Development of electrospun PVdF–PAN membrane-based polymer electrolytes for lithium batteries

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A B S T R A C T
Electrospun fibrous membranes of composites of polyvinylidene fluoride and polyacrylonitrile (PVdF–PAN–ESFMs) are prepared with different proportions of PAN (25, 50 and 75%, w/w). The morphology of the ESFMs is examined by field emission scanning electron microscopy (FESEM). FESEM image of PVdF–ESFM reveals that the fibers have uniform diameters and smooth surfaces. However, the fibers of PVdF–PAN–ESFMs are interconnected with large number of voids and cavities of different sizes. These voids are effectively utilized for the preparation of polymer electrolytes by loading lithium perchlorate dissolved in propylene carbonate. PVdF–PAN(25)–ESFM could load a high amount of lithium salt with electrolyte uptake of more than 300%. PVdF–PAN(25)–ESFM electrolyte exhibits a high conductivity of 7.8 mS cm −1 at 25 °C and electrochemically stable up to 5.1 V. Also, the addition of PAN into PVdF decreases the interfacial resistance with lithium electrode. PVdF–PAN–ESFM electrolytes have complementary advantageous characteristics of PVdF and PAN. The promising results reported here clearly indicate that polymer electrolytes based on PVdF–PAN–ESFMs are most suited for lithium batteries.

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1. Introduction

Polymer electrolytes have received wide spread attention due to their technological applications for a wide variety of solid-state electrochemical power sources, rechargeable batteries, fuel cells, super capacitors, etc. [1]. Polyvinylidene fluoride (PVdF), polyacrylonitrile (PAN), polyvinyl chloride, polymethyl methacrylate, polyurethane, etc. have been considered as the host polymers for the preparation of polymer electrolytes [2–4]. Among these, PVdF has received considerable attention due to its good electrochemical stability, affinity to electrolyte solutions and exhibits ionic conductivities in the range of 10 −4 to 10 −3 S cm −1 at room temperature [5]. PVdF has a high dielectric constant and electron withdrawing fluorine atoms in the backbone structure. These features are useful in dissociating the lithium salt to lithium ions while transforming into a polymer electrolyte.

One of the problems that restricts the use of PVdF-based polymer electrolytes is the formation of stable LiF and >\( \equiv \text{CF} \)–unsaturated bonds through interactions between the fluorine atoms in PVdF with lithium or lithiated graphite [6]. Also, PVdF is soluble in liquid electrolytes that are generally used for the preparation of polymer electrolytes [7]. This could result in a loss of mechanical strength and internal short-circuits. The crystalline part of PVdF hinders the migration of Li + ions and hence batteries with PVdF-based electrolytes have lower charge/discharge capacities and poor C-rate values [8].

On the other hand, PAN-based electrolytes have shown interesting characteristics like high ionic conductivity, thermal stability, good morphology for electrolyte uptake and compatibility with the lithium electrodes [9]. Besides these characteristics, PAN minimizes the formation of dendrite growth during the charging/discharging process of Li batteries [9]. Previous reports indicated that –\( \equiv \text{CN} \) groups in PAN could interact with –\( \equiv \text{O} \) groups of the liquid electrolytes (propylene carbonate (PC) or ethylene carbonate (EC)) as well with Li + ions [10,11]. The mechanism of Li + ion transport in PAN-based electrolytes with EC or PC as the plasticizer is rather complex as compared with other plasticizers [12]. Results from nuclear magnetic resonance, differential scanning calorimetry, FT-
IR spectroscopy studies on PAN-based electrolytes demonstrate the interactions between the groups in PC or EC and PAN [13–15]. The electrolyte behavior of PAN-based microporous membranes prepared by phase inversion method has been reported [16]. It is clear that PAN provides rigidity and other characteristics to the polymer electrolytes with augmented lithium ion conduction. However, PAN-based electrolytes have undesirable effects such as liquid extraction from the gel upon long storage. This could result in a decrease in ionic conductivity for the polymer electrolytes.

It is thus explicit from the literature that PAN and PVdF are individually having beneficial characteristics as host polymers in polymer electrolytes. Interestingly, PAN could provide few important characteristics towards polymer electrolytes which could not be derived from PVdF and vice versa. PAN is superior towards polymer electrolytes. Interestingly, PAN could provide few important characteristics as host polymers in polymer electrolytes. Recently, nanosize SiO$_2$ particles were incorporated into PVdF–HFP membrane during electrospinning [32]. An ionic conductivity of 4.3 mS cm$^{-1}$ at 25 °C was achieved. Composite electrospun membranes of polyimides with PVdF–HFP and PAN were reported [33]. Polyimide, which is used as a host matrix provides mechanical strength and the presence of gelling constituents, PVdF or PAN augment the ionic mobility. Li-ion cells fabricated using these gelled separators exhibited excellent cycling performance with no loss in capacity after 3 weeks of storage at room temperature and 50 °C. PAN-based electrospun polymer electrolytes were also developed and their electrochemical properties were reported [34].

In the present investigation, PVdF–PAN composite electrospun fibrous membranes (PVdF–PAN–ESFMs) were prepared with different wt.% of PAN and converted into the polymer electrolytes by loading lithium salts within the pores of ESFMs. The electrochemical characteristics of PVdF–PAN–ESFM-based polymer electrolytes were evaluated in the process of testing their suitability for application as electrolytes in lithium batteries.

2. Experiments

2.1. Materials

Polyvinylidene fluoride (PVdF; Mw 107,000), polyacrylonitrile (PAN; Mw 150,000), N,N-dimethylformamide (DMF), acetone, lithium perchlorate (battery grade, dry, 99.99%), propylene carbonate (anhydrous, 99.7% and the water content is <0.002%), lithium cobalt(III) oxide and N-methyl pyrrolidone were purchased from Sigma–Aldrich and used as such.

2.2. Preparation of the PVdF–PAN electrospun fibrous membranes (PVdF–PAN–ESFMs)

PVdF–PAN(x)–ESFMs (x represents the wt.% of PAN) were prepared with varying weight ratios of PAN in the composites. For instance, PVdF–PAN–ESFM with a wt.% of PAN as 25 is designated as PVdF–PAN(25)–ESFM. Likewise, composites were designated according to the wt.% of PAN as PVdF–PAN(50)–ESFM and PVdF–PAN(75)–ESFM. A typical procedure for the preparation of PVdF–PAN(25)–ESFM is outlined here. Solution of a mixture of PVdF and PAN was prepared by mixing the PVdF (7.5 g) and PAN (2.5 g) in DMF and acetone mixture (7:3, v/v). The solution was taken in the syringe and delivered with a flow rate of 10 mL h$^{-1}$. A potential difference of 25 kV was kept between the nozzle of the syringe and the collector (aluminum drum) at 25 °C. A metering pump was used to control the flow rate. A distance of 20 cm was kept between the syringe tip and the collector. Dry fibers that accumulated on the collector (drum) were collected as fibrous membranes.

2.3. Preparation of PVdF–PAN–ESFM electrolytes

PVdF–PAN–ESFMs were transformed into polymer electrolytes by soaking the fibrous membranes in a 1 M LiClO$_4$–PC solution at room temperature inside the glove box. The % of electrolyte uptake of ESFMs was determined by soaking the membranes in LiClO$_4$–PC solution and knowing the changes in mass of the membranes.

\[
% \text{ of electrolyte uptake} = \left( \frac{M_a - M_b}{M_b} \right) \times 100
\]
where $M_a$ and $M_b$ are mass of membranes after and before immersion in the liquid electrolyte, respectively.

2.4. Membrane characterization

Morphology of the ESFMs was analyzed by field emission scanning electron microscopy (FESEM, Hitach-530). Fourier transform infrared (FT-IR) spectra of the samples were recorded in KBr pellets using Bruker IFS 66 V FT-IR in the range of 400–4000 cm$^{-1}$. Differential scanning calorimetry data of the samples were collected using a TA 4000/Auto DSC 2910 over a temperature range $-50$ to $350^\circ$C at a scan rate of $10^\circ$C min$^{-1}$.

2.5. Porosity measurements

Porosity % of PVdF–PAN–ESFMs was determined using n-butanol uptake. For this purpose, PVdF–PAN–ESFMs were immersed in n-butanol for 2 h. The mass of PVdF–PAN–ESFMs before and after immersion was measured. The porosity % of the membrane was calculated using the equation:

$$\text{porosity} (\%) = \frac{m_a / \rho_a}{m_a / \rho_a + m_b / \rho_b} \times 100$$

where $m_a$ and $m_b$ are the mass of membranes after and before immersion in n-butanol, $\rho_p$ and $\rho_b$ are the density of the polymer and n-butanol, respectively.

2.6. Electrochemical measurements

An electrochemical cell was assembled by sandwiching PVdF–PAN–ESFM electrolytes between two stainless steel blocking electrodes (surface area: 2 cm$^2$) and sealed. Ionic conductivities were measured by recording the ac impedance spectra of SS/PVdF–PAN–ESFM/SS in the temperature between 25 and 80°C using EG&G PAR 283 Potentiostat/Galvanostat with FRA 1025 model. Electrochemical stability of the membrane electrolytes was determined using linear sweep voltammetry at a scan rate of 5 mV s$^{-1}$ with electrochemical cell consists of a SS working electrode, lithium metal as reference electrode as well as counter electrode. The interfacial resistance between lithium electrode and the fibrous polymer electrolyte was determined from the ac impedance spectrum recorded for Li/PVdF–PAN–ESFM/Li cell. The measurement was carried out over a frequency range of 5 MHz to 100 mHz, with an amplitude of 10 mV.

2.7. Charge/discharge studies

The charge/discharge studies were carried out with the pouch cell using WPG 100 (Potentiostat/Galvanostat) Won-A-Tech Instrument. The cell assembly was carried out inside the glove box filled with argon gas. The active cathode material was prepared by mixing LiCoO$_2$ in NMP with PVdF and carbon black and coated uniformly on a clean aluminum foil. Lithium foil pressed onto copper sheet was used as an anode. The thickness of cathode and anode after
3. Results and discussion

3.1. Characterization of PVdF–PAN–ESFMs

3.1.1. Morphology

Fig. 1 presents the FESEM images of PVdF–ESFM and PVdF–PAN–ESFMs. The fibers in PVdF–PAN–ESFMs are interconnected with a large number of voids and cavities of different sizes (Fig. 1b–d). The average diameter of the fibers of PVdF–PAN–ESFMs increases with increasing PAN content in the composite. The average diameters of PVdF–PAN(α)–ESFM having wt.% of PAN as 25, 50, 75 are ~250, ~300, ~400 nm, respectively. However, the fibers of PVdF–ESFM have uniform diameters of about 600 nm and smooth surface (Fig. 1a). It is important to note that there is no bead formation under the conditions selected by us for the electrospinning. The absence of uneven surface and variations in the diameter of the fibers indicate minimum axis symmetric instability of the polymer fluid during electrospinning [35].

Few more important features are noted in the morphology of PVdF–PAN–ESFMs. Firstly, the fibers of PVdF–PAN–ESFMs are more interconnected as the wt.% of PAN in the composite increases. Secondly, the fibers are not having the phase-separated microstructure even for a high content of PAN in the composite. FT-IR and DSC results are provided to discuss (later part of discussion) further about the phase mixing of PVdF and PAN during electrospinning. Thirdly, bead-fibers are absent in PVdF–PAN composites prepared with different compositions of PAN.

The interconnected network morphology for PVdF–PAN–ESFMs is expected to arise from the probable molecular level interactions between C–F (in PVdF) and –CN (in PAN) groups. These molecular interactions induce the phase mixing between PVdF and PAN. The absence of bead-fibers during electrospinning is due to several combinatorial factors. The high polarity of DMF (dipole moment of 3.80 D and dielectric constant of 36.7), low volatility of acetone (boiling point of 56.2 °C), polar nature of PVdF and PAN are the probable reasons [36].

3.1.2. FT-IR spectroscopy

FT-IR spectra of PVdF–ESFM and PVdF–PAN–ESFMs are presented in Fig. 2. FT-IR spectrum of PVdF–ESFM (Fig. 2a) shows peaks at 1400, 1200 and 472 cm⁻¹ and that are assigned to CF₂ bending, CF₂ stretching and CF₂ wagging, respectively [26]. FT-IR spectra of the PVdF–PAN–ESFMs (Fig. 2b–d) also show bands corresponding to CF₂ vibrations. However, band corresponding to bending mode vibration shifts to 1392 cm⁻¹ (1400 cm⁻¹ in PVdF) in the spectrum of PVdF–PAN–ESFMs. Further, band positions of wagging mode of CF₂ are found to be shifted to higher frequency with a decrease in the intensity, as compared to the bands in PVdF. Typically, the band of C–F stretch at 1200 cm⁻¹ is shifted to higher frequency. In addition, FT-IR spectra of composites show bands around 2940, 2238 and 1620 cm⁻¹ which correspond to the symmetrical –CH₂, –CN and asymmetrical –CH stretching vibrations of PAN, respectively. It is to be noted that the band of –CN stretching was observed at around 2244 cm⁻¹ in the case of PAN–ESFM [34]. These observations clearly indicate that there are molecular level interactions between the two polymers in the bicomponent fibers. These spectral features gave a hint for probable phase mixing between PVdF and PAN.

3.1.3. Differential scanning calorimetry

Further, to authenticate the miscibility of two polymers in ESFMs, DSC measurements were made. Table 1 presents the thermal properties of the ESFMs obtained from DSC measurements. PVdF–ESFM showed a sharp endothermic peak at ~42.8 °C corresponding to the glass transition temperature (Tg) and a strong melting endotherm at 165.59 °C. In the case of PAN–ESFM, Tg could be noticed at 118.2 °C. In addition to this, PAN–ESFM exhibited two exothermic peaks; a peak corresponding to less intense exothermic reaction at 252.81 °C and followed by a strong exotherm beyond 300 °C. The observed exothermic peaks are due to oxidation/cyclization of PAN [37]. PVdF–PAN(25)–ESFM and PVdF–PAN(50)–ESFM showed a single glass transition temperature, whereas PVdF–PAN(75)–ESFM exhibited two endothermic peaks at

![Fig. 2. FT-IR spectra of (a) PVdF–ESFM, (b) PVdF–PAN(25)–ESFM, (c) PVdF–PAN(50)–ESFM and (d) PVdF–PAN(75)–ESFM.](Image 83x525 to 317x773)

Table 1

<table>
<thead>
<tr>
<th>Electrosynthetic fibrous membranes⁴</th>
<th>PVdF</th>
<th>PAN</th>
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<tr>
<td></td>
<td>Tg (°C)</td>
<td>Tm (°C)</td>
</tr>
<tr>
<td>PVdF–ESFM</td>
<td>-42.8</td>
<td>165.59</td>
</tr>
<tr>
<td>PVdF–PAN(25)–ESFM</td>
<td>-39.3</td>
<td>164.99</td>
</tr>
<tr>
<td>PVdF–PAN(50)–ESFM</td>
<td>-40.7</td>
<td>164.55</td>
</tr>
<tr>
<td>PVdF–PAN(75)–ESFM</td>
<td>-42.6</td>
<td>163.19</td>
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<td>PAN–ESFM</td>
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⁴ The value in the parenthesis refers the wt.% of PAN in PVdF–PAN–ESFM.
−42.6 °C (more intense) and 113.5 °C (less intense) (Table 1). The thermal transition band became broader and \( T_g \) value moved to a higher temperature as PAN content in the blend increased. Nevertheless, \( T_g \) s of PVdF–PAN–ESFMs were lower than that observed for PVdF–ESFM. Generally, \( T_g \) of a polymer blend shifts when the polymers are miscible. Further, a decreasing trend in \( T_m \) for PVdF–PAN–ESFMs with increase in PAN content was noticed. The lower \( T_m \) reflects the decrease in crystallinity of PVdF in the PVdF–PAN–ESFMs. The presence of PAN in PVdF–PAN–ESFMs impedes the crystallization of PVdF and retains the amorphous domains. The existence of a single glass transition and the absence of any additional endothermic peak for PVdF–PAN(25)–ESFM confirms the miscibility of PAN with PVdF in the composite fibers.

3.2. Electrolyte characteristics of PVdF–PAN–ESFMs

3.2.1. Porosity measurements and electrolyte uptake

PVdF–PAN–ESFMs show 3D network with interconnected porous structure with varying porosity. This was inferred from porosity measurements. The porosity % of composite ESFMs decreased with increasing PAN (wt.%) contents. Also, the porosity % decreased (from 84.5 to 63.4%) with increasing fiber diameters [38]. Among the ESFMs, PVdF–PAN(25)–ESFM showed high porosity (~85%).

PVdF–PAN–ESFMs swell upon soaking into a solution of LiClO4 in PC. The electrolyte uptake % of PVdF–PAN–ESFMs in Li salt dissolved in PC was followed (Fig. 3). PVdF–PAN–ESFMs exhibited different rates of electrolyte uptake. A high liquid uptake % (>300%) was witnessed for PVdF–PAN(25)–ESFM as compared to pristine PVdF–ESFM (~200%). However, PVdF–PAN(25)–ESFM with increasing PAN content showed a decreasing liquid uptake of the electrolyte. The average diameter of the fibers was determined before and after immersion in the liquid electrolyte (Table 2).

![Fig. 3. Electrolyte uptake characteristics of (a) PVdF–ESFM, (b) PVdF–PAN(25)–ESFM, (c) PVdF–PAN(50)–ESFM and (d) PVdF–PAN(75)–ESFM.](image)

![Fig. 4. Dependence of ionic conductivity of (a) PVdF–PAN(25)–ESFM, (b) PVdF–PAN(50)–ESFM and (c) PVdF–PAN(75)–ESFM with temperature.](image)

The average diameter of the fibers increased significantly after the liquid uptake. Further, PVdF–PAN–ESFMs showed good retention ability of the liquid electrolyte. For an example, nearly 84% of liquid electrolyte was retained in PVdF–PAN(25)–ESFM. PVdF–PAN–ESFMs exhibited good dimensional stability even after liquid uptake and consequent swelling. The high retention ability and faster penetration of liquid electrolyte into the fibrous membranes are due to the unique pores generated from the interconnected fibers. The interconnected network structure in PVdF–PAN–ESFMs also provides the dimensional stability to the membrane even at the swollen states.

3.2.2. Ionic conductivity

The ionic conductivities of the PVdF–PAN–ESFMs were determined at different temperatures by ac impedance spectroscopy (Fig. 4). PVdF–PAN(25)–ESFM electrolyte exhibited a high conductivity of about 7.8 mS cm\(^{-1}\) at 25 °C. The value of ionic conductivity for PVdF–PAN(25)–ESFM is much higher than PVdF-based electrolytes reported in literature [39–42]. In the case of PVdF, high crystalline content of PVdF may impede migration of lithium ions and decrease the conductivity. It is to be noted that existence of PAN in the PVdF–PAN–ESFMs resulted in diminishing of crystalline domains of PVdF. Ultimately, an increase in ionic conductivity was

| Table 2 Physical properties and ionic conductivity of PVdF–PAN–ESFMs |
|--------------------------|------------------|------------------|------------------|
| Electrosyn fibrous membranes | Porosity (%) | Average fiber diameter\(^b\) (nm) | Ionic conductivity (mS cm\(^{-1}\)) |
| PVdF–ESFM | 56.2 | 600 ± 05 | Before immersion | 660 ± 05 | After immersion | 1.0 |
| PVdF–PAN(25)–ESFM | 84.5 | 250 ± 15 | Before immersion | 290 ± 25 | After immersion | 7.8 |
| PVdF–PAN(50)–ESFM | 76.2 | 300 ± 10 | Before immersion | 345 ± 10 | After immersion | 5.6 |
| PVdF–PAN(75)–ESFM | 63.4 | 400 ± 20 | Before immersion | 465 ± 10 | After immersion | 3.8 |

\(a\) The value in the parenthesis refers the wt.% of PAN in PVdF–PAN–ESFM. 
\(b\) Average fiber diameter was measured (using FESEM) before and after immersion in 1 M LiClO4 dissolved in PC for 50 h.
Witnessed. In addition to this, increase in ionic conductivity is attributed to arise from the combined influence of higher content of electrolyte uptake into the pores of the membranes and augmented lithium ion mobility in the gelled state. Further, the interconnected networks in the PVdF–PAN–ESFMs restrict the leakage of the liquid electrolyte.

3.2.3. Electrochemical stability

The electrochemical stability of the PVdF–PAN–ESFMs was evaluated by linear sweep voltammetry measurements (Fig. 5). The PVdF–PAN(25)–ESFM exhibited an anodic stability up to 5.1 V versus Li. Whereas, PVdF–PAN(50)–ESFM and PVdF–PAN(75)–ESFM have anodic stabilities as 4.8 and 4.7 V, respectively. An anodic stability of about 4.5 V has earlier been reported for the PVdF–ESFM electrolyte [29]. The increase in electrochemical stability for PVdF–PAN–ESFMs than PVdF–ESFM may be due to the combined presence of PVdF and PAN in the composite membrane.

In order to have a comparative account and to demonstrate the high electrochemical stability of PVdF–PAN–ESFMs, microporous PVdF and PAN membranes were prepared individually through phase inversion method [21] (porosity: 44 and 48%, respectively) and they were transformed into electrolytes by soaking the porous membranes in 1 M LiClO₄–PC solution at 25 °C. The microporous PVdF and PAN membranes showed anodic stability of about 4.38 and 4.25 V, respectively. The electrolyte uptake of PVdF and PAN were about 180 and 195%, respectively. These results clearly indicate that PVdF–PAN–ESFMs posses enhanced electrochemical stability than that of conventional porous membranes and are expected to be stable within the operating voltage of a lithium polymer battery. Furthermore, the low residual current and the absence of additional peaks at lower voltages indicate that the PVdF–PAN–ESFMs are highly pure.

3.2.4. Interfacial characteristics

The electrochemical impedance spectra of the symmetric Li cell constructed with the PVdF–PAN–ESFMs as polymer electrolyte are presented in Fig. 6a–c. The cole–cole plot for the symmetric cells was used to obtain the interfacial resistance (Rᵢ) between the lithium and PVdF–PAN–ESFM [43]. We could observe variation in the Rᵢ, which may be attributed to the growth of a passivating film on the Li electrode surface due to the reaction of Li metal with PVdF–PAN–ESFM. Nevertheless, Rᵢ of the PVdF–PAN–ESFMs decreases as the wt.% of PAN increases, irrespective of the storage time. PVdF membranes have been reported to have Rᵢ of about 150 Ω which increased with storage time [38,44]. Rᵢ of PVdF–PAN–ESFM is much lower than PVdF-based gel polymer electrolyte [38,44]. In the present case, the mechanism of the inhibition effect of PAN on passive layer formation is unknown. One of the possibilities is that existence of PAN in the composite ESFMs might increase the viscoelasticity of the gel and that could suppress the formation of passive film.

Although, the resistance of the passive film increases as a function of time (aging time), the ESFM with 75% of PAN...
showed a lower interfacial resistance as compared to other ESFMs. Typically, after 28 days of storage time, the interfacial resistance of PVdF–PAN(25)—ESFM, PVdF–PAN(50)—ESFM and PVdF–PAN(75)—ESFM were 280, 170 and 120 \(\Omega\), respectively. The lower amount of organic liquid (PC) entrapped inside the PVdF–PAN(75)—ESFM could also be the reason for the decrease in interfacial resistance than the other ESFMs.

3.2.5. Battery performances

In order to evaluate the electrochemical performance of PVdF–PAN–ESFM as electrolyte in lithium-cells, pouch cells were fabricated with Li as anode and LiCoO\(_2\) as cathode. The assembled cells were subjected to cycle tests. The cell was charged/discharged at 0.1C rate between 2.8 and 4.25V. Fig. 7(i) shows the charge–discharge profile (first cycle) of the Li/LiCoO\(_2\) pouch cell using PVdF–PAN–ESFM at 25 \(^\circ\)C. A capacity of 120.4 mAh g\(^{-1}\) was achieved. The experimental capacity of the cell is close to the theoretical capacity of LiCoO\(_2\) (125 mAh g\(^{-1}\)). The discharge capacity versus cycle number for the cell subjected to 150 cycles is shown in Fig. 7(ii). The decline in the discharge capacity was not significantly pronounced for all the ESFMs. The decrease in capacity was at the rate of about 0.05, 0.07 and 0.09% per cycle (for PVdF–PAN(x)—ESFM; x = 25, 50 and 75%, respectively) with the number of discharge cycles. In the case of PVdF–PAN(25)—ESFM, at the 150th cycle, 93% of the initial capacity (120.4 mAh g\(^{-1}\)) was retained. These results confirm the excellent efficiency of the PVdF–PAN–ESFM to conduct the ions between electrodes during cycling processes. This PVdF–PAN–ESFMs have good compatibility with electrodes, especially to lithium metal.

The rate capability of the pouch cell was also evaluated. Inset in Fig. 7(ii) shows the discharge curves of the cell with PVdF–PAN(25)—ESFM obtained at different current rates. The cell was charged at 0.1C rate. It is evident from the figure that the cell at 0.2C rate could achieve a capacity of 112.38 mAh g\(^{-1}\). However, the discharge capacity was found to gradually decrease with increasing current rates, due to polarization. It is estimated that the cell retained ~72% of discharge capacity at 2C rate, as compared to that at 0.1C rate. These results demonstrate that PVdF–PAN–ESFMs can effectively be used as polymer electrolytes in rechargeable Li batteries.

4. Conclusions

Electrospun fibrous membranes (ESFMs) of the composites of PVdF and PAN were prepared. PVdF–PAN–ESFMs have interconnected fibrous morphology with voids/pores. PVdF–PAN–ESFMs exhibit a high uptake of liquid electrolyte (lithium salt in PC) and transform into gel type ESFMs. The PVdF–PAN(25)—ESFM showed a high ionic conductivity (7.8 mS cm\(^{-1}\)) at 25\(^\circ\)C and high anodic stability (5.1 V vs. Li). PVdF–PAN–ESFMs exhibited higher liquid electrolyte uptake with adequate dimensional stability, lower interfacial resistance and higher electrochemical stability window than the PVdF–ESFM. The performance characteristics of PVdF–PAN–ESFMs as polymer electrolytes in lithium batteries are much superior to the membranes of individual polymers (PAN and PVdF). Thus, the present methodology of composite preparation using electrospinning can be extended for the preparation of wide range of other polymer composites membranes.

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