Poly(vinylidene fluoride)–polydiphenylamine composite electrospun membrane as high-performance polymer electrolyte for lithium batteries

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1. Introduction

Polymer electrolytes consist of salts dissolved in solid polymers hold a key role in realizing the major goal of an all-solid-state rechargeable lithium battery [1–3]. Amorphous polymer electrolytes have been studied intensively for more than 30 years, however, the performance of the electrolyte has not increased substantially over that period. Conductivity in the order of $\sim 1$ mS cm $^{-1}$ was achieved in these systems. To enable high performance of the lithium battery, a polymer electrolyte should possess ionic conductivity greater than that period. Conductivity in the order of $\sim 1$ mS cm $^{-1}$ was achieved in these systems. To enable high performance of the lithium battery, a polymer electrolyte should possess ionic conductivity greater than $\sim 1$ mS cm $^{-1}$, good dimensional and thermal stability, an electrochemical stability window of $\geq 5.0$ V, chemical compatibility with Li electrodes, ability to afford Li cycling (recharge) at an efficiency of greater than 99%. Therefore, it is essential to develop polymer electrolytes to suit for the modern needs in the power sources.

Poly(vinylidene fluoride), PVdF with its high mechanical stability and chemical inertness has been used as polymer electrolytes in lithium batteries [4]. PVdF is inherently polar due to the presence of electronegative fluorine atoms in the backbone structure [5]. The crystalline domains in PVdF hinder migration of lithium ions and lower the ionic conductivity. Polydiphenylamine (PDPA), a polymer of N-substituted aniline, is more soluble in common organic solvents [6], exhibits different redox characteristics than other poly(N-substituted anilines) [7,8]. Recent studies show that backbone units of PDPA can be grafted with other polymeric chains to have novel functional properties [9].

Electrospinning is an efficient fabrication process that gives fibrous and porous membranes with an average diameter ranging from 100 nm to 5 μm [10], which are at least one or two order of magnitude smaller than the fibers produced from melt or solution spinning. Electrospinning technology has recently been extended in various fields like preparation of porous filters, biomedical materials, reinforcing components, cloths for electromagnetic wave shielding, sensors, electronic devices, etc. [11–13]. Reports on using electrospinning for making non-woven mats of polymer composites consisting of conducting polymer and a conventional polymer are scarce. Blends of polyaniline with poly(ethylene oxide) in chloroform were electrospun to produce filaments in the range of 4–20 nm [14]. PEO provides adequate viscosity to the composite solution to achieve electrospinning.

In the present study, PVdF–PDPA composite nanofibrous membranes (PVdF–PDPA–CFM) were prepared though electrospinning. β-Naphthalene sulfonic acid (NSA)-doped PDPA is fairly soluble in DMF in which PVdF (10% w/w) can form viscous solution and...
this suits for electrospinning the composite [15]. The migration of lithium ions in PVdF is expected to be enhanced by forming composites with PDPA that can have physicochemical interactions with C–F groups in PVdF. Improved ion mobility and ionic conductivity are therefore expected. Further, the presence of PDPA can also reduce the bulk resistance of the electrolyte.

2. Experimental

2.1. Preparation of polymer electrolytes

Polydiphenylamine was prepared by the oxidative polymerization of diphenylamine (50 mM in 1 M NSA) with potassium peroxodisulfate (0.2 M in 1 M NSA) at 5 °C [16]. The green colored precipitate (NSA-doped PDPA) was filtered, washed with 1 M NSA and dried in vacuum oven. Adequate amounts of PVdF and NSA-doped PDPA were dissolved in DMF/acetone mixture (7:3 v/v). Electrospun composite membranes were prepared by using the methodology, as described elsewhere [15]. Electrospinning of the composite solution was performed at a flow rate of 10 mL/h with a potential difference of 25 kV. A distance of 15 cm was kept between the syringe tip and collector. Membranes were accumulated on the collector (drum) over the aluminium foil. Electrospun membranes with different amounts of PDPA (0.5%, 1% and 2% w/w) were made. Also, membranes with different thickness ranging from 20 μm to 60 μm were made by manipulating the time for the electrospinning. Polymer electrolyte was prepared by soaking the electrospun PVdF–PDPA-CFM in 1 M LiClO₄–PC solution at 25 °C in the glove box. The methodology adapted for the fabrication of PVdF–PDPA-CFM is presented in Scheme 1.

2.2. Membrane characterization

The morphology of the membranes was examined by field emission scanning electron microscope (FESEM)-Hitachi S-4300 with a field emission gun operated at 200 kV. Fourier transform infrared spectra were recorded at ambient temperature using Bruker IFS 66v FT-IR spectrophotometer with a wave number resolution of 4 cm⁻¹. Samples for FT-IR were made by casting the membrane directly on KBr pellets and then simultaneously dried at 120 °C for 48 h.

2.3. Electrochemical characterization

The polymer electrolyte membranes for electrochemical measurements were obtained by soaking the electrospun PVdF–PDPA-CFM in 1 M LiClO₄–PC solution for 24 h at 25 °C. Ionic conductivities of the PVdF–PDPA-CFM were measured by recording the ac impedance spectra of the symmetric SUS316 cell (area: 3.14 cm²) in the temperature range of 0–80 °C (sweep: 100 Hz to 0.1 MHz and ac amplitude: 5 mV). The symmetrical cell was then fixed in an airtight double wall glass tube, through the outer jacket of which thermostated water was circulated for measurements at different temperatures. All electrochemical measurements were performed using EG and G PAR 283 Potentiostat/Galvanostat with FRA 1025. For electrochemical measurements, a cell was constructed by sandwiching the electrospun membrane electrolyte between two symmetrical lithium metal electrodes. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed at a sweep rate of 1 mV s⁻¹. For dc polarization measurement, a constant potential difference of about 10 mV was applied across the cell and the current was measured as a function of time until it reaches a constant value. By considering the potential drop occurring at surface layers on the electrode, the cation transport number, \( t_+ \), was determined. As impedance spectra were recorded before and after the current relaxation measurement without interruption of the dc bias [17]. For charge–discharge studies, pouch cell battery prototypes were assembled by laminating in sequence the three components, i.e. the graphite anode, PVdF–PDPA-CFM as a electrolyte (typically of 60-μm thickness) and the LiCoO₂ cathode.

3. Results and discussion

3.1. Morphology and structure

Fig. 1 shows the FESEM images of electrospun fibrous membranes depicting the morphological variations between pristine

![Scheme 1. Schematic representation for the fabrication of PVdF–PDPA-CFM.](image-url)
PVdF membrane and PVdF–PDPA-CFM. PVdF membrane is white in color, whilst PVdF–PDPA-CFM is green in color (viewed through optical microscope). FESEM images clearly show the morphological variations between pristine PVdF membrane and PVdF–PDPA-CFM. Electrospun PVdF fibrous membranes have a nearly straightened and tubular structure with an average diameter of ~500 nm (Fig. 1a). However, PVdF–PDPA-CFM has interconnected multifibrous layers with ultrafine porous structures (Fig. 1b and c). The average diameter of PVdF–PDPA-CFM (~200 nm) with 0.5 wt.% of PDPA in the composite (Fig. 1b) is far lesser than pristine PVdF membrane (Fig. 1a). There is inter-fiber twisting in the PVdF–PDPA-CFM that generates microcavities. PVdF–PDPA-CFM with 1 wt.% of PDPA in the composite has much lower (~<200 nm) fiber diameters and more entanglements between the fibers (Fig. 1c). The fibers appeared to be uniform in composition without having any phase separated microstructure or beads which are due to the miscibility of PVdF and PDPA.

Now, it becomes relevant to analyze the reason for the differences in morphology between PVdF membrane and PVdF–PDPA-CFM. It is generally known that the distance between the nozzle of the syringe and the collector, applied voltage, viscosity of the polymer solution and dielectric constant of the solvent are the parameters that influence the morphology of electrospun fibers. In the present study, the first three factors in the above list were maintained constant while electrospinning and hence cannot be the reason for the morphological differences. Hence, we envisage the following reasons. The incorporation of PDPA can increase the dielectric of the medium for electrospinning. Electrospin jets are therefore easily formed (in comparison to a lesser dielectric PVdF solution) at the nozzle of the syringe for PVdF–PDPA composite solution and cause formation of fibers with lower diameter without beads from the composite solution [15]. Interconnected fibrous morphology for the PVdF–PDPA-CFM is expected to arise from the probable intermolecular interactions between the protonated amine or imine groups in PDPA [7,8] and electronegative fluorine atoms in PVdF.

FT-IR spectrum of PVdF–PDPA-CFM (Fig. 2) shows main bands corresponding to the oxidized form of PDPA consisting of diphenquinodimine (quinoid) and diphenyl benzidine (benzenoid) structures [7,8]. However, the benzenoid and quinoid C=N vibrational bands that appeared 1494 cm\(^{-1}\) and 1595 cm\(^{-1}\), respectively for PDPA are found to be shifted to 1498 cm\(^{-1}\) and 1598 cm\(^{-1}\) in the PVdF–PDPA-CFM. Similarly, the band corresponding to CF\(_2\) bending mode of vibration that appeared in 1400 cm\(^{-1}\) for PVdF [18,19] is found to be shifted to 1375 cm\(^{-1}\) in the PVdF–PDPA-CFM. Further, new vibrational bands are found around 1670 cm\(^{-1}\) and 1734 cm\(^{-1}\) for the composite. The above observations indicate that there are molecular level interactions between the nitrogen atoms in benzenoid or quinoid structures of PDPA and electronegative fluorine atoms in PVdF.

3.2. Swelling behaviour

PVdF–PDPA-CFM was transformed into polymer electrolyte membrane by soaking the porous mats into an electrolyte solution (1 M LiClO\(_4\) in propylene carbonate) (Fig. 3). PVdF–PDPA-CFM with 2% PDPA (w/w) has higher uptake (>280 wt.%) of liquid electrolyte.
over PVdF membrane (≈200 wt.%). To the best of our knowledge, PVdF–PDPA-CFM has the highest liquid uptake for PVdF-based polymer electrolyte [20–24]. A maximum of 70% liquid uptake for PVdF and PVdF–HFP membranes has been reported [20,21]. For PVdF–HFP and PVdF–HFP-g-P MMA membranes, a liquid uptake of about 45% and 75%, respectively have been reported [22,23]. A maximum liquid uptake of about 260 wt.% for electropun PVdF has been reported [24]. At the swelled state, PVdF–PDPA-CFM showed good dimensional stability. The higher liquid uptake for PVdF–PDPA-CFM mainly arises from the interconnected network morphology that increased the stability of pores.

3.3. Ionic conductivity

The ionic conductivity of a polymer electrolyte membrane depends on the effective number of carrier ions and the ion mobility. The effective number of carrier ions is related to the concentration of the dissolved ions. The ion mobility in a polymer electrolyte formed by the dissolution of ions in polymer is facilitated by the segment mobility of the polymer chains.

Ionic conductivities of the PVdF–PDPA-CFM were determined by ac impedance spectroscopy as a function of temperature. The mechanism of ionic conduction for PVdF–PDPA-CFM is mainly in accordance with Vogel–Tammann–Fulcher (VTF) relationship. VTF relationship to ion transport in PVdF–PDPA-CFM signifies the coupling of the charge carriers with the segmental motion of the polymer chains. PVdF–PDPA-CFM with 2% PDPA (60-μm thickness) exhibits an ionic conductivity of 3.6 mS cm$^{-1}$ at 25°C, the highest reported value for PVdF-based electrolyte [24–28].

The high ionic conductivity for PVdF–PDPA-CFM (2% PDPA) is attributed to arise from the combined influence of higher content of electrolyte (>280 wt.%) incorporated into the pores of the membrane and augmented lithium ion mobility in the membrane. Doped PDPA has positively charged nitrogen sites (protonated diphenylquinone diimine units) [7,8] that have molecular level interactions with the electronegative fluorine atoms present in PVdF. This environment provides (i) new path for Li$^+$ ion migration in the composite, (ii) interconnected network morphology between PDPA and PVdF and (iii) compact porous structure to hold more amount of the liquid electrolyte. The recombination possibility of Li$^+$ ion with ClO$_4^-$ ion is expected to be hindered in the presence of PDPA and hence facile Li$^+$ ion mobility becomes possible. A portion of the ClO$_4^-$ ions is expected to be immobilized at the protonated amine or imine sites of PDPA by replacing the organic dopant, naphthalene sulfonate anions. The bulky naphthalene sulfonate anion has lesser mobility than ClO$_4^-$ ion. As a result, Li$^+$ ions in the PVdF–PDPA membrane matrix can freely move to result higher ionic conductivity.

The electrochemical stability window of the polymer electrolyte is one of the important parameters that must be considered for application in rechargeable lithium batteries. This parameter can be determined by means of a linear sweep voltammetry. Generally, LSV is performed by the fabrication of a laminated electrode cell with two inert blocking electrodes at an ambient temperature. The blocking electrode is polarized anodically and the electrochemical stability is identified by the rapid increase of the anodic current observed when the decomposition of the polymer electrolyte, i.e., typically the oxidation of the electrolyte anion, takes place. The working potential range or practical lithium rechargeable batteries are generally between +1.8 V and +3.5 V vs. Li.

In the present study, to ascertain the electrochemical stability of PVdF–PDPA-CFM, LSV was performed. Fig. 4 shows the current–voltage response obtained for PVdF–PDPA-CFM electrolytes. The onset of current flow is associated with the decomposition voltage of the electrolyte. From the magnitude of the current response, the decomposition voltage of PVdF–PDPA-CFM was found to be 5.0 V, 5.1 V and 5.18 V vs. Li (PDPA: 0.5%, 1% and 2%, respectively). It can be seen that the electrochemical stability of the membrane is influenced by the amount of PDPA content. LSV measurements of PVdF–PDPA-CFM reveals an increased anodic limit voltage (5.18 V), which is higher than the electrospun PVdF membrane (4.6 V; Fig. 4a) and reported values of PVdF-based electrolytes [24,29–31]. The composite nanofibrous structure increases the oxidation potential of liquid electrolyte by ≈1.6 V (generally 3.6 V vs. Li) and gives a higher anodic stability to the electrolyte membrane. The negligible contribution of current beyond 4.3 V for the PVdF–PDPA-CFM arises from the electronic contribution of PDPA. In the present study, the presence of PDPA has a beneficial effect to widen the electrochemical stability window of the resultant electrolyte membrane.

3.5. Reversibility of Li/Li$^+$ couple

Cyclic voltammetry was performed to study the reversibility of Li deposition–stripping process of the PVdF–PDPA-CFM. Fig. 5 shows the repetitive cyclic voltammograms for Li/PVdF–PDPA-CFM/Li electrode cell performed at an ambient temperature. The sweep rate was kept as 1 mV s$^{-1}$. The onset potential for Li depo-
position was about $-0.4 \text{ V}$ and that can be taken as cathodic limit for the membrane electrolyte.

On sweeping the electrode potential, a cathodic peak was observed at around $-0.4 \text{ V}$, which corresponds to the plating of lithium onto the electrode. On the reverse scan, stripping of lithium was observed at around $0.38 \text{ V}$. The high currents along with peaks in both anodic and cathodic direction indicate the establishment of reversibility of Li/Li$^+$ couple. The reaction

$$\text{Li}^+ + e^- \leftrightarrow \text{Li}$$

is facile at the interface between the lithium electrode and PVdF–PDPA-CFM. The separation in peak potentials being large may be due to the fact that there is no reference electrode used.

It is observed that, although the process remains reversible upon cycling, the amount of cycled lithium progressively decreases. This phenomenon may be attributed to the formation of a passive layer on the electrode, which is similar to those commonly experienced in liquid organic electrolytes. The formation of passive layer is also envisaged from the impedance response of the lithium electrode with PVdF–PDPA-CFM. The reversibility of the membrane demonstrates that the PVdF–PDPA-CFM is electrochemically stable and hence can be safely used as the polymer electrolyte in the rechargeable lithium batteries.

### 3.6. Transport number

The transport number of an electrolyte is an important index of its conductive behaviour. For intercalation/de-intercalation of lithium ions throughout the host compound lattice, electrolytes with a Li$^+$ transference number ($t_+$) close to unity are desirable to avoid a concentration gradient during charge–discharge cycling. Therefore, evaluation of the transference number is important for characterizing electrolyte materials for lithium polymer battery applications.

Cation transference number, $t_+$ of the composite electrolyte was determined by the application of 10 mV dc potential across the test cell (Li/(PVdF–PDPA-CFM)/Li). The current decays immediately and asymptotically approaches steady state. The decrease in current may be due to the growth of passivating layers at the electrode [2,3]. The transference number of Li$^+$ ions was determined and presented in Table 1. The $t_+$ value of PVdF–PDPA-CFM with 2% PDPA was determined to be 0.48. The reported $t_+$ values for SPEs range from 0.06 to 0.2 [21]. For gel polymer systems, $t_+$ values in the order of 0.4–0.5 have been reported. Cationic transport number ranging between 0.2 and 0.4 has been reported for PVdF–HFP-based electrolyte membrane [32–35].

### 3.7. Interfacial behaviour

Compatibility with the electrode materials is an essential parameter in the cyclability and the reliability of rechargeable lithium battery. ac impedance studies performed for the symmetrical non-blocking Li/PVdF–PDPA-CFM/Li and Li/PVdF membrane/Li cells under open-circuit conditions provide useful information on the charge transfer and diffusion of lithium ions [36]. The intercept at high frequency is assigned to bulk resistance ($R_b$) and the intercept at the lower frequency side corresponds to resistance at the interface arising from the passivation of membrane ($R_i$) at the electrode. PVdF electrospun membrane has $R_b$ as 0.46 k$\Omega$ (at 25 $^\circ$C), whereas the PVdF–PDPA-CFM (2% PDPA) shows a lower $R_b$ of about 0.32 k$\Omega$ (at 25 $^\circ$C) (Fig. 6a). Further, it can be seen that the $R_b$ increases as a function of time (aging time) and decreases with PDPA content in the membrane. The increase in $R_b$ can be attributed to the growth of a passivating film on the lithium surface.

![Fig. 5. Cyclic voltammograms of PVdF–PDPA-CFM with 2% PDPA.](image1)

![Fig. 6. (i) Plot of interfacial resistance ($R_i$) with PDPA content in PVdF–PDPA-CFM; (ii) ac impedance spectra of Li/PVdF–PDPA-CFM (2% PDPA)/Li cell at different temperatures: (a) 25 $^\circ$C, (b) 30 $^\circ$C, (c) 40 $^\circ$C, (d) 50 $^\circ$C, (e) 60 $^\circ$C and (f) 70 $^\circ$C. Inset shows the influence of temperature on $R_i$ and $i_0$.](image2)
Generally, the C–F bonds in PVdF react with lithium or lithiated graphite to form stable LiF and/or \( >\text{C–F} \)-type unsaturated bonds [37] and cause instability to the negative electrode of the lithium and lithium ion batteries and also result thermal runaway problems. In the PVdF–PDPA-CFM, a portion of C–F bonds is intermolecularly bound to protonated amine or imine part of PDPA units and hence suppress the adverse effect of C–F interaction with Li electrode.

Further, to understand the effect of temperature on the Li/PVdF–PDPA-CFM interface, impedance measurements were conducted at different temperatures between 25°C and 70°C (Fig. 6b). The Nyquist plots reveal that the interfacial resistance \( (R_i) \) decreases with temperature and consequently the exchange current density \( (i_0) \) increases with temperature. This indicates that the properties of the interfacial film at higher temperatures are conducive for a facile charge transfer and this may be based on the breakdown of the passivating film. It is obvious from the impedance results that the PVdF–PDPA-CFM exhibits good compatibility with lithium metal electrode.

PVdF–PDPA-CFM exhibited improved performance characteristics than electrospun PVdF and other PVdF-based polymer electrolyte membranes. A comparison with respect to the electrochemical characteristics of PVdF–PDPA-CFM with other PVdF-based electrolytes was made and presented in Table 2.

### Table 2

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<th>Value 3</th>
<th>Value 4</th>
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<tr>
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<td>0.28</td>
<td>0.34</td>
<td>0.34</td>
<td>0.48</td>
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3.8. Battery performances

In order to explore the usefulness of the PVdF–PDPA-CFM as electrolyte in rechargeable lithium batteries, pouch cells consisting of graphite as anode, LiCoO\(_2\) as cathode and PVdF–PDPA-CFM as an electrolyte were constructed and the performance was evaluated. A typical charge and discharge curves of the pouch cell with PVdF–PDPA-CFM (2% PDPA) at 25°C is shown in Fig. 7. The cell was cycled between the cut-off voltages, 4.2 V and 3.0 V at 1 C rate. The charge–discharge profile is similar to what is observed in lithium ion batteries in general [38], which ensures a good contact between the electrodes and PVdF–PDPA-CFM. An open-circuit voltage as high as 4.15 V is achieved at 25°C and the charging–discharging voltages are quite reproducible over the entire set of cycles.

Fig. 8a shows the discharge curves for the cells with PVdF–PDPA-CFM (PDPA: 1% and 2%) as electrolyte at various rates. A high-rate capability is realized in the cell with PVdF–PDPA-CFM as an electrolyte, which is due to the high ionic conductivity and highly porous morphology of PVdF–PDPA-CFM. A good fraction of the capacity is delivered at 0.2 C and the cell is still able to operate even at 2 C. Typically, at 1 C rate, the cell can deliver about 90% of its 0.2 C capacity. Even at a high 2 C rate, the cell can still deliver about ~70% of its 0.2 C capacity. Further, the cell was subjected to cycle tests with cut-off voltages of 4.2 V (upper limit) and 3.0 V (lower limit) at 1 C rate. Fig. 8b reveals that the cell with PVdF–PDPA-CFM as electrolyte has a very steady charge–discharge behaviour without significant loss in capacity under the voltage conditions (1 C rate at 25°C). Also, a high charge–discharge efficiency (ratio between charge and discharge capacity) is observed, which confirms the good interfacial stability between the electrode and the PVdF–PDPA-CFM. Thus, the pouch cell with PVdF–PDPA-CFM as an electrolyte shows low impedance, excellent rate capability and good cyclability and displays a superior potential for rechargeable lithium batteries.

### 4. Conclusions

PVdF–PDPA composite nanofibrous membranes were prepared by electrospinning and the polymer electrolytes were prepared by soaking the porous mats into an electrolyte solution. The polymer electrolyte based on PVdF–PDPA-CFM shows superior performances in terms of ionic conductivity, electrochemical stability window and good interfacial behaviour with electrode and proved to be a promising material component for high-performance lithium batteries.

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