into an oven at 160 ^oC for 2 h, and then peeled off from the plate. The thickness of the resultant membranes was about 90±3 μm. After that, the membrane was dipped into 500 ml of lithium hydroxide aqueous solution (40 g $LiOH·H_2O$ in 500 ml of de-ionized water) at 80 ^oC for 6 h. Then, the obtained PFSA membrane with Li^+ form (PFSA-Li) was washed by de-ionized water at room temperature until neutrality of the washing water was obtained. Since the sensitivity of the membrane properties to water content, the dehydration process of the PFSA-Li membrane was carried out in the glove-box under argon atmosphere. The membrane sample was left in contact with 20 ml anhydrous propylene carbonate in the presence of 20 g activated 3A 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.

The ionic conductivity was determined with two electrodes AC impedance method by using Autolab PGSTA302 electrochemical test system (Eco Chemie, Netherland). The conductivity measurement cell containing two stainless steel electrodes was employed. The sample was removed from PC solvent 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 80 ^oC. 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 s^{-1} and at 25 ^{o}C, 50 ^{o}C and 80 ^{o}C, respectively. All the test cells were assembled and sealed in the glove box.

The 2016-coin type battery of Li/PC-PFSA-Li/Li was used to measure the interfacial stability of the PC swollen lithiated perfluorinated sulfonic membranes (PC-PFSA-Li) with a lithium metal anode. The battery was stored at room temperature and the interfacial impedance was tested at 45 ^{o}C by using Autolab PGSTAT302 electrochemical test system (Eco Chemie, the Netherlands). The fitting of the spectra was made using the non-linear least-squares fit software developed by Autolab.

$LiFePO_4$ electrode materials with carbon treatment were purchased from ZTE Pylon Technologies Co., Ltd., China. The $LiFePO_4$ electrodes were prepared by mixing the $LiFePO_4$ material powder (90 wt%) with 5 wt% carbon black and 5 wt% poly(vinylidene fluoride) in N-methylpyrrolidone. The mixed slurry was then coated onto aluminium foil collector and vacuum dried at 120 ^{o}C for 2 h. The dried electrode was compresses by a roller at room temperature to make a smooth and compact film structure. Then the electrode disks (1.5386 cm^2) were punched out of the larger coated foil sheets and weighted. The $LiFePO_4$/Li half-cell was fabricated with 2016-coin type cells in the argon-filled glove box and the PC swollen PFSA-Li membrane was used as separator and electrolyte. The charge-discharge behaviour was tested at the constant current mode over the range of 2.5-4.2 V by Land CT2001A tester.

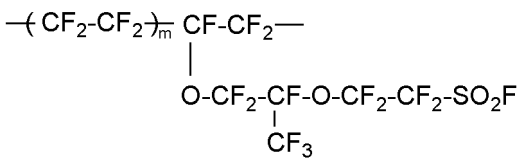

Fig. S-1 The structure formula of perfluorinated sulfonic precursor, m is about 5-7.

Reference

1. Y. Luan, H. Zhang, Y. Zhang, L. Li, H. Li and Y. Liu, J. Membr. Sci., 2008, **319**, 91.