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Organic di-radical rechargeable battery with an ionic liquid-based gel polymer electrolyte

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Abstract−We employed 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI)-based gel polymer electrolyte (ILPE) of low viscosity to prevent the instability of the di-TEMPO organic (DTO) electrode with enhancement of the cycle ability and rate-capability. The gel polymer electrolyte was prepared by electrospinning process. The DTO//ILPE//Li cell showed high initial capacity of 80 mAh g^{-1} for 1 C and 68 mAh g^{-1} for 10 C-rate, which corresponds to 100 and 85% of theoretical capacity, respectively. The cycle ability and rate-capability were much improved by using of EMImTFSI-based gel polymer electrolyte without self-discharge.

Keywords: EMImTFSI, Di-TEMPO Electrode, Cycle Ability, Rate-capability, Organic Batteries

INTRODUCTION

2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), which contains the nitroxide radical and is used as the repeating unit of polymers, exhibited reversible redox behavior with aprotic solvents [1]. The TEMPO-based polymers were actively studied for electron spin resonance, molecular motion, polymeric stabilizer, oxidants of alcohols, and electrode materials [2]. Currently, various TEMPO-based polymer structures are prepared for organic rechargeable batteries (ORBs). Advantage of TEMPO-based electrodes for organic batteries is the rapid redox reactions with an electron-transfer rate constant of the order of 10^{-1} cm s^{-1} [2,3]. The electrochemical behavior of TEMPO has been mostly studied in liquid electrolytes of organic solvents. However, the liquid electrolyte type ORB induced high self-discharge when they were maintain during a week [4]. Therefore, several solutions such as brush type electrode, ionic liquid, polymers composite electrode, and carbon composite electrode were considered to prevent the self-discharge of TEMPO-based electrodes [4-7]. Among them, ionic liquid electrolyte application is an easy method for improving the stability of TEMPO-based electrode. There are some reports wherein the ionic liquid (hereafter IL) was reported as solvent, and its CV performance was compared with organic solvents. CV of TEMPO in 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$) shows $\Delta E=0.24$ V, which corresponds to the reversible reaction of one-electron [8]. It is revealed that the electrochemical reaction of TEMPO is not significantly changed in ILs, though the effect of the high viscosity of IL results in slow ion diffusion of the electrochemical reaction and the resulting low redox current and high cell resistance [9-11]. Also, we used 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide (BMImTFSI) complexed with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as electrolyte for CF_3SO_3 anion-based di-TEMPO organic electrode. Even though the stability of ORB was improved by using ionic liquid electrolyte, the rate-capability was remarkably decreased [4].

In this study, we employed low viscosity ionic liquid electrolyte to satisfy both stability and rate-capability that is 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI), which has low viscosity of <30 cP and high ionic conductivity. Moreover, the EMImTFSI electrolyte in combination with the LiTFSI salt is applied on gel polymer electrolyte (GPE), based on activation of electrospun poly(vinylidenefluoride-co-hexafluoropropylene) [P(VdF-HFP)] membrane. The di TEMPO-based organic cathode of PF_6 anion with the ionic liquid-based gel polymer electrolyte significantly enhanced the cycle performance without self-discharge.

EXPERIMENTS

The di TEMPO-based organic active materials (DTO) were presented in previous study [12,13]. 4-Hydroxy-TEMPO was reacted with 1,4-dibromobutane in acetone and in the presence of NaH at 25 °C for 3 h. The bromide adduct thus obtained was refluxed with imidazole in 2 : 1 molar ratio for 48h in acetone in the presence of K_2CO_3. Subsequently, anion exchange was carried for 72 h at room temperature with KPF_6 in acetonitrile to obtain 1,3-bis(4-(2,2,6,6,-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium trifluorosulfonate (Fig. S1). Purity >95% (TLC), mp ~220 °C. ^{1}H NMR spectrum [δ 1.21 (s, 12H), 1.31 (s, 12H), 1.40-1.62 (m, 8H), 1.78-2.04 (m, 8H), 3.43 (t, J=6.3 Hz, 2H), 3.49 (t, J=5.7 Hz, 2H), 3.54-3.65 (m, 2H), 4.22 (t, J=7.5 Hz, 4H), 7.36 (s, 2H), 8.88 (s, 1H)]. ^{13}C NMR spectrum (δ 135.5, 122.6, 71.0, 67.4, 59.5, 50.1, 44.9, 32.4, 27.8, 26.6, 20.8).

The porous membrane of P(VdF-HFP) polymer was prepared by electrospinning process under conditions optimized in our laboratory [14]. A 17 wt% solution of P(VdF-HFP) (Kynar Flex 2801) in a mixed solvent (7 : 3 by wt ratio) of acetone and N,N dimethy-

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lacetamide (HPLC grade, Aldrich) was electrospun in a common setup at room temperature. Ionic liquid-based polymer electrolyte (ILPE) was prepared by soaking the membrane for 1 min with a solution of 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl) imide (EMImTFSI: supplied by Aldrich) in 0.5 M LiTFSI (supplied by Aldrich) under argon atmosphere in a glove box (H_2O <10 ppm).

The di-radical organic active material was characterized by ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectroscopy by recording spectra on Varian 300 spectrometer using TMS as internal standard. The surface morphology of samples was studied with scanning electron microscope (SEM) (JEOL JSM 5600). The thermal stability was analyzed by thermo-gravimetric analysis (TGA) (SDT Q600 TA) in nitrogen atmosphere at a heating rate of 10 °C/min from 20 °C to 400 °C. Ionic conductivity was measured by Solartron 1470E. The cathode was fabricated by blending the di-radical organic active material (DTO), Super-P carbon black (Aldrich) and poly(vinylidene fluoride) (PVdF: Aldrich) binder in a ratio of 40 : 50 : 10 by weight. The thin film so prepared (~20 μm thick) was cut into circular discs with an area of 0.95 cm^2 to evaluate its use as a cathode material. Two-electrode electrochemical coin cells were assembled with a lithium metal (300 μm thickness, Cyprus Foote Mineral Co.) anode, radical cathode and GPE of 0.5M LiTFSI in EMImTFSI-based electrospun electrolyte. The cell was assembled under an argon atmosphere in a glove box with a level of H_2O<10 ppm. The charge-discharge and cycling properties of the batteries were evaluated between 2.5 and 4.0 V at different current densities using an automatic galvanostatic charge-discharge unit, WBCS-3000 battery cycler (WonA Tech. Co.), at 25 °C.

RESULTS AND DISCUSSION

The molecular structure and good thermal stability of DTO are revealed from scheme and TGA of Fig. 1 with an initial decomposition temperature of 235 °C and a peak decomposition temperature of 285 °C. The radical centers in DTO do not undergo any change up to the decomposition temperature of DTO. Thus, TEMPO-based organic material is reported to have very good long-term storage stability with no appreciable change in radical concentration, even up to one year [15]. The inserted SEM image of Fig. 1 presents the morphology of the electrospun fibrous PVdF-HFP membrane. The membrane prepared by electrospinning process is made up of inter-laid fibers of average diameter 800 nm. The interlaying of fibers creates a microporous structure in the SEM image with a porosity of 58%. The surface area and pore size of electrospun fibrous PVdF-HFP membrane are determined by BET method as presented in Fig. S2. The surface area and average pore size are 15.4 m^2 g^{-1} and 700 nm, respectively. An electrolyte uptake of 250% is exhibited by the membrane within 1 min when soaked in 0.5 M LiTFSI/EMImTFSI electrolyte. The fully interconnected pore structure of the membrane is beneficial in achieving good wettability, sufficient mechanical strength and self-standing properties. The ILPE exhibits a relatively high ionic conductivity of 9.9×10^{-3} S cm^{-1} at 25 °C and good flexibility (Fig. S3).

Fig. 2 compares the SEM images of the DTO cathodes before cycling, and after subjecting to charging process with varying charge-discharge cycles. In Fig. 2(a), the as-prepared DTO cathode shows well-defined, uniform particle morphology, with spherical particles of average size 100 nm. The conductive carbon particles being spherical with an average size of 40 nm [14], the observed morphology of DTO cathode shows the uniform coating of carbon with a thin layer of DTO. After charging with several cycles, the cathode morphology of Fig. 2(b) becomes less uniform with an agglomeration of particles forming larger domains, but a significant morphology change caused by dissolution of active material and unde-

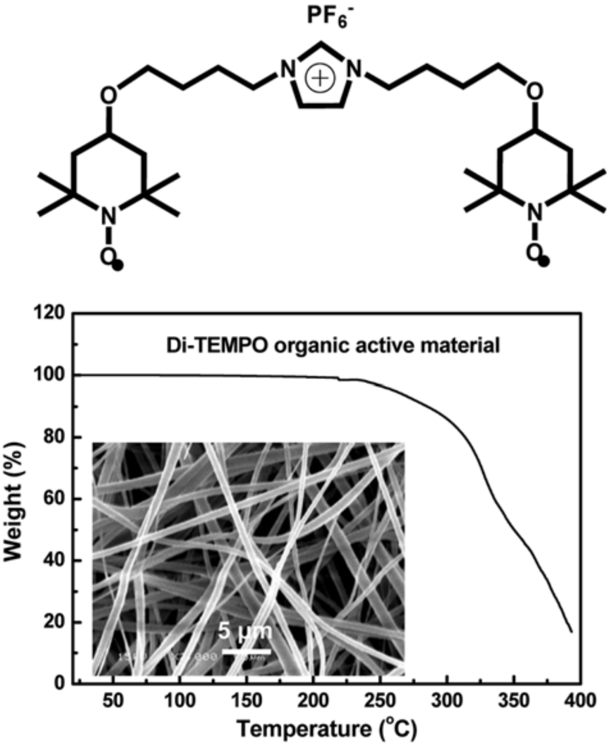

Fig. 1. Scheme and TGA curve of 1,3-bis(4-(2,2,6,6,-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium hexaflurophosphate (Inserted figure is SEM image of electrospun PVdF-HFP host).

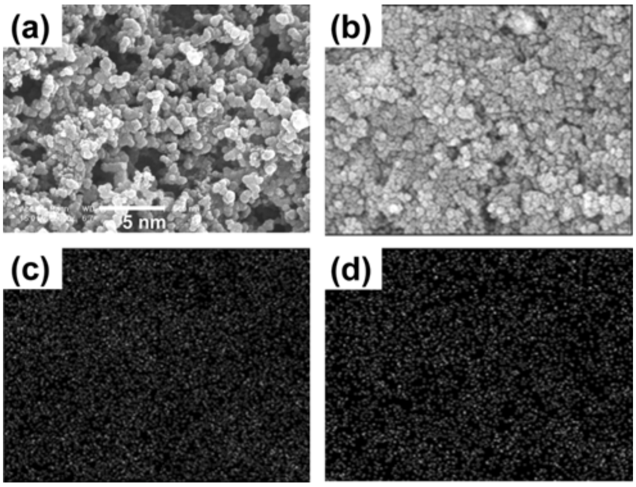

Fig. 2. SEM images of DTO-based cathode before (a) and after (b) cycling, and EDX mapping of (c) C and (d) F after charging.

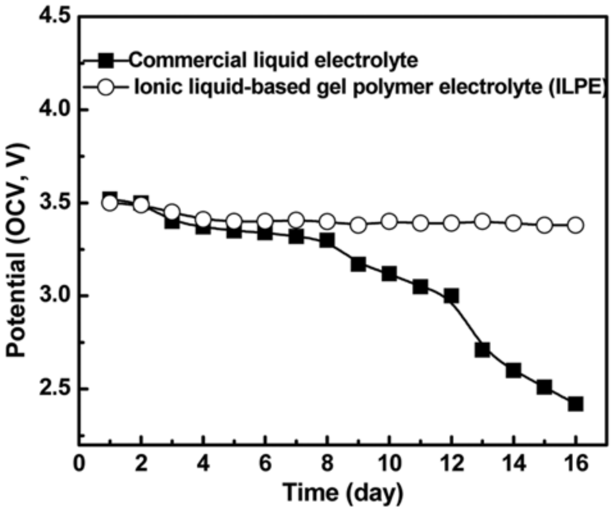

Fig. 3. Open circuit voltage (OCV) of the commercial liquid electrolyte and ionic liquid-based gel polymer electrolyte batteries over teen days.

sired reaction between DTO and electrolyte is not observed. That is because of strong ions interaction and low donor ability of ionic liquid [4,12,16]. The homogeneity of chemical composition as determined by SEM-EDX mapping is presented in Fig. 2(c), (d). The elemental mapping images obtain for C and F match with that of the corresponding SEM image. With charge process the TFSI^- [$N(SO_2CF_3)_2^-$] interacted with nitroxy radical of TEMPO conjugation, and the performance is well exhibited with F mapping althouth the electrode surface is washed with ethanol.

Self-discharge is one of the important properties of rechargeable batteries that relates to life-time, using time and efficiency of battery [17]. Namely, high self-discharge markedly decreases the life-time and efficiency of the battery. The self-discharge mainly comes from the dissolution of electrode active material and is investigated by change of open-circuit-voltage (OCV), as shown in Fig. 3. The DTO//ILPE//Li cell is charged to 100% state-of-charge (SOC) and the OCV is observed with disconnection of current. The OCV of ILPE cell is stabilized at 3.4 V, whereas commercial liquid electrolyte continuously decreases from initial voltage. The result indicates the use of ILPE is able to prevent the dissolution of organic active material effectively.

Galvanostatic charge-discharge curves for DTO//ILPE//Li cell in the voltage window 2.5-4.0 V are shown in Fig. 4(a). At 1C-rate the cell demonstrated a single charge-discharge plateau around 3.45 V reflecting a low cell resistance without undesired reaction. For the 10 C-rate the voltage separation between the charge and discharge increases to ~0.1 V from 0.04 V at 1 C as a result of increased cell resistance and the first discharge capacity is decreased to 68 mAh g^{-1} from 80 mAh g^{-1} at 1 C. The capacity retention at 10 C-rate is higher than other ionic liquid-based electrolytes [4]. Moreover, the irreversible capacity loss between the charge and discharge reaction is less than 2 mAh g^{-1} at both 1 and 10 C, and the Coulombic efficiency is almost 99% for the DTO cell with ILPE (Fig. S5).

The cycling performance of the DTO cell with 0.5 M LiTFSI in

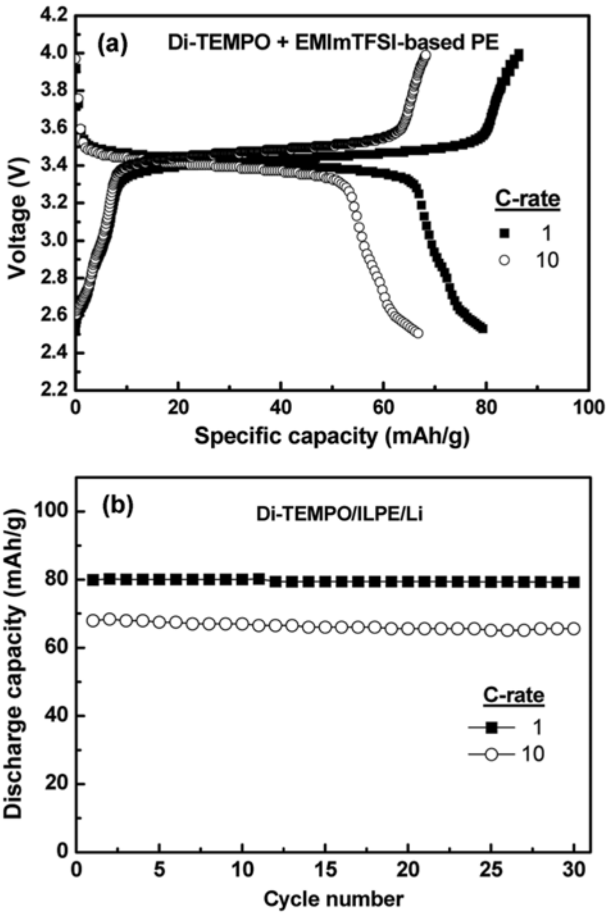

Fig. 4. Charge-discharge curve (a) and cycle performance (b) of Li/ILPE/DTO cells at 1 and 10 C-rate (room temperature).

EMImTFSI-based gel polymer electrolyte at room temperature under 1 and 10 C-rates is presented in Fig. 4(b). At both 1 and 10 C-rate the cell shows a very stable cycling performance over the 30 cycles made in this work. For the 1 and 10 C-rate the energy efficiency is corresponding to 100 and 85%. The discharge capacity fade for the DTO/OLPE/Li cell calculated on basis of the initial and 30th cycle capacities is ~0.08% per cycle at 1 C. Although the capacity fade is increased at 10 C-rate, the capacity retention is still above 96% after 30 cycles. The cycle ability and rate-capability is much improved by using of EMImTFSI ionic liquid, compared with previous BMImTFSI-based gel polymer electrolyte [12]. The excellent electrochemical performance of DTO cell with the EMImTFSI-based gel polymer is promising and reflects an improvement of thermal stability and electrochemical stability of the organic rechargeable batteries together with good cycle ability and rate-capability.

CONCLUSION

We proposed EMImTFSI-based gel polymer electrolyte (ILPE) in order to prevent the instability of the DTO electrode, while the cycle ability and rate-capability were enhanced. The ILPE could also improve the flexibility of the battery. The EMImTFSI-based gel polymer electrolyte cell showed good electrochemical properties at moderate C-rates, although the regular performance decreased at higher C-rate due to an intrinsic high viscosity of the ionic liquid. The capacity at high C-rate is higher than commercial batteries with using ionic liquid electrolyte, whereas at low C-rate the capacity is lower than commercial electrode materials. Therefore, this system could not be suitable for commercial rechargeable batteries but might attract an attention for micro-batteries.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

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The nitroxyl radicals of TEMPO are oxidized to form a cation and join an electrolyte anion ($TFSI^-$ in the present case) to form oxoammonium salt during the anodic stage and its reverse reaction occurs during cathodic stage.

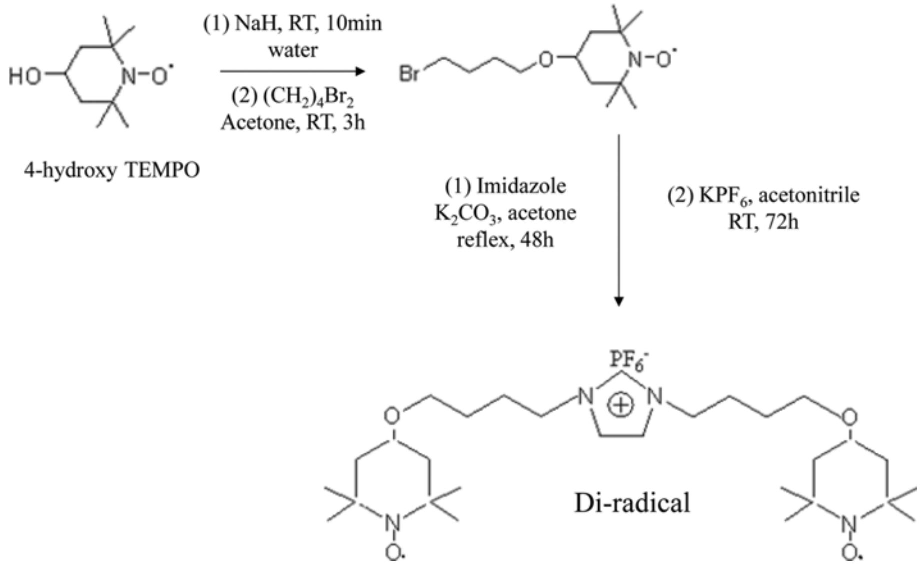

Fig. S1. Synthesis of 1,3-bis(4-(2,2,6,6,-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium hexaflurophosphate.

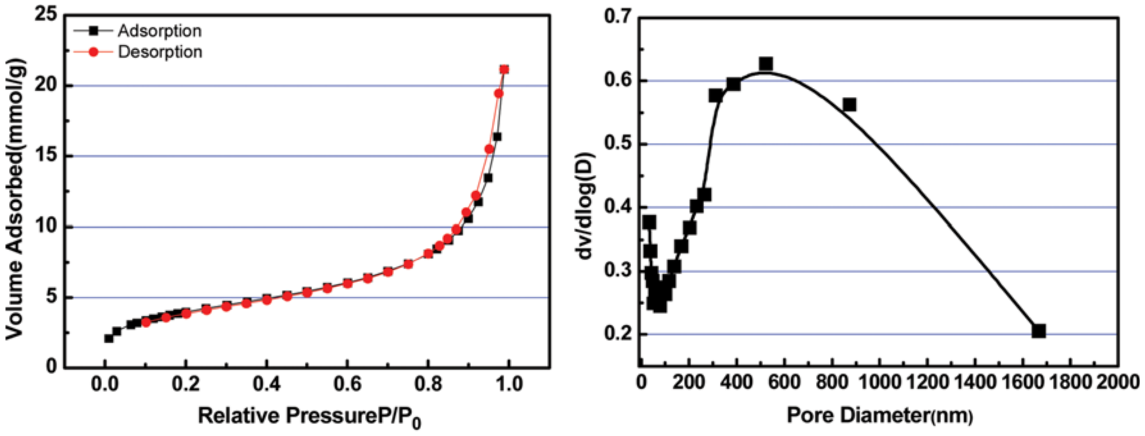

Fig. S2. BET surface area and pore size distribution of the electrospun fibrous PVdF-HFP membrane.

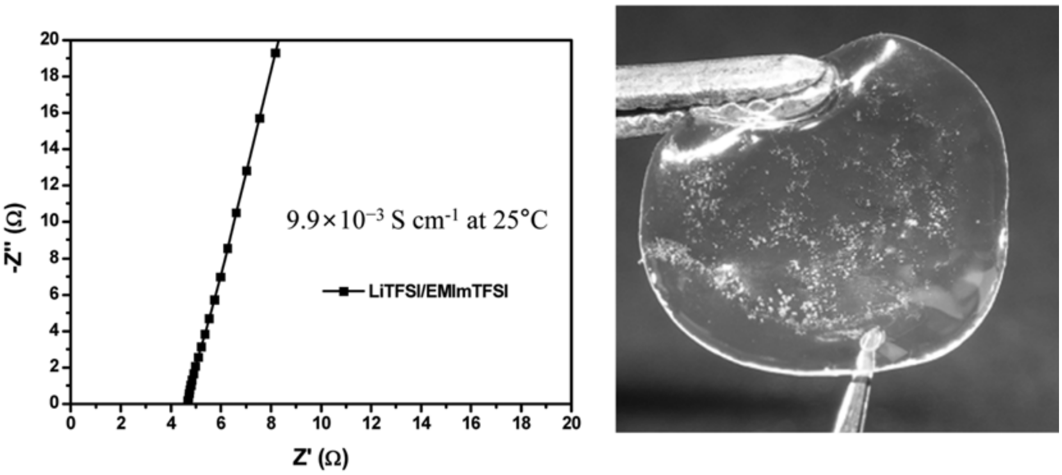

Fig. S3. Ionic conductivity and photograph of ILPE.

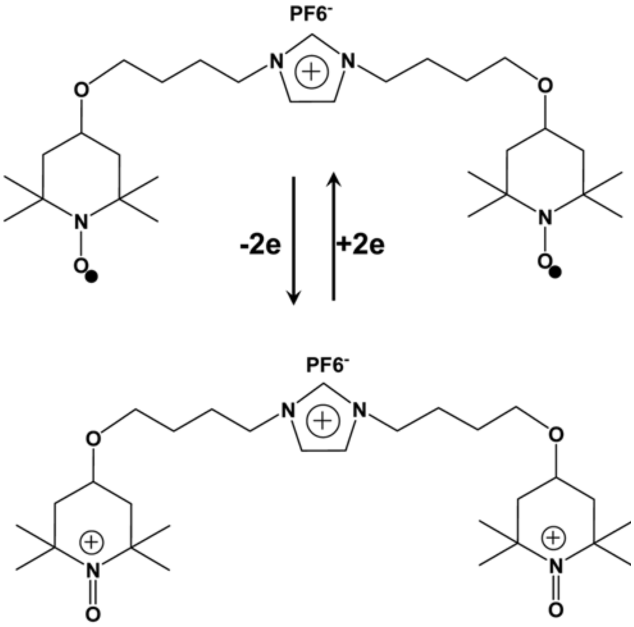

Fig. S4. Electrochemical reaction of of 1,3-bis(4-(2,2,6,6,-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium hexaflurophosphate based on nitroxide radical.

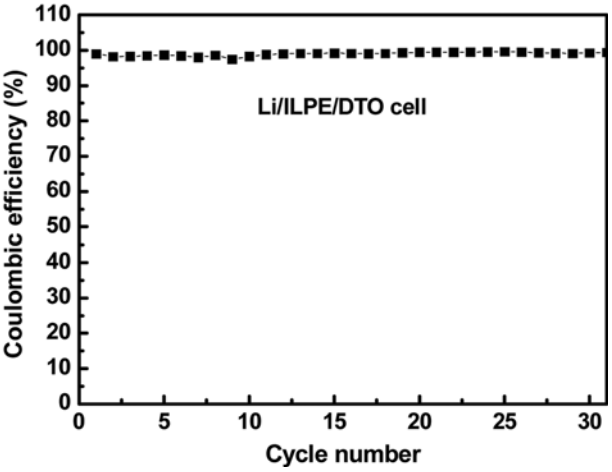

Fig. S5. Coulombic efficiency of Li/ILPE/DTO cell at 25 °C with cycles.