

# Electrospun polymer membrane activated with room temperature ionic liquid: Novel polymer electrolytes for lithium batteries

Gouri Cheruvally<sup>a</sup>, Jae-Kwang Kim<sup>a</sup>, Jae-Won Choi<sup>a</sup>, Jou-Hyeon Ahn<sup>a,\*</sup>,  
Yong-Jo Shin<sup>a</sup>, James Manuel<sup>a</sup>, Prasanth Raghavan<sup>a</sup>, Ki-Won Kim<sup>b</sup>,  
Hyo-Jun Ahn<sup>b</sup>, Doo Seong Choi<sup>c</sup>, Choong Eui Song<sup>c</sup>

<sup>a</sup> Department of Chemical and Biological Engineering and ITRC for Energy Storage and Conversion, Gyeongsang National University, 900 Gajwa-dong, Jinju 660-701, Republic of Korea

<sup>b</sup> School of Nano and Advanced Materials Engineering and ITRC for Energy Storage and Conversion, Gyeongsang National University, 900 Gajwa-dong, Jinju 660-701, Republic of Korea

<sup>c</sup> Institute of Basic Science and Department of Chemistry, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Gyeonggi-do, Suwon City, Republic of Korea

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## Abstract

A new class of polymer electrolytes (PEs) based on an electrospun polymer membrane incorporating a room-temperature ionic liquid (RTIL) has been prepared and evaluated for suitability in lithium cells. The electrospun poly(vinylidene fluoride-*co*-hexafluoropropylene) P(VdF-HFP) membrane is activated with a 0.5 M solution of LiTFSI in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI) or a 0.5 M solution of LiBF<sub>4</sub> in 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>). The resulting PEs have an ionic conductivity of  $2.3 \times 10^{-3}$  S cm<sup>-1</sup> at 25 °C and anodic stability at >4.5 V versus Li<sup>+</sup>/Li, making them suitable for practical applications in lithium cells. A Li/LiFePO<sub>4</sub> cell with a PE based on BMITFSI delivers high discharge capacities when evaluated at 25 °C at the 0.1C rate (149 mAh g<sup>-1</sup>) and the 0.5C rate (132 mAh g<sup>-1</sup>). A very stable cycle performance is also exhibited at these low current densities. The properties decrease at the higher, 1C rate, when operated at 25 °C. Nevertheless, improved properties are obtained at a moderately elevated temperature of operation, i.e. 40 °C. This is attributed to enhanced conductivity of the electrolyte and faster reaction kinetics at higher temperatures. At 40 °C, a reversible capacity of 140 mAh g<sup>-1</sup> is obtained at the 1C rate.

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**Keywords:** Polymer electrolyte; Electrospinning; Porous membrane; Room temperature ionic liquid; Lithium batteries

## 1. Introduction

There is a great demand for developing a suitable polymer electrolyte (PE) for application in lithium metal polymer batteries (LMPBs). When compared with presently available lithium-ion batteries, LMPBs offer advantages in terms of lighter weight, higher specific energy, flexibility in design, and improved safety. However, the most ideal, ‘dry’, solid PE based on the complex formed by blending poly(ethylene oxide) (PEO) with lithium salt (LiX) has limited ionic con-

ductivity at lower temperatures [1,2] and hence demands an operating temperature of >70 °C for successful utilization in LMPBs. Use of gel PEs prepared by incorporating liquid electrolyte in the porous membrane of a host polymer has received great attention since they possess higher ionic conductivity and sufficient mechanical integrity for handling. Poly(vinylidene fluoride) (PVdF) and its copolymer, poly(vinylidene fluoride-*co*-hexafluoropropylene) {P(VdF-HFP)} are particularly preferred as polymer hosts because of their thermal and electrochemical stability and affinity for electrolytes [3]. The porous membranes are prepared by different methods that include solution casting [4], phase inversion [5,6], plasticizer extraction [7,8], and electrospinning [9–14]. The size and distribution of the pores are important factors that decide the membrane’s ability for elec-

\* Corresponding author. Tel.: +82 55 751 5388; fax: +82 55 753 1806.  
E-mail address: [jhahn@gsnu.ac.kr](mailto:jhahn@gsnu.ac.kr) (J.-H. Ahn).

trolyte uptake. The process of electrospinning is particularly suitable for producing thin and homogenous polymer membranes with pores in the nano- to micro-meter size range. Since the membranes possess high porosity, they exhibit relatively high electrolyte uptake that results in improved ionic conductivity. A few recent studies [9–14] have reported the suitability of gel PEs based on electrospun polymer membranes for lithium batteries.

The use of molecular solvents as electrolyte components always causes concern with respect to the safety aspects of the battery. There has been much interest in recent years to replace them with suitable room-temperature ionic liquids (RTILs), which are non-volatile, non-flammable molten salts with low melting points [15]. RTILs generally exhibit high ionic conductivity, high thermal and chemical stability, a wide electrochemical window and low toxicity. They are thus preferred as electrolyte components in batteries and capacitors [15]. RTILs based on organic cations like imidazolium [16–18], pyrrolidinium [19–23] and piperidinium [24,25] have been studied and the results have been extremely encouraging. In some of these studies, RTIL is incorporated in PEO-LiX solid PEs to achieve a substantial increase in ionic conductivity at low temperatures [19–22].

In an earlier study, we optimized the electrospinning parameters for obtaining a microporous P(VdF-HFP) membrane and investigated PE prepared by activating it with organic liquid electrolytes [14]. In the present study, we evaluate the suitability of a PE based on activation of electrospun P(VdF-HFP) membrane with 1-butyl-3-methylimidazolium (BMI)-based RTILs, which are non-volatile. BMI-based RTILs have been chosen based on our earlier studies that showed good properties for the PEs prepared by incorporating them in PEO-LiX [26,27].

## 2. Experimental

### 2.1. Preparation of PEs

A microporous membrane of P(VdF-HFP) (Kynar 2801) was prepared by means of electrospinning as per the procedure standardized in our laboratory [14]. A 16 wt.% solution of P(VdF-HFP) in a mixed solvent of acetone and *N,N*-dimethylacetamide (7/3, w/w) was electrospun by applying an electric voltage of 18 kV at room temperature. A thin film of ~80  $\mu\text{m}$  thickness was collected on an aluminum foil. The electrospun membrane was vacuum dried at 60 °C for 12 h before further use. The RTILs, i.e., 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>), were prepared by a reported procedure [28]. The PEs were prepared by immersing the electrospun membrane in a 0.5 M solution of LiTFSI in BMITFSI or a 0.5 M solution of LiBF<sub>4</sub> in BMIBF<sub>4</sub> for a period of 20 min at 40 °C and then slowly cooling to room temperature. Activation of the membrane to prepare the PEs was carried out in argon-filled glove box under conditions of <10 ppm moisture level.

### 2.2. Characterization and electrochemical evaluation

The surface morphology of the membrane was observed with a scanning electron microscope (SEM-JEOL JSM 5600). Electrolyte uptake was determined by soaking a circular piece of the membrane (diameter 1.5 cm) in the electrolyte solutions kept at 40 °C for 20 min. A higher temperature was employed to facilitate the easy penetration of the pores of the membrane by the electrolytes, which are very viscous at room temperature. The wetted membranes were slowly cooled to 25 °C and the excess electrolyte remaining on the surface of each membrane was removed by wiping softly with a tissue paper. The electrolyte uptake ( $\varepsilon$ ) was calculated using the relation:

$$\varepsilon(\%) = \frac{M - M_0}{M_0} \times 100 \quad (1)$$

where  $M_0$  is the mass of the dry membrane and  $M$  is the mass after soaking with electrolyte [10]. The ionic conductivities of the PEs, over the temperature range –20 to 80 °C, were measured by the ac impedance method using stainless-steel (SS) Swagelok® cells with an IM6 frequency analyzer. The measurements were carried out over the frequency range of 100 mHz to 2 MHz, at an amplitude of 10 mV.

Cyclic voltammetry (CV) of the electrolyte sandwiched between lithium electrodes was measured at room temperature at a scan rate of 1 mV s<sup>-1</sup> between –1 and +1 V. Electrochemical stability was determined by linear sweep voltammetry (LSV) of a Li/PE/SS cell at a scan rate of 1 mV s<sup>-1</sup>, over the range of open-circuit voltage to 6 V. Two-electrode coin cells were assembled by sandwiching PE between a lithium metal anode (300  $\mu\text{m}$  thickness, Cyprus Foote Mineral Co.) and a carbon-coated lithium iron phosphate (LiFePO<sub>4</sub>) cathode in SS Swagelok® circular cells of 23 mm diameter. LiFePO<sub>4</sub> was prepared in-house by mechanical activation followed by solid state reaction at high temperature [29]. The Li/PE/LiFePO<sub>4</sub> cell was subjected to CV at 25 and 40 °C at a scan rate of 0.1 mV s<sup>-1</sup> between 2.0 and 4.5 V. Electrochemical performance tests were carried out using an automatic galvanostatic charge–discharge unit, WBCS3000 battery cyler (WonA Tech. Co.), between 2.0 and 4.2 V at 25 and 40 °C, at different current densities that ranged from 0.1 to 1 C.

## 3. Results and discussion

### 3.1. Electrolyte uptake and ionic conductivity

The morphology of a P(VdF-HFP) membrane prepared by electrospinning is presented in Fig. 1. The membrane is made up of a network of interlaid fibers with an average diameter (AFD) of 1  $\mu\text{m}$ . The zig–zag interlaying of the fibers imparts sufficient mechanical strength for handling the membrane. The presence of fully-interconnected micron-sized pores in the structure makes it ideal for application as a host matrix for the preparation of gel polymers. The membrane exhibits an electrolyte uptake of 750% with a 0.5 M solution of LiTFSI in BMITFSI and 600% with a 0.5 M solutions of LiBF<sub>4</sub> in BMIBF<sub>4</sub>. The high electrolyte uptake shown by the electrospun P(VdF-HFP) membrane results

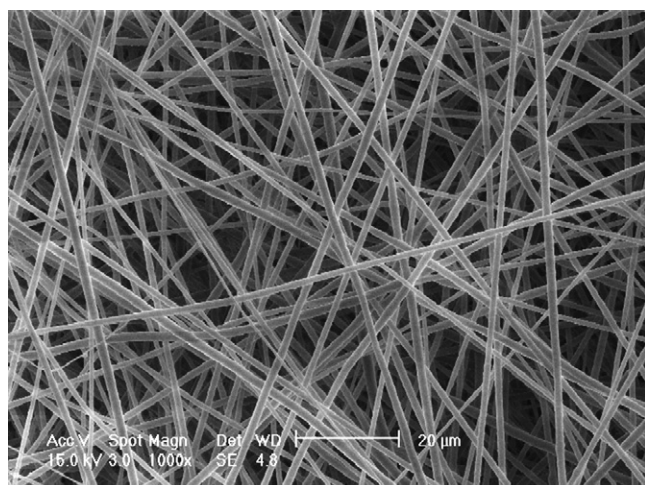


Fig. 1. SEM image of electrospun P(VdF-HFP) membrane.

from: (i) the high surface area provided by the uniform fibers of micron and sub-micron size diameters; (ii) the easy penetration of liquids into the inner cavities through the interconnected pores of the membrane; (iii) the high density of the RTILs used as electrolytes. The fact that the uptake of electrolyte based on BMITFSI is higher than that based on BMIBF<sub>4</sub> is attributed to the lower viscosity of the former RTIL, as given in Table 1.

The high electrolyte uptake exhibited by electrospun membranes naturally raises a concern regarding their ability to retain the liquid electrolyte on ageing or under mechanical stress. Kim et al. have evaluated the leakage behaviour (under mechanical stress) of electrospun PVdF [10] and P(VdF-HFP) [13] membranes that contained LiPF<sub>6</sub> in mixed organic solvents as the electrolyte. The membranes showed good electrolyte retention properties that should be acceptable for practical battery applications. A decrease in AFD resulted in a decrease in leakage rate; thus, membranes with <1 μm AFD exhibited a high retention of ~80% of its initial absorption ratio even after 120 min of the leakage test [10,13]. It was also observed that, compared with PVdF membranes, P(VdF-HFP) membranes showed lower leakage which is attributed to the higher amorphous content in the polymer [10]. Hence, the high affinity of P(VdF-HFP) polymer for the electrolyte, the large surface area provided by the fibers of 1 μm AFD and the unique network structure of the electrospun membrane studied here are expected to result in a high electrolyte retention ability for PEs based on these membranes.

The temperature dependence of the ionic conductivity of the PEs incorporated with BMITFSI and BMIBF<sub>4</sub> is shown in

Table 1  
Properties of BMITFSI and BMIBF<sub>4</sub> [15]

Properties	BMITFSI	BMIBF <sub>4</sub>
Molecular weight (g mol <sup>-1</sup> )	419	225.8
Density (g cm <sup>-3</sup> )	1.429 <sup>(19)</sup>	1.210 <sup>(25)</sup>
Melting point (°C)	-4	-81 <sup>a</sup>
Viscosity (cP)	52 <sup>(20)</sup>	180 <sup>(25)</sup>
Conductivity (mS cm <sup>-1</sup> )	3.9 <sup>(20)</sup>	3.5 <sup>(25)</sup>

Superscripts refer to temperature at which property is measured.

<sup>a</sup> Determined in laboratory.

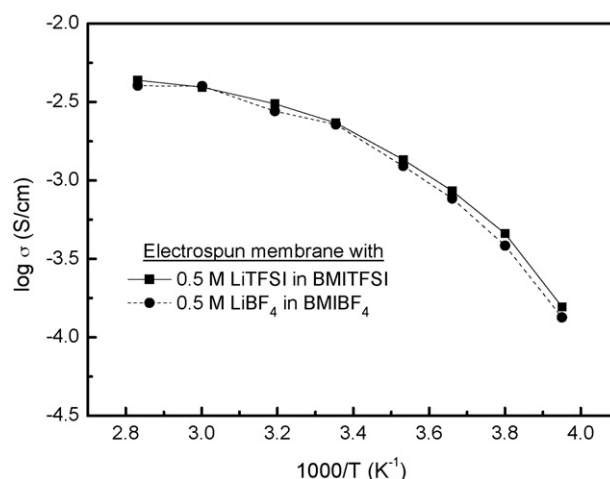


Fig. 2. Variation of ionic conductivity with temperature of PEs based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI and 0.5 M LiBF<sub>4</sub> in BMIBF<sub>4</sub>.

Fig. 2. The ionic conductivities of these two PEs are nearly the same over the entire temperature range (-20 to 80 °C) studied here. A conductivity of >10<sup>-3</sup> S cm<sup>-1</sup> is achieved at a minimum of 10 °C. Thus, at 25 °C, the PEs exhibit an ionic conductivity of 2.3 × 10<sup>-3</sup> S cm<sup>-1</sup>, which is quite high for a PE. Although BMITFSI and BMIBF<sub>4</sub> possess ionic conductivities that are ≥3.5 × 10<sup>-3</sup> S cm<sup>-1</sup> at 25 °C (Table 1), the processes of adding lithium salts to them and further absorbing of the electrolyte solutions within the pores of the polymer membrane are expected to decrease the ionic conductivity. Nevertheless, the extent of conductivity loss incurred upon absorption of liquid electrolyte solution due to the presence of the electrospun membrane in the PE has been found to be much lower than that reported for PEs based on microporous membranes prepared by the phase-inversion method [14]. The high porosity of the electrospun membrane, and more importantly the interconnectivity of micron-sized pores, assist the easy migration of ions and this results in high ionic conductivity even at lower temperatures.

### 3.2. Electrochemical stability

LSV data of PEs sandwiched between Li and SS electrodes are shown in Fig. 3. The voltage corresponding to the onset of a steady increase in the observed current indicates the anodic stability limit of the electrolyte. A PE incorporating BMITFSI shows stability up to 5.3 V. This is better than the PE with BMIBF<sub>4</sub> which is stable up to 4.7 V. The anodic current corresponds to the oxidation of the anions TFSI<sup>-</sup> and BF<sub>4</sub><sup>-</sup> in the respective electrolytes. Compared with BF<sub>4</sub><sup>-</sup>, TFSI<sup>-</sup> is better stabilized by the resonance structures in which the negative charge is fully delocalized over its atoms. Nevertheless, the PE containing BMIBF<sub>4</sub> also exhibits an anodic stability at >4.5 V, which is high enough to employ it in combination with most of the presently used cathode materials in lithium batteries.

Compatibility with the lithium electrode is an essential requirement for employing the PEs in LMPBs. CV studies of Li/PE/Li cells can provide a good understanding of the redox processes taking place in the cell. BMITFSI and BMIBF<sub>4</sub> are

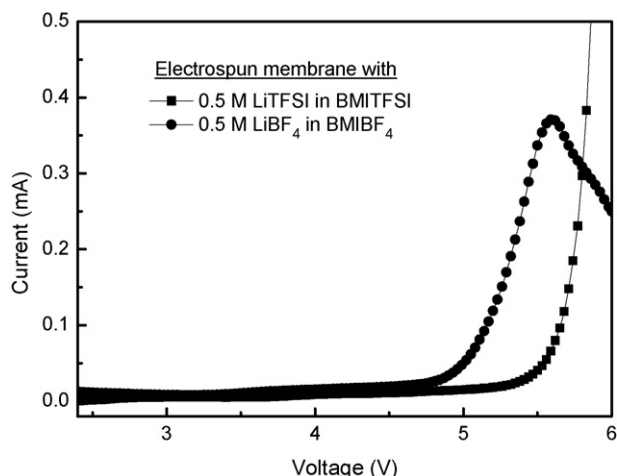


Fig. 3. Anodic stability of PEs based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI and 0.5 M LiBF<sub>4</sub> in BMIBF<sub>4</sub> by LSV (Li/PE/SS cells, scan rate: 1 mV s<sup>-1</sup>; voltage range: open-circuit voltage to 6 V).

reported to have electrochemical stability windows of 4.6 and 4.2 V, respectively [15]. Thus, BMITFSI has a cathodic limit of -2.0 V and an anodic limit of 2.6 V versus Ag/Ag<sup>+</sup> [30], which is equivalent to 1.2 and 5.8 V versus Li/Li<sup>+</sup>. BMIBF<sub>4</sub> has cathodic limit of 1.2 V and an anodic limit of 5.0 V versus Li/Li<sup>+</sup> [31]. The positive cathodic limit of these RTILs with respect to lithium suggests the unsuitability for using them in lithium metal batteries. This feature has also been reported [17] for ethyl-methylimidazole (EMI)-based RTILs. However, our earlier studies [26,27] have shown that when BMITFSI and BMIBF<sub>4</sub> are incorporated in PEO-LiTFSI blend, the resulting PEs are capable of exhibiting a well-defined lithium reduction process at ~-0.5 V and are stable up to -1.0 V versus Li/Li<sup>+</sup>. The enhancement of the cathodic limit results from the effective suppression of reduction of the organic cation of RTIL by the lithium salt in the electrolyte [19,26,27]. The PEs prepared by activation of electrospun P(VdF-HFP) membranes with BMITFSI or BMIBF<sub>4</sub> also exhibit well-defined anodic and cathodic peaks in the CVs, as shown in Fig. 4. The oxidation and

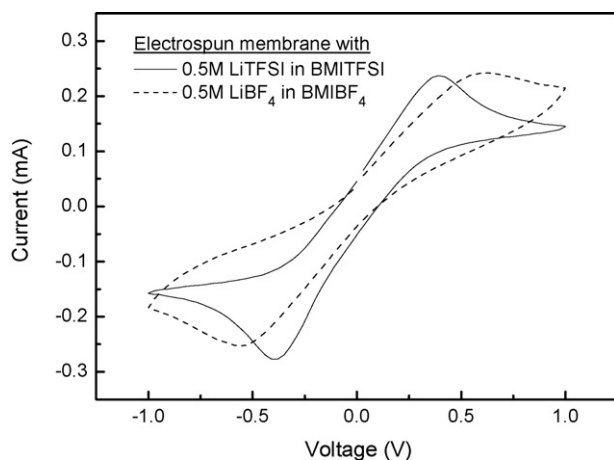


Fig. 4. CV profiles of PEs based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI and 0.5 M LiBF<sub>4</sub> in BMIBF<sub>4</sub> (Li/PE/Li cells, scan rate: 1 mV s<sup>-1</sup>; voltage range: -1 to +1 V).

reduction peaks are at 0.39 and -0.38 V, respectively, for the PE containing BMITFSI; the corresponding peaks are at 0.60 and -0.56 V for PE containing BMIBF<sub>4</sub>. Thus, a PE with BMITFSI supports better, reversible redox behaviour with a lower peak separation of 0.77 V compared with PE with BMIBF<sub>4</sub> that has a peak separation of 1.16 V. It is noteworthy that the PEs with RTILs exhibit only a low reduction current (<0.2 mA) at -1.0 V versus Li<sup>+</sup>/Li, which indicates that the bulk reduction of RTILs has not occurred appreciably at this voltage and the PEs are sufficiently stable at this voltage.

### 3.3. Evaluation in Li/LiFePO<sub>4</sub> cell

LiFePO<sub>4</sub> is a cathode active material of increasing attention in recent years since it is a safe, cheap and non-toxic material that provides a relatively high theoretical capacity of 170 mAh g<sup>-1</sup> with good cycle performance. We have synthesized carbon-coated LiFePO<sub>4</sub> by a modified mechano-chemical activation followed by a thermal treatment procedure. This material gives a high-discharge capacity and good cycle performance when evaluated as a cathode in lithium metal batteries with liquid electrolytes at room temperature [29]. In the present study, the suitability of PE for a Li/LiFePO<sub>4</sub> cell has been studied under varying C-rate and operation temperatures. Fig. 5 presents the CV profile of a cell with PE containing BMITFSI at 25 and 40 °C. The oxidation and reduction peaks representing the redox reactions of LiFePO<sub>4</sub> as a cathode material are observed at 3.7 and 3.1 V, respectively, with a mean redox potential at 3.4 V. The areas under the cathodic and anodic peaks remain nearly the same, which indicates that the extraction and insertion of lithium ions from/to the material proceeds to the same extent. It is observed that the redox current is enhanced by an increase in operation temperature of the cell. Thus, the cell at 40 °C has a redox current that is ~17% higher than that at 25 °C. This is attributed to the enhanced kinetics of charge transfer as well as increased ionic conductivity at the higher temperature.

The initial discharge capacities of the cells with PEs containing the two RTILs at the 0.1C rate (0.08 mA cm<sup>-2</sup>) at 25 °C are

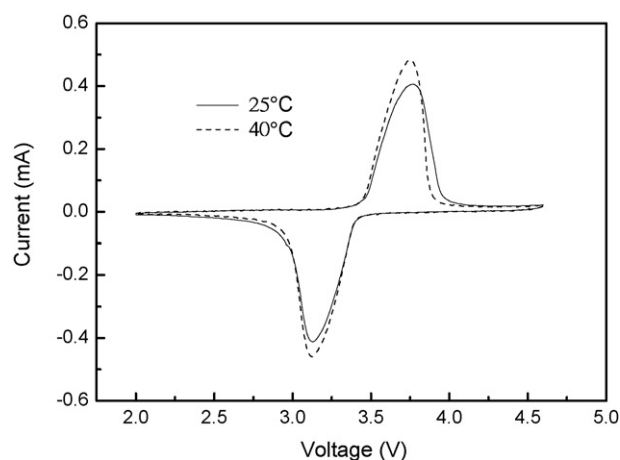


Fig. 5. CV of Li/PE/LiFePO<sub>4</sub> cell at 25 and 40 °C (PE based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI; scan rate: 0.1 mV s<sup>-1</sup>; voltage range: 2.0–4.5 V).

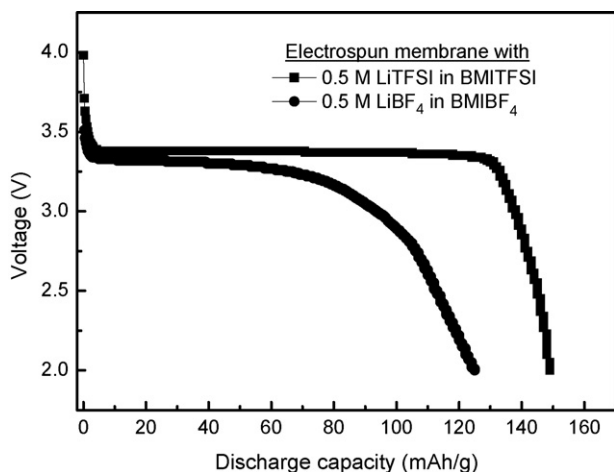


Fig. 6. Initial discharge capacities of PEs based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI and 0.5 M LiBF<sub>4</sub> in BMIBF<sub>4</sub> (Li/PE/LiFePO<sub>4</sub> cells, 0.1C rate, 25 °C).

compared in Fig. 6. The PE with BMITFSI delivers a capacity of 149 mAh g<sup>-1</sup>, which is 87.6% of the theoretical capacity of LiFePO<sub>4</sub>. This is a remarkable performance since the PE is able to serve the purpose excellently at such low temperatures. In an

earlier study with a PEO-based PE incorporating BMITFSI in Li/LiFePO<sub>4</sub> cell at 25 °C, only 32% of theoretical capacity could be realized at 0.05C rate [27]. The efficiency of the electrospun membrane to hold a large quantity of electrolyte and provide high ionic conductivity is the key factor contributing to this excellent performance. The PE with BMIBF<sub>4</sub> delivers a discharge capacity of 125 mAh g<sup>-1</sup>, which is significantly lower than the PE with BMITFSI. This could be the result of reduced compatibility of the electrolyte containing BF<sub>4</sub><sup>-</sup> with the electrodes in the cell. With PEO-based electrolytes incorporating RTILs, it was observed earlier [26] that the system with BMIBF<sub>4</sub> leads to higher electrode/electrolyte interfacial resistance in the cell, probably due to the formation of a thick, passivating layer on the lithium electrode by the reaction of F<sup>-</sup> ions usually present along with BF<sub>4</sub><sup>-</sup> ions [26]. Further electrochemical evaluations have been carried out with the better-performing PE that incorporates BMITFSI.

The Li cell with PE incorporating BMITFSI has been evaluated for cycleability property at the 0.1C rate at 25 °C and the results are shown in Fig. 7(a). The cell displays a very stable performance with nearly identical charge and discharge capacities. After 24 cycles, the cell exhibits a charge–discharge capacity of

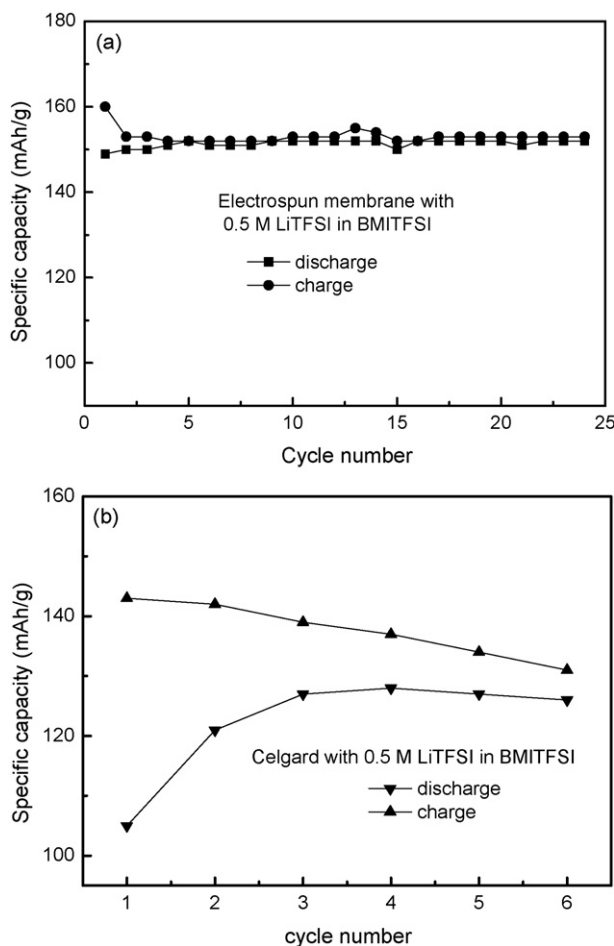


Fig. 7. Cycle performance (charge and discharge capacities) of (a) PE based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI and (b) Celgard separator activated with 0.5 M LiTFSI in BMITFSI (Li/PE/LiFePO<sub>4</sub> cells, 0.1C rate, 25 °C).

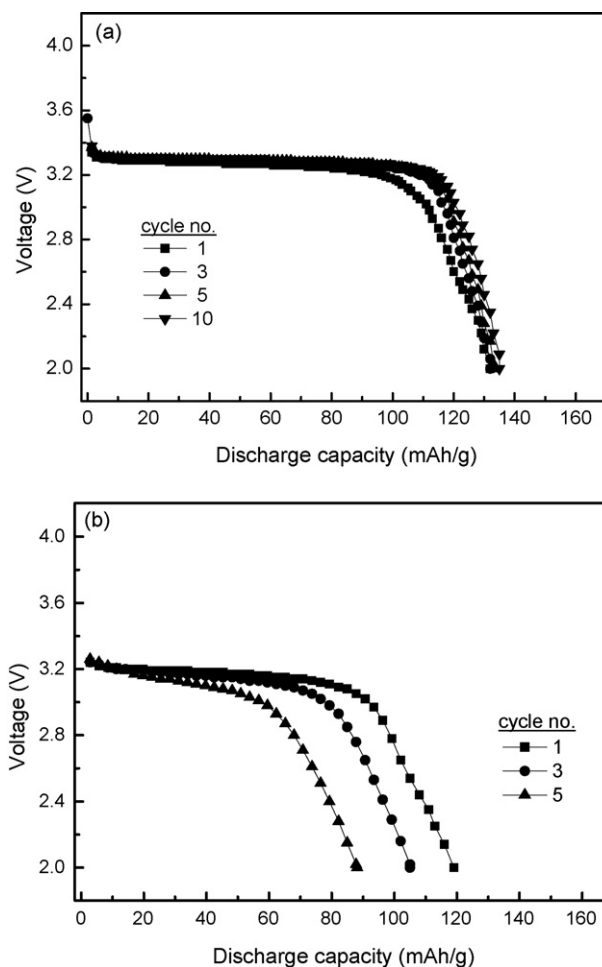


Fig. 8. Discharge capacity during cycling of Li/PE/LiFePO<sub>4</sub> cell at 25 °C (a) 0.5C rate, and (b) 1C rate (PE based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI).

152 mAh g<sup>-1</sup>, corresponding to 89.4% of theoretical capacity. Fig. 7(b) shows the cycle performance of the cell under identical conditions using a Celgard separator activated with 0.5 M LiTFSI in BMITFSI. The specific capacity of the cell is lower (by at least 20%) than that of the cell based on an electrospun P(VdF-HFP) membrane. The cell exhibits a tendency towards better reversibility after a few initial cycles; probably resulting from a better stabilization of the system as a whole. The fully-interconnected pore structure of the electrospun membrane with higher porosity and the resultant higher ionic conductivity of the PE contribute to the performance enhancement compared with the electrolyte based on the Celgard separator.

The cell performance in terms of discharge capacity on cycling at 0.5 and 1 C at 25 °C is shown in Fig. 8(a) and (b), respectively. The initial discharge capacity of 132 mAh g<sup>-1</sup> at the 0.5C rate is well retained after repeated cycling. At the higher current density of 1 C, however, the cell shows rapid degradation in performance. The first cycle capacity of 119 mAh g<sup>-1</sup> is lowered to 88 mAh g<sup>-1</sup> in just five cycles. The LiFePO<sub>4</sub> cathode material is known to suffer the limitation of lower performance at higher C-rate and reduced temperatures due to slow Li<sup>+</sup> ion diffusion at the solid, two-phase boundary of LiFePO<sub>4</sub>/FePO<sub>4</sub> [32]. Nevertheless, with the use of a liquid electrolyte (1 M

LiPF<sub>6</sub> in EC/DMC) in a Li/LiFePO<sub>4</sub> cell at 25 °C [29], a higher discharge capacity of 142 mAh g<sup>-1</sup> at 1 C and a better cycle performance was realized. Hence, the lower performance of the present cell using PE at 25 °C could be mainly due to insufficient ionic conduction levels. To validate this, the cell was operated at 1 C and 40 °C. The performance in terms of discharge capacity and cycling is shown in Fig. 9(a) and (b), respectively. An initial discharge capacity of 140 mAh g<sup>-1</sup> is delivered, which is 100% retained on cycling. The enhanced performance at 40 °C compared with that at 25 °C results from the higher ionic conductivity of the electrolyte as well as enhanced kinetics (i.e., rate of electrode reactions) at higher temperature. A CV comparison of the cell (Fig. 5) also shows a higher redox current resulting from the cell at 40 °C. The performance of the cell under study at 40 °C at 1 C is nearly the same as that of the cell with a liquid electrolyte at 25 °C at the same C-rate, as obtained previously [29]. Thus, this study shows that a PE based on an electrospun P(VdF-HFP) membrane with BMITFSI is suitable for satisfactory performance of Li/LiFePO<sub>4</sub> cells at room temperature and low current densities (<1 C), and at a moderately high temperature of 40 °C at a higher current density of 1 C.

#### 4. Conclusions

An electrospun P(VdF-HFP) membrane has been activated by incorporating the RTILs, BMITFSI or BMIBF<sub>4</sub>, to prepare novel PEs. The presence of thin fibers with a large surface area and fully-interconnected micron-sized pores in the membrane is conducive to high uptake of the electrolytes based on a lithium salt dissolved in BMITFSI or BMIBF<sub>4</sub>. The PEs possess high ionic conductivity of  $2.3 \times 10^{-3}$  S cm<sup>-1</sup> at 25 °C, which is suitable for room temperature applications of lithium batteries. Good compatibility with lithium metal electrodes showing well-defined peaks for lithium insertion and extraction is observed for the PEs. Anodic stability at >4.5 V is obtained and this indicates their usefulness in lithium metal batteries with presently used cathode materials. The PE incorporating BMITFSI performs better than that incorporating BMIBF<sub>4</sub>. A Li/LiFePO<sub>4</sub> cell using a PE based on BMITFSI gives an initial discharge capacity at 25 °C of 149 and 132 mAh g<sup>-1</sup> at 0.1 and 0.5 C, respectively, along with a stable cycle property. The cell performance decreases at higher C-rate at 25 °C, which indicates an insufficient level of ionic conductivity of the PE at low temperature as well as a limitation to the rate of lithium ion diffusion in the cathode material at higher C-rate. The cell performance is improved appreciably by enhancing the operating temperature to 40 °C. The study shows that the PE based on an electrospun P(VdF-HFP) membrane incorporating BMITFSI is suitable for operation of Li/LiFePO<sub>4</sub> cells at 25 °C and at low current densities.

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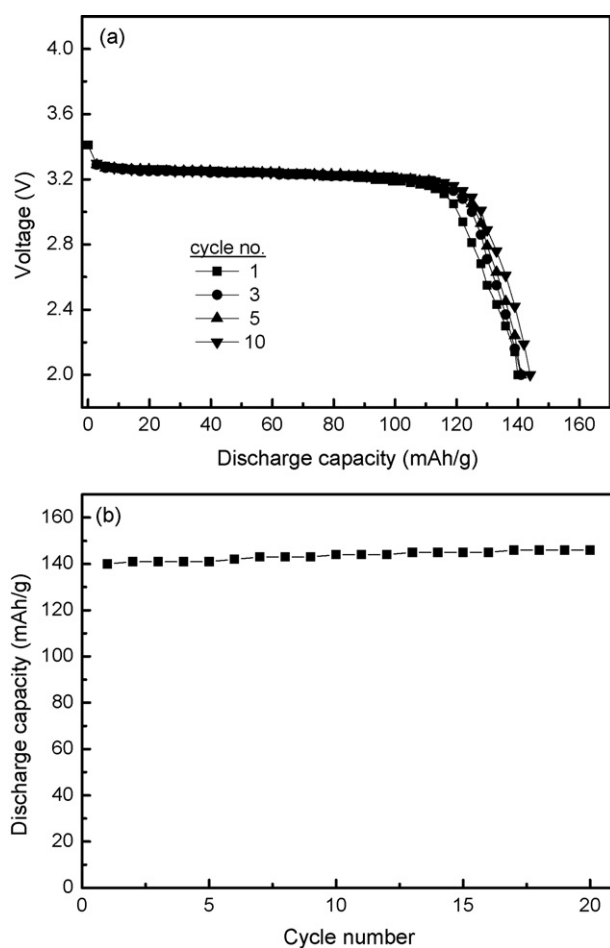


Fig. 9. (a) Discharge capacity during cycling of Li/PE/LiFePO<sub>4</sub> cell at 40 °C at 1C rate, and (b) cycle performance at 40 °C at 1C rate (PE based on electrospun P(VdF-HFP) membrane activated with 0.5 M LiTFSI in BMITFSI).

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## References

- [1] G.B. Appetecchi, F. Croce, J. Hassoun, B. Scrosati, M. Salomon, F. Cassel, *J. Power Sources* 114 (2003) 105.
- [2] J.H. Shin, Y.T. Lim, K.W. Kim, H.J. Ahn, J.H. Ahn, *J. Power Sources* 107 (2002) 103.
- [3] Z. Jiang, B. Carroll, K.M. Abraham, *Electrochim. Acta* 42 (1997) 2667.
- [4] Z. Wang, Z. Tang, *Mater. Chem. Phys.* 82 (2003) 16.
- [5] A. Subramania, N.T. Kalyanasundaram, G. Vijayakumar, *J. Power Sources* 153 (2006) 177.
- [6] J.W. Choi, J.K. Kim, G. Cheruvally, J.H. Ahn, H.J. Ahn, K.W. Kim, *Electrochim. Acta* 52 (2007) 2075.
- [7] J.M. Tarascon, A.S. Gozdz, C. Schmutz, F. Shokoohi, P.C. Warren, *Solid State Ionics* 86–88 (1996) 49.
- [8] J.W. Choi, J.H. Kim, G. Cheruvally, J.H. Ahn, K.W. Kim, H.J. Ahn, J.U. Kim, *J. Ind. Eng. Chem.* 12 (2006) 939.
- [9] S.W. Choi, S.M. Jo, W.S. Lee, Y.R. Kim, *Adv. Mater.* 15 (2003) 2027.
- [10] J.R. Kim, S.W. Choi, S.M. Jo, W.S. Lee, B.C. Kim, *Electrochim. Acta* 50 (2004) 69.
- [11] S.S. Choi, Y.S. Lee, C.W. Joo, S.G. Lee, J.K. Park, K.S. Han, *Electrochim. Acta* 50 (2004) 339.
- [12] S.W. Lee, S.W. Choi, S.M. Jo, B.D. Chin, D.Y. Kim, K.Y. Lee, *J. Power Sources* 163 (2006) 410.
- [13] J.R. Kim, S.W. Choi, S.M. Jo, W.S. Lee, B.C. Kim, *J. Electrochem. Soc.* 152 (2005) A295.
- [14] X. Li, G. Cheruvally, J.K. Kim, J.W. Choi, J.H. Ahn, K.W. Kim, H.J. Ahn, *J. Power Sources* 167 (2007) 491.
- [15] M. Galinski, A. Lewandowski, I. Stepniak, *Electrochim. Acta* 51 (2006) 5567.
- [16] B. Garcia, S. Lavalley, G. Perron, C. Michot, M. Armand, *Electrochim. Acta* 49 (2004) 4583.
- [17] H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara, *J. Electrochem. Soc.* 150 (2003) A695.
- [18] Y.S. Fung, R.Q. Zhou, *J. Power Sources* 81–82 (1999) 891.
- [19] J.H. Shin, W.A. Henderson, S. Passerini, *J. Electrochem. Soc.* 152 (2005) A978.
- [20] J.H. Shin, W.A. Henderson, S. Scaccia, P.P. Prosini, S. Passerini, *J. Power Sources* 156 (2006) 560.
- [21] J.H. Shin, W.A. Henderson, S. Passerini, *Electrochem. Solid-State Lett.* 8 (2005) A125.
- [22] J.H. Shin, W.A. Henderson, G.B. Appetecchi, F. Alessandrini, S. Passerini, *Electrochim. Acta* 50 (2005) 3859.
- [23] J.H. Shin, W.A. Henderson, S. Passerini, *Electrochem. Commun.* 5 (2003) 1016.
- [24] L.X. Yuan, J.K. Feng, X.P. Ai, Y.L. Cao, S.L. Chen, H.X. Yang, *Electrochem. Commun.* 8 (2006) 610.
- [25] H. Sakaebe, H. Matsumoto, *Electrochem. Commun.* 5 (2003) 594.
- [26] Y.H. Kim, G. Cheruvally, J.W. Choi, J.H. Ahn, K.W. Kim, H.J. Ahn, D.S. Choi, C.E. Song, *Macromol. Symp.* 249–250 (2007) 183.
- [27] J.W. Choi, G. Cheruvally, Y.H. Kim, J.K. Kim, J. Manuel, P. Raghavan, J.H. Ahn, K.W. Kim, H.J. Ahn, D.S. Choi, C.E. Song, *Solid State Ionics* 178 (2007) 1235.
- [28] V. Farmer, T. Welton, *Green Chem.* 4 (2002) 97.
- [29] J.K. Kim, J.W. Choi, G. Cheruvally, J.U. Kim, J.H. Ahn, G.B. Cho, K.W. Kim, H.J. Ahn, *Mater. Lett.* 61 (2007) 3822.
- [30] A. Lewandowski, I. Stepniak, *Phys. Chem. Chem. Phys.* 5 (2003) 4215.
- [31] T. Nishida, Y. Tashiro, M. Yamamoto, *J. Fluorine Chem.* 120 (2003) 135.
- [32] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.