Short communication

Preparation and electrochemical characterization of electrospun, microporous membrane-based composite polymer electrolytes for lithium batteries

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Abstract

Poly(vinylidene fluoride-co-hexafluoropropylene) {P(VdF-HFP)} membranes incorporating 0, 6 and 10 wt.% of nano-meter sized particles of SiO_2 were prepared by electrospinning. These membranes served as host matrix for the preparation of polymer electrolytes (PEs) by activating with the non-volatile and safe room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) (BMITFSI). The membranes consisted of layers of fibers with average fiber diameter of 2–5 μm and had a porosity of ∼87%. PEs with SiO_2 exhibited higher ionic conductivity with a maximum of 4.3×10^{-3} S cm^{-1} at 25 °C obtained with 6% SiO_2. The optimum PE based on the membrane with 6% SiO_2 exhibited better compatibility with lithium metal electrode on storage and resulted in enhanced charge–discharge performance in Li/LiFePO$_4$ cells at room temperature, delivering the theoretical specific capacity of 170 mAh g^{-1} at 0.1 C-rate. The PEs exhibited a very stable cycle property as well, demonstrating their suitability for lithium battery applications.
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1. Introduction

The development of suitable polymer electrolytes (PEs) with sufficient mechanical strength, high ionic conductivity at ambient temperature and good compatibility with lithium electrodes is actively pursued world-wide to meet the applications in lithium metal/ion polymer batteries. Different PEs such as (i) the dry, solid-type PEs based on the blend of poly(ethylene oxide) (PEO) and lithium salt, (ii) the composite PEs incorporating high surface area nano-sized ceramic particles, and (iii) the gel/plasticized PEs based on a polymer host membrane activated with liquid electrolytes, are being explored extensively. Although the dry and composite types of PEs are highly desirable in view of their mechan-

ical/handling strength and safety, they possess relatively low ionic conductivity (typically $<10^{-4}$ S cm^{-1}) at room temperature which limits their practical applications. The gel PEs exhibit higher ionic conductivity (∼10^{-3} S cm^{-1} at 25 °C), but are less advantageous with regard to mechanical strength and safety.

Electrospun polymer membranes are receiving increasing attention in recent years as host matrices for preparation of porous PEs [1–8]. Polymer membranes consisting of fibers of micron and submicron scale diameters and high porosities can be readily prepared by the electrospinning process under properly controlled parameters. Such membranes with large surface area fibers and fully interconnected pore structures are suitable for incorporation of large amounts of liquid electrolyte and hence can attain high ionic conductivity at room temperature. PEs based on electrospun poly(vinylidene fluoride) (PVdF) [1–4], its copolymer, poly(vinylidene fluoride-co-hexafluoropropylene) {P(VdF-HFP)} [5–7] and poly(acrylonitrile) (PAN) [8] have

been evaluated and found to be suitable for application in lithium metal/ion batteries.

In an earlier study we optimized the conditions to prepare electrospun P(VdF-HFP) microfibrous membrane and prepared the PE by activating the membrane with a liquid electrolyte based on organic solvents for conducting a preliminary evaluation of its performance in lithium metal battery at room temperature [6]. Since molecular solvents as electrolytes are a cause of concern in the safe operation of batteries, their replacement with the non-volatile, non-flammable and safe room temperature ionic liquids (RTILs) is studied with increasing interest [7,9–14]. Our previous study based on this approach demonstrates the suitability of the novel PE consisting of the electrospun P(VdF-HFP) membrane as matrix and a RTIL as electrolyte for lithium cells [7]. It has been well demonstrated by various researchers that the incorporation of sub-micron sized ceramic fillers (like SiO_2, Al_2O_3, TiO_2) to form the composite PE can enhance the handling strength and ionic conductivity of the PE and lead to better compatibility with lithium metal electrode [15–21]. In the present study, P(VdF-HFP) microporous composite membranes incorporating SiO_2 have been prepared for the first time by electrospinning process and the membrane properties as well as the electrochemical properties of the PEs based on them are evaluated and compared with that of the PE without SiO_2.

2. Experimental

Microporous membranes of P(VdF-HFP) (Kynar Flex 2801, $M_w = 4.77 \times 10^5$, VdF/HFP ratio: 88/12, Elf Atochem) were prepared at room temperature by electrospinning of 16 wt.% polymer solution in acetone/N,N-dimethylacetamide (7/3, w/w) at 18 kV applied voltage, using a standard set up [6]. For preparing membranes with SiO_2, a 16 wt.% solution of the polymer was blended with 6 or 10 wt.% of silica particles (Aldrich, fumed SiO_2, particle size: 3–12 nm, surface area: 200 m^2 g^{-1}) by mechanical ball milling at room temperature for 90 min and the homogenous solution so obtained was subjected to electrospinning under the same conditions. The collected membranes were vacuum dried at 60 °C for 12 h. Homogenous, fibrous membranes of 100–120 μm thickness were obtained. The surface morphology of the membranes was examined with a scanning electron microscope (SEM-JEOL JSM 5600) and the average fiber diameter (AFD) was estimated from SEM images. The porosity (%) of the membranes was evaluated following the

n-butanol uptake method by immersing the dry membrane in n-butanol for 1 h [6].

The RTIL, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) (BMITFSI) was synthesized by the procedure reported by Farmer et al. [22], by the reaction of 1-butyl-3-methylimidazolium chloride with LiTFSI. PEs were prepared by activating the electrospun membranes with the liquid electrolyte of 0.5 M solution of lithium bis(trifluoromethanesulfonylimide) (LiTFSI, Aldrich) in BMITFSI at 25 °C. The liquid electrolyte was first heated to a temperature of 40 °C to reduce its viscosity and then a definite quantity (40 μL) of the electrolyte was added using a microsyringe onto the membrane positioned appropriately and then slowly cooled to 25 °C. The ionic conductivity of the PEs at 25 °C was measured by the ac impedance analysis using SS Swagelok® cells with an IM6 frequency analyzer, over 100 mHz to 2 MHz frequency range at an amplitude of 10 mV. Cyclic voltammetry (CV) measurement of Li/PE/Li cell was performed at 25 °C at a scan rate of 1 mV s^{-1} between −1 and +1 V. The interfacial resistance between the PE and lithium metal electrode was measured by analyzing the impedance response over the frequency range of 10 mHz to 2 MHz of Li/PE/Li cell kept at room temperature for a period of up to 7 days.

The prototype lithium cell was assembled by sandwiching the PE between lithium metal anode (300 μm thick, Cyprus Foote Mineral Co.) and carbon-coated lithium iron phosphate (LiFePO$_4$) cathode in Swagelok® type circular cells of 23 mm diameter. LiFePO$_4$ cathode active material was synthesized in-house [23] and the cathode was prepared as its blend with conductive carbon and PVdF binder in the ratio 80:10:10 by wt. Electrochemical tests of the Li/PE/LiFePO$_4$ cells were conducted in an automatic galvanostatic charge–discharge unit, WBCS3000 battery cycler (WonA Tech. Co.) between 2.5 and 4.0 V at 25 °C at a current density of 0.1 C. The activation of electrospun membrane to prepare PE and the fabrication of test cells were carried out in argon-filled glove box with a moisture level <10 ppm.

3. Results and discussion

P(VdF-HFP) membranes prepared by electrospinning consist of multi-fibrous layers with a number of interstices/pores between the fibers, as shown in Fig. 1. The membrane without SiO_2 exhibits a comparatively uniform morphology with an AFD of 2 μm. AFD is higher for the membranes contain-
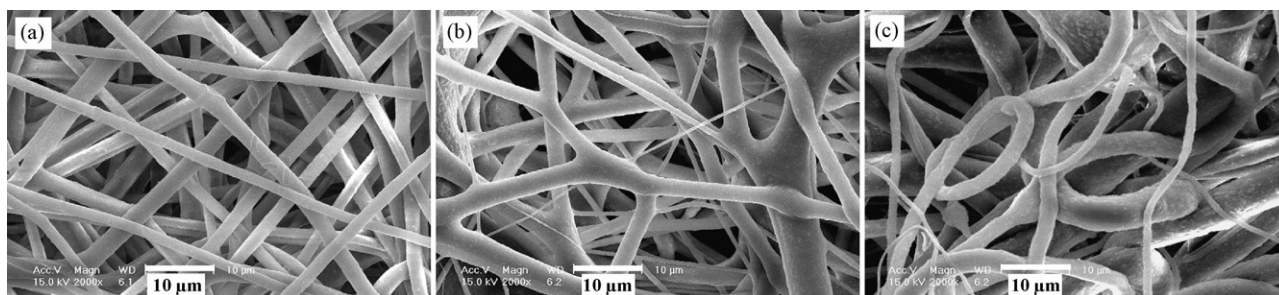

Fig. 1. SEM images of electrospun P(VdF-HFP) membranes with varying SiO_2 contents: (a) 0 wt.%, (b) 6 wt.%, and (c) 10 wt.%.

ing SiO$_2$: 3 and 5 μm, respectively, with 6 and 10% SiO$_2$. With the incorporation of SiO$_2$, more branching of fibers is observed and the fiber size distribution tends to be less uniform. Thus, the membrane with 10% SiO$_2$ consists of fibers of different sizes with branches and some bending as well. The formation of membranes with fibers of larger size is attributed to the substantial increase in viscosity of the polymer solution resulting from blending with particulate filler. A higher viscosity of the electrospinning polymer solution leads to the ejection of a larger fluid jet from the needle and a consequent deposition of fibers with larger diameters [24]. It is anticipated that by decreasing the polymer concentration and/or optimizing the spinning voltage, SiO$_2$-containing membranes with a better fiber size distribution would be formed; such a study forms part of a future investigation.

P(VdF-HFP) membrane without SiO$_2$ exhibits a porosity of 88% as determined by *n*-butanol method. Since the non-polar *n*-butanol does not have any interaction with the polymer fibers in the membrane, it penetrates and occupies all the pore spaces available and gives a measure of the total pore volume in the material. The presence of large, interconnected pores is evident from the SEM image of this membrane and this contributes to the high pore volume. Although such well-defined, large pores are less conspicuous in the SEM images of the membranes with SiO$_2$, they also have nearly the same porosity, ∼87%. This suggests that the less efficient packing of non-uniform, thicker fibers in the layers of these membranes leads to a large number of smaller pores which add up to give a high pore volume.

In order to have a better comparison of the electrochemical properties of the PEs based on the electrospun membranes containing varying SiO$_2$ contents, experiments were performed using PEs containing a fixed quantity of the liquid electrolyte, 0.5 M LiTFSI in BMITFSI. The electrolyte-soaked membranes were sandwiched between the desired electrodes for various tests. The addition of 40 μL of liquid electrolyte based on the relatively dense BMITFSI (density = 1.429 at 19 °C [25]) corresponds to ∼80% of liquid electrolyte content in the PE which is equivalent to ∼400% of liquid uptake by the dry membrane in forming the PE.

Fig. 2 presents the ac impedance data obtained at 25 °C for the PEs. Straight lines inclined towards the real-axis representing the electrode/electrolyte double layer capacitance behavior are obtained for all the samples over the whole range of frequency evaluated. This response is typical of electrolytes with a major contribution towards total resistance from bulk resistance (R_b) and only a minor contribution from grain boundary resistance. The intercept on real-axis representing R_b of the electrolyte varies between 1.6 and 3.0 Ω; it is the lowest for the membrane with 6% SiO$_2$. From the impedance data, the ionic conductivities of the membranes at 25 °C (in mS cm^{-1}) are calculated as: 2.3 (without SiO$_2$), 4.3 (with 6% SiO$_2$) and 3.4 (with 10% SiO$_2$). Thus, the PEs exhibit high ionic conductivities at room temperature making them candidate materials for practical battery applications. The use of the RTIL, BMITFSI in the PE leads to the presence of additional mobile ions that can also contribute for the high ionic conductivity. The results of the electrochemical tests could provide an evidence, though indirectly, for the high
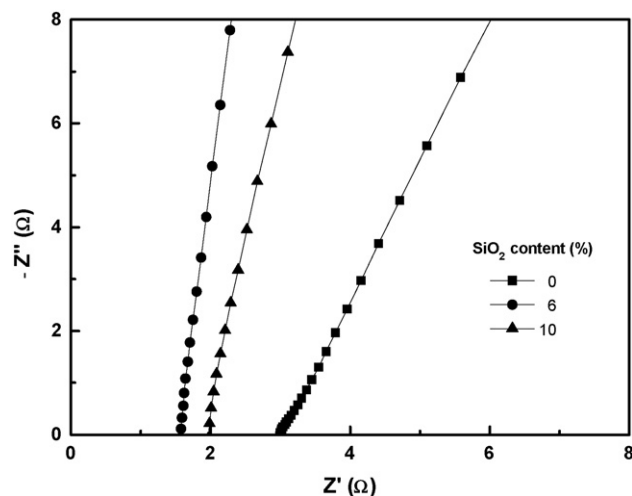

Fig. 2. ac impedance spectra at 25 °C of PEs based on electrospun P(VdF-HFP) membranes with different SiO$_2$ contents.

mobility of Li$^+$ ions in the PEs. Incorporation of ceramic fillers in PEs has been demonstrated by different researchers as a successful way to enhance the ionic conductivity. The conductivity enhancement in such composite electrolytes has been attributed mainly to the decreased polymer crystallinity (and consequent increase in amorphous content) in the presence of the inorganic particles [18–21] and also to the Lewis acid–base type interactions between the filler and the polar groups of the polymer chains [15,18]. A similar effect is observed in the present study also, where the inclusion of small amounts of SiO$_2$ enhances the ionic conductivity of the PE by a factor of 1.5–2.0.

The successful use of an electrolyte in lithium metal battery requires good electrochemical stability and an excellent compatibility with the lithium metal used as the anode material [26]. An initial understanding of the behavior of lithium electrode in the PE is made by the CV data of Li/PE/Li cell. Fig. 3 presents the CV curves during 1–5 cycles of the PE based on the membrane with 6% SiO$_2$, which is representative of the PEs studied here. The redox peaks corresponding to
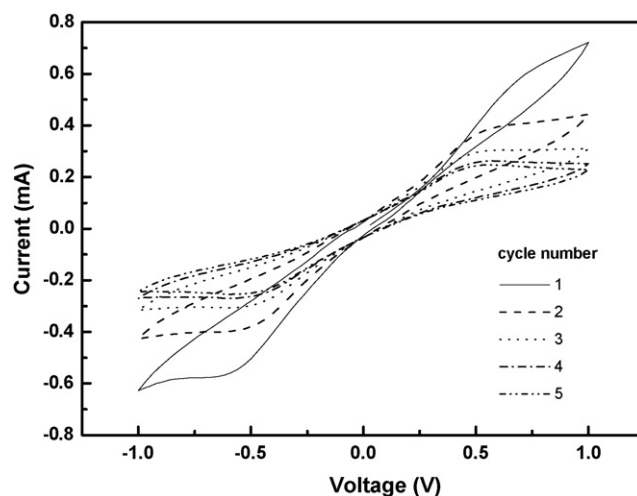

Fig. 3. CV curves during 1–5 cycles with PE based on electrospun P(VdF-HFP) membrane containing 6% SiO$_2$ (Li/PE/Li cell, 25 °C, −1 to +1 V).

anodic oxidation at $+0.55$ V and cathodic reduction at -0.59 V occur versus Li^+/Li. On cycling, there is no substantial change in the redox peak voltages. The peak currents tend to decrease markedly during the initial cycles and stabilize afterwards. This indicates that following the initial stabilization period, the PE is able to support fully reversible redox process. Another useful observation that can be made from the CV data is the stability of the PE against decomposition at -1 V which is even lower than the lithium plating voltage. Although the RTIL, BMITFSI, as such has a cathodic limit of -2 V versus Ag^+/Ag [27], which is equivalent to 1.2 V versus Li^+/Li, its incorporation in PEs by blending with PEO-LiTFSI [13] and P(VdF-HFP)-LiTFSI [7] resulted in enhanced reduction stability, well below -1 V. Studies reported by Shin et al. on PEs based on PEO-LiX incorporating pyrrolidinium-based RTIL also demonstrated a similar effect [9]. The improved cathodic stability has been attributed to the presence of lithium salt in the electrolyte which effectively suppresses the reduction of the organic cation of RTIL by forming a stable, Li^+ ion-conducting, passivation layer on the lithium surface that prevents further reaction of RTIL [7,9,13].

LiFePO$_4$ is attracting much attention in recent years as the next-generation cathode-active material to substitute the transition metal oxides that are currently employed. LiFePO$_4$ is a safe, cheap and non-toxic material with a theoretical capacity of 170 mAh g^{-1} and an operating voltage of 3.4 V. Our earlier studies with the in-house synthesized LiFePO$_4$ have shown high discharge capacity and stable cycle performance in lithium batteries using liquid electrolytes at 25 °C [23,28]. The PEs prepared in this study have been evaluated for performance in Li/LiFePO$_4$ cells at 25 °C, at 0.1 C-rate (corresponding to 0.07 mA cm^{-2}). A comparison of the performance of the cells during the first cycle charging and discharging is presented in Fig. 4. Charge and discharge reactions occur at 3.5 and 3.4 V respectively with the characteristic, flat charge–discharge profile of LiFePO$_4$ cathode-active material arising from the LiFePO$_4$/FePO$_4$ two-phase redox reaction [23,28]. The charge capacities of cells with PEs based on the membrane without SiO$_2$

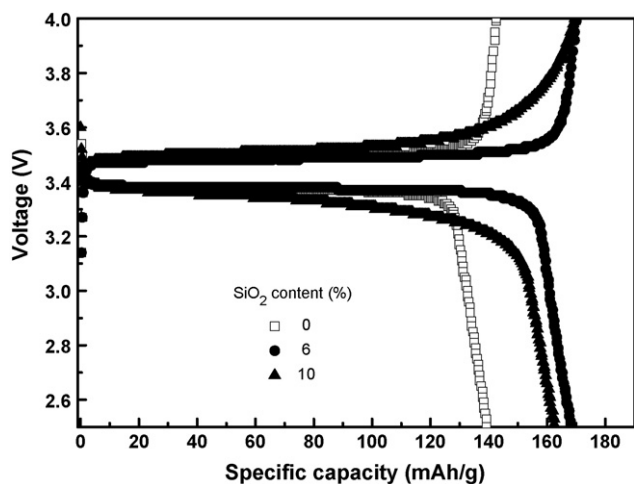Fig. 4. First cycle charge and discharge capacities of Li/LiFePO$_4$ cells with PEs based on electrospun P(VdF-HFP) membranes containing varying SiO$_2$ contents (25 °C, 0.1 C-rate, 2.5–4.0 V).
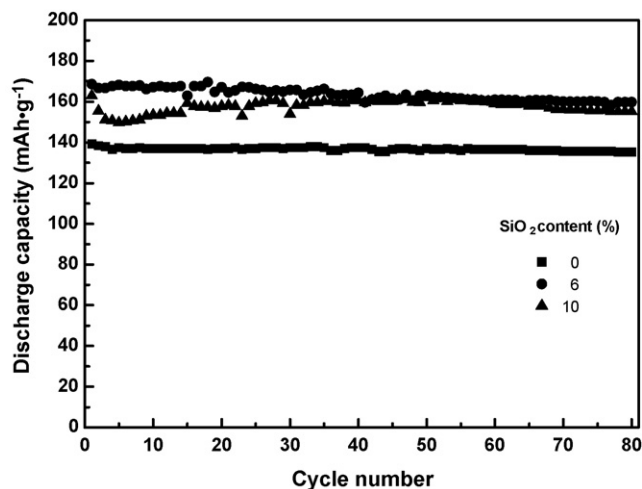

Fig. 5. Cycle performance of Li/LiFePO$_4$ cells with PEs based on electrospun P(VdF-HFP) membranes containing varying SiO$_2$ contents (25 °C, 0.1 C-rate, 2.5–4.0 V).

and with 6 and 10% SiO$_2$ are 143, 170 and 170 mAh g^{-1}, respectively. The corresponding discharge capacities are 139, 169 and 163 mAh g^{-1}, respectively. Thus, the membrane with 6% SiO$_2$ delivers the highest specific capacity (which corresponds to 100% active material utilization) under the test conditions. Since all other contributing factors remain almost constant, the higher performance shown by the membranes with SiO$_2$ compared to that without SiO$_2$ could be a direct consequence of the higher ionic conductivity of these PEs.

The performance of Li/PE/LiFePO$_4$ cells on repeated cycling is presented in Fig. 5. All PEs exhibit a stable cycle property, studied here up to 80 cycles. Thus, the % fade in discharge capacity (calculated based on the initial and 80th cycle capacities) for the PEs is <0.07% per cycle. The observed cycle performance is comparable to that we obtained earlier for Li/LiFePO$_4$ cells under similar test conditions (at 0.1 C-rate) using the liquid electrolyte 1 M LiPF$_6$ in EC/DMC (~0.08% per cycle evaluated for 100 cycles) [23], and PE based on electrospun P(VdF-HFP) activated with 1 M LiPF$_6$ in EC/DMC (~0.04% per cycle evaluated for 100 cycles) [6]. The remarkably good cycle property of the cell in the present study confirms the excellent efficiency of the microporous membrane-based PEs to conduct the ions between electrodes freely without any decrease in the property on cycling. This, in turn indicates that the electrolytes have good compatibility with both the electrodes, especially lithium metal.

The formation of a stable solid electrolyte interface (SEI) on the lithium metal that can conduct Li^+ ions freely and at the same time prevent any undesired interaction between the electrolyte components and lithium leading to dendrite formation is essential for attaining good cycle performance. The compatibility of the PE with lithium metal has been analyzed by evaluating the variation of impedance of symmetrical Li/PE/Li cells over storage up to 7 days. Fig. 6(a) and (b) depict the impedance spectra observed for the PEs without SiO$_2$ and with 6% SiO$_2$, respectively. The PEs exhibit a single semi-circle impedance pattern, typical of liquid/gel electrolytes having high ionic conductivity with contributions from bulk resistance of the electrolyte (R_b)
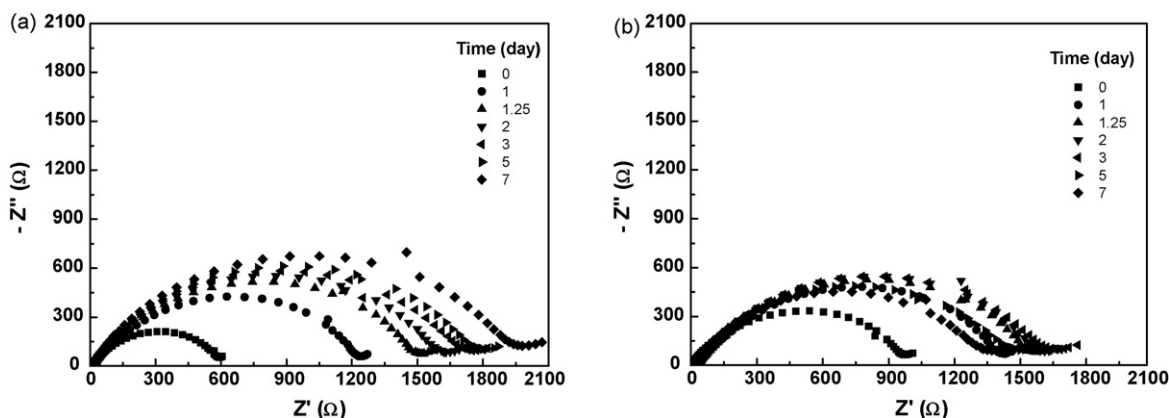
Fig. 6. Variation of impedance behavior of PEs with storage time: (a) membrane without SiO_2; (b) membrane with 6% SiO_2 (Li/PE/Li cells, 25 °C, 10 mHz to 2 MHz).

and electrode/electrolyte interfacial resistance (R_f). The real-axis intercept at the high-frequency end corresponding to R_b is very low for the PEs and it does not show much change with storage time: varies between 8 and 18 Ω for the PE without SiO_2 and between 8 and 32 Ω for the PE with 6% SiO_2. Earlier studies with PEs based on electrospun membranes have also reported nearly constant values for R_b with storage time [1,2,6]. This confirms that the PEs consisting of fully interconnected pores and fibrous swollen structure function efficiently as ion transporting media between the electrodes and maintains the property over storage also.

Unlike R_b, R_f shows a significant variation with time, as shown in Fig. 7. Initial R_f is determined by the properties of the passivation layer spontaneously formed on the lithium surface when it comes in contact with the electrolyte and its value for the PE without SiO_2 is lower than that of PE with SiO_2 (582 Ω versus 962 Ω). It is presumed that the presence of insulative SiO_2 particles in the PE adversely affects the free passage of Li^+ ions by functioning as a barrier at the electrode/electrolyte interface and results in higher R_f. With advancing time, R_f shows a continuously increasing trend for PE without SiO_2 and reaches 1971 Ω after 7 days. The initial increase in R_f with time is inevitable in lithium metal batteries as it indicates the formation and growth of the passivation layer on the metal surface by reaction with the electrolyte components, impeding the passage of ions [29]. The PE without SiO_2 shows the tendency to form a stable SEI as time proceeds, but rather slowly. On the contrary, for the PE with 6% SiO_2, R_f shows an initial increase during 3 days time to reach 1661 Ω, and then it further decreases. For this PE, R_f is 1377 Ω after 7 days, which is only 43% higher than its initial value and is 30% less than the corresponding R_f of the PE without SiO_2. Hence, PE with SiO_2 demonstrates a much better compatibility with lithium electrode on continued storage, which could be considered as equivalent to repeated cycling of the cell. A similar observation of enhanced interfacial stability with lithium metal electrode is reported by Yang et al. for PVdF-based gel electrolyte with Al_2O_3 filler [17] and by He et al. for P(VdF-HFP)-based gel electrolyte with in situ generated SiO_2 filler [19]. The enhancement is attributed to the ability of nano-sized filler particles with high surface area that can effectively hold the electrolyte solvent by capillary force leading to a decreased interaction between the electrolyte and lithium metal and stabilization of the interface gradually [17]. The improved rigidity of the membrane containing inorganic particles leading to a better retention of its adhesion with the lithium electrode on cycling could also be a contributing factor to its better compatibility [19]. The enhanced electrochemical performance of the PE based on the membrane with SiO_2 is thus attributed to a combination of its higher ionic conductivity and better compatibility with lithium electrodes. The results in the present study indicate that (i) BMITFSI-based, non-volatile and safe electrolytes are suitable candidates to replace the molecular solvent-based electrolytes, and (ii) electrospun P(VdF-HFP) membrane having high porosity and good mechanical strength, containing small quantities of dispersed ceramic particles, could serve as suitable host matrix for preparing PEs that lead to satisfactory performance in lithium metal batteries at room temperature at reasonable C-rates.
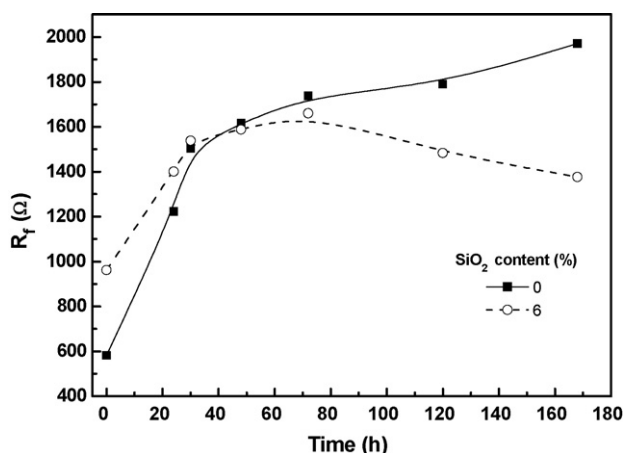

Fig. 7. Variation of R_f of PEs with storage time (Li/PE/Li cells, 25 °C, 10 mHz to 2 MHz).

4. Conclusions

Micro-fibrous composite membranes of P(VdF-HFP) containing nanometer sized particles of SiO_2 were prepared by

electrospinning of polymer solution containing the dispersed ceramic filler. The incorporation of SiO_2 resulted in forming larger size fibers with a less homogenous morphology, but with the same porosity level as the membrane without SiO_2. PEs based on the membranes activated with 0.5 M LiTFSI in BMITFSI showed high ionic conductivities in the range of 2.3–4.3 mS cm^{-1} at 25 °C and exhibited well-defined redox peaks in CV demonstrating their suitability for application in lithium metal batteries. PE based on the membrane with 6% SiO_2 showed the best charge–discharge performance when evaluated in Li/LiFePO$_4$ cells at room temperature, with an initial discharge capacity of 170 mAh g^{-1} (corresponding to 100% active material utilization) and a very stable cycle performance (<0.07% capacity fade per cycle) at 0.1 C-rate. The PE containing SiO_2 also showed good compatibility with lithium electrode with a faster stabilization of the electrode/electrolyte interface. The study demonstrates the suitability of the electrospun, SiO_2-containing P(VdF-HFP)-based membrane activated with the safe and non-volatile BMITFSI as a promising PE for lithium metal batteries.

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