Preparation and characterization of electrospun poly(acrylonitrile) fibrous membrane based gel polymer electrolytes for lithium-ion batteries

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ABSTRACT

Electrospun, non-woven membrane of high molecular weight poly(acrylonitrile) (PAN) is demonstrated as an efficient host matrix for the preparation of gel polymer electrolytes for lithium-ion batteries. Electrospinning process parameters are optimized to get a fibrous membrane of PAN consisting of bead-free, uniformly dispersed thin fibers with diameter in the range 880–1260 nm. The membrane with good mechanical strength and porosity exhibits high uptake when activated with the liquid electrolyte of 1 M LiPF$_6$ in a mixture of organic solvents and the gel polymer electrolyte shows ionic conductivity of 1.7×10^{-5} S cm^{-1} at 20 °C. Electrochemical performance of the gel polymer electrolyte at 20 °C is evaluated in lithium-ion cell with lithium cobalt oxide cathode and graphite anode. Good performance with a low capacity fading on charge–discharge cycling is demonstrated.

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1. Introduction

Polymer electrolytes (PEs) have received wide spread attention due to their technological applications for a variety of solid-state electrochemical power sources, rechargeable batteries, fuel cells and supercapacitors [1]. In the field of rechargeable lithium-ion batteries, they have gained immense importance as they hold the promise for safer, lighter and higher-performance batteries. Although a lot of research has been carried out on the development of true solid PEs based on lithium salt incorporated poly(ethylene oxide) (PEO) and similar polymers/oligomers, they could not succeed well because of the limitation of ionic conductivity that could be achieved at ambient temperature with such systems [2]. Later on, the gel PEs that have characteristics in between the solid and liquid electrolytes got wide spread attention and have been successfully used in the lithium-ion polymer batteries marketed by a few manufacturers [3].

The gel PE is prepared by activating the host polymer matrix with the conventional liquid electrolyte consisting of the lithium salt solution in organic solvents. A number of parameters like good ionic conductivity under ambient conditions, wide electrochemical window with sufficient anodic and cathodic stability resisting degradation during the charge–discharge operations of the cell, compatibility with the electrodes, good thermal stability and

sufficient mechanical strength enabling its easy handling, etc. are to be satisfied by the gel PE for its useful application in a lithium-ion cell. Poly(vinylidene fluoride) (PVdF), its copolymer with hexafluoro propylene (PVdF-co-HFP), poly(acrylonitrile) (PAN), PEO, poly (methyl methacrylate) (PMMA), etc. are some of the polymers that have gained importance as the host matrices for realizing gel PEs [2]. Among these, PVdF-co-HFP and PAN have several of the desirable properties including good thermal stability and wide electrochemical window.

Different techniques are being adopted to prepare the porous polymer membrane to function as the host matrix for gel PE. These include solvent casting, plasticizer extraction, phase separation using a non-solvent, and more recently, electrospinning. Because of the uniqueness and desirable features of the membrane that can be prepared by electrospinning, this technique stands out as a method of choice. A few studies have been reported on the usefulness of electrospun polymer membranes as host matrices for gel PEs [4–9]. Generally, membranes prepared by electrospinning of lower molecular weight polymers exhibit poor mechanical properties, attributed to their non-woven texture made up of fibers without any inter-fiber bonding. Improvement in properties, to some extent, is achieved by suitable thermal treatment [10,11].

Earlier studies have reported that PAN-based gel PEs are suitable for application in lithium-ion batteries. The interactions between the nitrile (–C≡N) groups in PAN and Li$^+$ ions in the electrolyte contribute to enhanced ionic conductivity of the gel PE [12–17]. The porous PAN membrane, however, suffers from brittleness due to the reduced flexibility of the main chain arising from the interactions of the adjacent nitrile groups that lead to an increase in

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resistance for the interior rotation of the main chain. Studies are presently being undertaken by various research groups to improve the performance of PAN based PEs [18].

In the present investigation, electrospinning technique was chosen to prepare the porous membrane of PAN having a sufficiently high molecular weight of 4×10^5 expecting to get the host matrix with good mechanical strength and porosity. The electrospinning process parameters were optimized first to prepare the membrane with required characteristics. The gel PE was then prepared by activation of the membrane with liquid electrolyte. The detailed characterization of the PE together with its electrochemical evaluation in lithium-ion cell demonstrating its application as a separator-cum-electrolyte is presented here.

2. Experimental

2.1. Materials

Poly(acrylonitrile) with M_n 4×10^5 and density $1.2 \, \text{g cm}^{-3}$ was produced at Vikram Sarabhai Space Centre, India. Lithium cobalt oxide (M/s. Tianjin B&M Science and Technology Joint-Stock Co. Ltd., China) graphite (M/s. BTR Energy Corporation, China), conductive carbon (M/s. Timcal, Switzerland), Celgard 2320 (M/s. Celgard, USA), polyvinylidene fluoride, lithium hexafluorophosphate (LiPF$_6$), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), n-butanol (all from M/s. Aldrich, USA), and N,N-dimethyl formamide (DMF) (M/s. S.d. Fine Chemicals, India) were used as received.

2.2. Instrumental

Electrospinning was performed using the semi-automated, ESPIN NANO equipment (M/s. Physics Instruments Company, India). The characterization of electrospun membrane was done using the Environmental Scanning Electron Microscope (ESEM Model EVO-50, M/s. Carl Zeics SMT EVO Technology), Fourier Transform Infrared Spectrometer (Perkin Elmer Spectrum GX A FTIR) and INSTRON 5569 Universal Testing Machine. The preparation and evaluation of PE was performed in a glove box (M/s. Mbraun, Germany) with moisture and oxygen levels <1 ppm. The ionic conductivity of PE was evaluated using electrochemical impedance spectroscope (Solartron 1260 A Impedance/gain phase analyzer, 1287A Electrochemical Interface, Solartron Analytical, UK). The electrochemical evaluation of test cells was performed in a battery test station (M/s. Arbin Instruments, USA).

2.3. Preparation of electrospun PAN membrane

Poly(acrylonitrile) was vacuum dried at 60 °C for 8 h before use. It was dissolved in DMF by magnetic stirring at room temperature to get homogenous solution of concentration varying in the range 6–14 wt.%. Fibrous membranes of PAN were prepared by electrospinning method at room temperature. A thin aluminium foil was used as the substrate for deposition of fibers. This was wound over a metallic collector drum (which forms one of the electrodes) kept at a distance of about 17 cm from the other electrode which is the metallic needle of the syringe containing the polymer solution. The collector was kept rotating at a constant speed of 1500 rpm. The solution flow rate through the needle could be programmed between 0.1 and 2 ml min^{-1}. Experiments were performed under varying process parameters like polymer concentration, solution flow rate and applied voltage.

2.4. Characterization of electrospun PAN membrane

The electrospun membranes were removed from the collector drum and dried at 60 °C under vacuum prior to further use. They were characterized for thickness (measured by thickness gauge – Mitutoyo make), surface morphology, spectral and mechanical properties and porosity. Tensile strength, Young's modulus and percentage elongation were evaluated using rectangular samples of 80 mm × 25 mm dimension with an effective gauge length of 25 mm. Porosity of the membrane was determined by the n-butanol uptake method [19].

2.5. Preparation and characterization of gel PE based on electrospun PAN membrane

The electrospun membrane was used as the host matrix for preparation of gel PEs. The compatibility of the membrane with the liquid electrolyte of composition 1 M LiPF$_6$ in EC:DMC:DEC (0.25:1:1, v/v) was tested by immersing a small piece of the membrane in the liquid electrolyte for 30 min and observing the physical changes for the membrane, if any. The PE was prepared by activating the membranes with the liquid electrolyte. The capacity of the membrane to imbibe the liquid electrolyte (electrolyte uptake, ε) was measured by soaking a sample of the membrane in the electrolyte and weighing it at regular intervals of time after removing the excess electrolyte by wiping with tissue paper. The electrolyte uptake (ε) was calculated as

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

where M_0 is the mass of the dry membrane and M the mass after soaking in electrolyte. The efficiency of the membrane to hold the absorbed electrolyte over a period of time is defined in terms of the relative absorption ratio R_A. This is measured by soaking the membrane in the electrolyte for 4 h to reach saturation and then recording the weight changes with respect to time when the swollen membrane is kept under a load. The parameter, R_A is then calculated as:

$$R_A = \frac{M_{PE}}{M_{PE,saturated}} \tag{2}$$

where $M_{PE,saturated}$ is the mass of the PE when the membrane is fully saturated with the electrolyte and M_{PE} that of the PE after a time interval when the saturated PE has been squeezed by pressing it under load.

The ionic conductivity of the gel PE was evaluated at room temperature (20 °C). The electrolyte sample was placed in between two gold plated copper electrodes and the resistance (R, ohm) measurements were performed over the frequency range of 1 MHz to 1 kHz at amplitude of 10 mV. Ionic conductivity (σ) of the sample was calculated as

$$\sigma = \frac{L}{RA} \tag{3}$$

where 'L' is the thickness of the gel PE and 'A' is the cross sectional area.

2.6. Electrochemical performance evaluation of gel PE in Li-ion cell

The suitability of the electrospun, PAN membrane based gel PE in lithium-ion cell was tested by assembling and evaluating prismatic cell (electrode size: ~60 mm × 40 mm) with lithium cobalt oxide as positive electrode and graphite as negative electrode. In addition to the above active materials, the electrodes contained PVdF as the polymeric binder and carbon as the conductive agent. The electrodes were prepared by coating the slurry of the materials
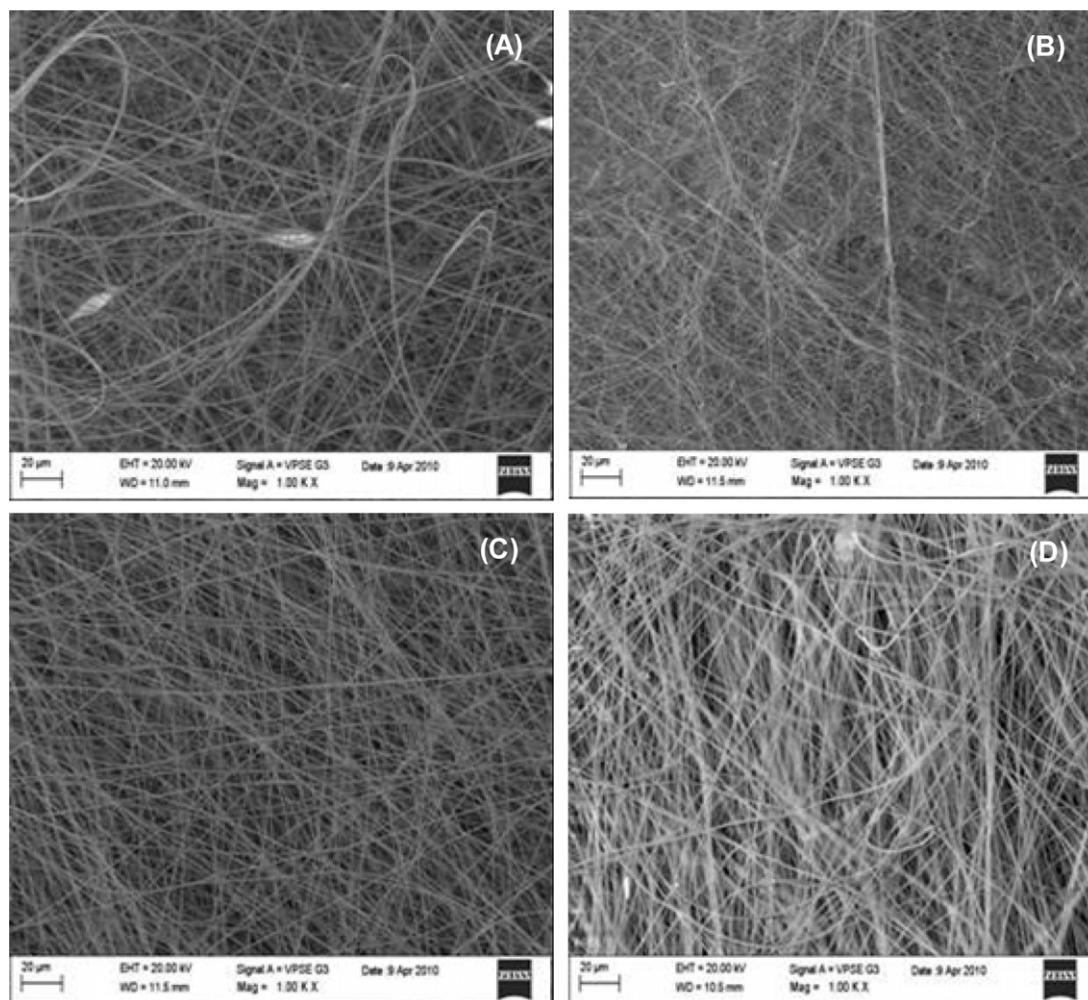
Fig. 1. ESEM images of PAN membranes prepared by electrospinning (A) PAN-1, (B) PAN-2, (C) PAN-3 and (D) PAN-4.

over aluminium (for cathode) and copper (for anode) foils. The gel PE functioned as a separator-cum-electrolyte in the cell, the assembly of which was done inside a glove box. The cell was cycled between 2.8 and 4.1 V at 8 mA current density, corresponding to C/20 rate. The charge–discharge cycling evaluation was performed at 20 °C.

Lithium-ion cell with graphite anode, LiCoO$_2$ cathode, Celgard separator and 1 M LiPF$_6$ in EC:DMC:DEC (1:1:1) electrolyte was assembled as a reference cell and evaluated for electrochemical performance with charge–discharge cycling between 2.8 and 4.0 V at C/20 rate.

3. Results and discussion

3.1. Preparation and characterization of PAN electrospun membrane

For getting the fibrous membrane of a polymer with desired morphology by electrospinning technique, a number of parameters like applied electric voltage, concentration, viscosity and surface energy of polymer solution, flow rate, orifice size of the needle ejecting the solution, distance through which the solution jet travels before deposition, rotating speed of the collector, etc. need to be optimized. The fiber formation, its orientation and diameter as well as uniformity of deposition are all governed by the spinning parameters. In the present study, the experiments were aimed at achieving highly porous membranes of PAN composed

of bead-free, continuous fibers of uniform size with submicron diameter. For this, a few parameters like distance between the needle and collector (17 cm), syringe capacity (10 ml) and needle orifice (0.5 mm) were kept fixed based on the preliminary experiments done. Process optimization was done by changing the three important parameters: polymer concentration (6–14 wt.%), flow rate (0.5–2.0 ml h^{-1}) and applied voltage (8–20 kV). Under each condition, PAN membranes were spun to about 200–250 μm thickness.

It was observed that electrospinning of PAN solution of low concentration (<8 wt.%) resulted in a large number of beads in the fibers and a non-uniform distribution of fibers in the structure. Moreover, the handling of the membrane was extremely difficult. Solution concentration >12 wt.% resulted in thicker fibers with non-uniform morphology. Applied voltage in the range of 10–18 kV and flow rate between 1.0 and 2.0 ml h^{-1} were found to be most conducive for getting thin, bead-free and uniform fibers. Table 1 presents in nutshell the experimental conditions adopted and the observations made regarding the membrane formation and characteristics.

The morphological features of a few of the selected membranes observed in ESEM are shown in Fig. 1. The images reveal that ultrafine fibrous structures of PAN can be easily realized by electrospinning process. The interlaying of the fibers builds up the thickness for the membrane and results in the formation of a large number of micron and submicron sized pores in the structure. Although thin fibers with closely packed structure resulted by spinning 8 wt.% PAN solution (ESEM images A and B in Fig. 1), these
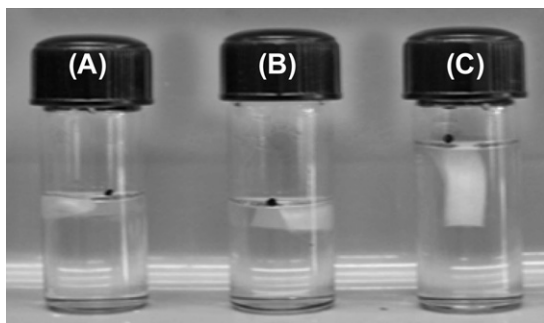
Table 1
Effect of electrospinning parameters on the characteristics of membranes obtained.

Membrane identification	PAN solution concentration (wt.%)	Applied voltage (kV)	Solution flow rate (ml h^{-1})	Observations
PAN-1	8	10	2.0	Fibers formed with beads in between, nearly uniform distribution, flimsy membrane, difficult to handle
PAN-2	8	17	2.0	Thin fibers formed, nearly uniform distribution, better strength compared to PAN-1, difficult to handle
PAN-3	10	15	1.5	Fibers formed with uniform distribution, reasonably good handling strength
PAN-4	10	15	2.0	Fibers formed with uniform distribution and closer packing, stronger membrane with better handling strength than PAN-3
PAN-5	12	18	1.0	Thicker fibers formed with non-uniform distribution

Fig. 2. ESEM image of PAN-4 showing the range of fiber diameters.

Fig. 3. FTIR spectra of PAN before electrospinning and PAN electrospun membrane.

membranes lacked sufficient mechanical strength for easy handling. Stronger membranes with better morphology were formed with 10 wt.% solution (ESEM images C and D in Fig. 1). Among all the membranes, PAN-4 exhibited the best combination of morphological features and handling strength. The ESEM image of PAN-4 taken at a higher magnification is given in Fig. 2. The range of fiber diameters observed has been marked in this image; values range between 880 nm and 1260 nm, with an average fiber diameter of 900 nm. The thickness of PAN-4 membrane is 250 μm.

For further studies on preparation and evaluation of gel PEs, PAN-4 membrane (hereafter referred to as PAN membrane) was selected. To confirm that the applied high electrical field does not cause any change in the chemical structure of PAN during the electrospinning process, the FTIR spectra of PAN before and after spinning are compared (Fig. 3). The two spectra are identical showing the presence of characteristic peak of –C≡N at 2243 cm^{-1}.

Mechanical properties like tensile strength, percentage elongation and Young's modulus of PAN membrane in both machine direction and transverse direction were determined at room temperature and the values are included in Table 2. The properties are high enough enabling the easy handling of the membrane for

practical purposes. Fig. 4 shows the typical stress–strain curve for the sample tested in machine direction under tensile load. It can be observed that the sample behaved in ductile manner and was able to take up good strain levels (from ~10 to 65%) at the highest load of 30 kg cm^{-2}. Thus, by electrospinning process, it is possible to prepare porous PAN membrane with good flexibility, in contrast to the brittle ones obtained by other methods like solution casting. This is probably because the molecular chains get oriented

Fig. 4. Representative stress–strain curve for PAN electrospun membrane tested in the machine direction under tensile load.

Table 2
Mechanical properties of the electrospun PAN membrane.

Properties	Machine direction	Transverse direction
Tensile strength (kg cm^{-2})	38	22
Young's modulus (kg cm^{-2})	74	55
Elongation at break (%)	92	68

Fig. 5. Solubility test of PAN electrospun membrane in liquid electrolyte of varying compositions of EC:DMC:DEC (by volume) (A) 1:1:1, (B) 0.5:1:1 and (C) 0.25:1:1.

Fig. 6. Electrolyte uptake vs. time for electrospun PAN membrane.

in the direction of the electric field during spinning and prevents interaction between the adjacent nitrile groups. As a result, the internal rotation and flexibility of the main chain are preserved. Also, the mechanical properties determined in the machine direction are higher than those in the transverse direction, indicating the uniform alignment of the fibers in the machine direction. The higher fiber content per unit area in the machine direction enables those samples to take up more load resulting in higher mechanical properties.

3.2. Gel PE based on electrospun PAN membrane

The porosity of the PAN membrane was determined to be 81%. The porosity is thus at least two times higher when compared with the commercial Polypropylene/Polyethylene/Polypropylene trilayer separator (Celgard 2320, porosity 35%, determined by the same procedure under similar conditions) which is most widely used in the state-of-the-art lithium-ion cells. The gel PE prepared by activating the polymer host membrane with liquid electrolyte has to remain stable in the electrochemical cell during repeated charge–discharge cycling. For this, it is essential that the polymer membrane does not dissolve in the liquid electrolyte or chemically react with it. 1 M solution of $LiPF_6$ in a mixture of organic solvents EC, DMC and DEC (in varied proportions to meet user requirements) has been the most widely used liquid electrolyte in lithium-ion cells. In the present study, the compatibility of electrospun PAN membrane with the liquid electrolyte of compositions of EC:DMC:DEC in 1:1:1, 0.5:1:1 and 0.25:1:1 (by volume), was tested by observing its solubility/change in dimensions after keeping immersed in the electrolyte for 30 min; the results are shown in Fig. 5. Results indicated that PAN membrane remains unaffected in the composition 0.25:1:1, whereas, it slowly disintegrated in the compositions containing higher proportion of EC. Thus, the liquid electrolyte of 1 M $LiPF_6$ in EC:DMC:DEC of 0.25:1:1 composition was used for preparation of gel PE and further evaluation. The properties of the gel PE based on electrospun PAN membrane are given in Table 3.

Fig. 6 shows the electrolyte uptake of the membrane as a function of time. The porous nature of the membrane helps to uptake a large amount of the electrolyte within a short interval of time. Thus, an electrolyte uptake of 1100% is attained within 20 min. Under similar conditions, the Celgard separator shows an uptake of 200%. The higher uptake of electrospun PAN membrane results from its
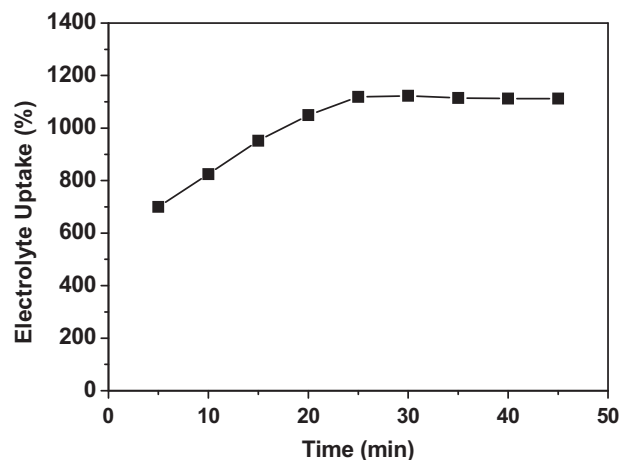
higher porosity as well as the high surface area of the submicron fibers which can also absorb the liquid electrolyte. The change in relative absorption ratio R_A of the gel PE with time is depicted in Fig. 7. The gel PE shows a substantial leakage in the electrolyte when subjected to load, showing a decrease in R_A value with time. The leakage is high during the initial period, but gets stabilized to R_A value of 0.15 after about 90 min. In contrast, the commercial separator Celgard showed a relatively high R_A value of 0.68 which remained stable throughout the experiment. This indicates that the interconnected pore structure of electrospun membrane is not able to retain the whole amount of absorbed electrolyte when subjected to external load. With a stabilized R_A value of 0.15, PAN membrane can hold ~165% (1100×0.15) of electrolyte which is marginally better than Celgard which can hold ~136% (200×0.68).

Based on the above studies, the gel PE was prepared by activating the electrospun PAN membrane with the liquid electrolyte by keeping for 1 h and then squeezing out the excess electrolyte by subjecting to a mechanical load for about 90 min. The ionic conductivity of the gel PE was determined to be 1.7×10^{-5} S cm^{-1} at 20 °C; this value was found to be better than that of Celgard in the same electrolyte 1.1×10^{-5} S cm^{-1}. The results indicate that electrospun membrane based gel PE can function satisfactorily providing easy transport of ions between the electrodes in lithium-ion cells.
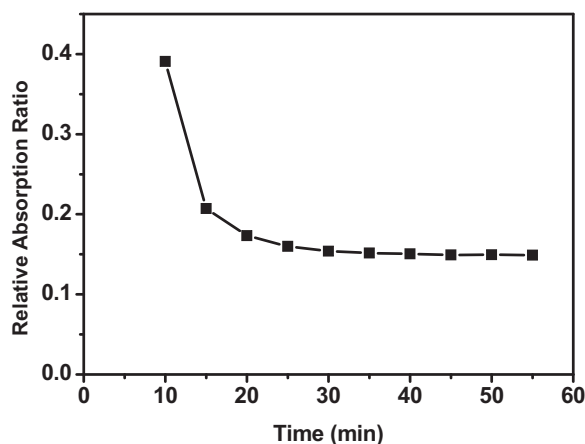
Table 3
Properties of the gel PE based on electrospun PAN membrane.

Properties	Value
Electrolyte uptake (max.) (%)	1100
Relative absorption ratio of electrolyte	0.15
Ionic conductivity at 20 °C (S cm^{-1})	1.7×10^{-5}

Fig. 7. Relative absorption ratio of electrolyte vs. time for electrospun PAN membrane.

Fig. 9. Charge-discharge profile of the lithium-ion cell with electrospun PAN based gel PE for the first 200 h.

Fig. 10. Comparison of discharge capacity of the cell on cycling for lithium-ion cells with electrospun PAN based gel PE and with Celgard separator and liquid electrolyte.
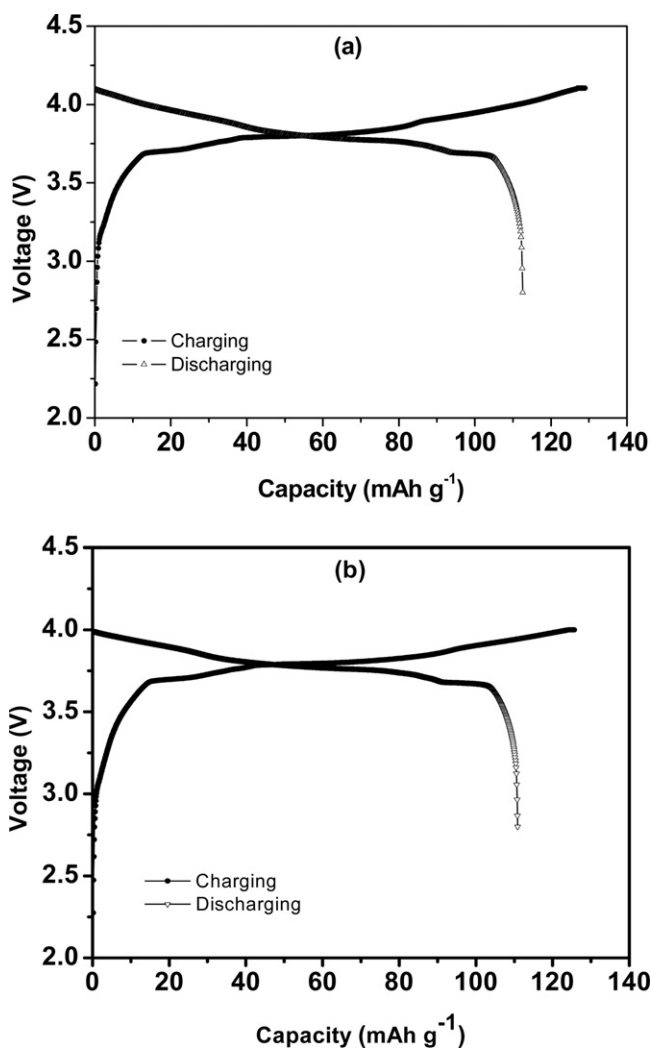
Fig. 8. First cycle charge and discharge performance of the lithium-ion cell (a) with electrospun PAN based gel PE and (b) with Celgard separator and liquid electrolyte.

3.3. Electrochemical performance of gel PE in lithium-ion cell

The charge–discharge characteristics of a lithium-ion prismatic cell (dimensions 60 mm × 40 mm) with $LiCoO_2$ as cathode and graphite as anode were evaluated using the electrospun PAN membrane based gel PE functioning as the separator-cum-electrolyte. Fig. 8(a) demonstrates the first cycle charge and discharge performance of the cell at a current of 8 mA, which corresponds to C/20 rate. Initial charge and discharge capacities were 128 and 113 mAh g^{-1}, respectively. These are comparable with the initial charge and discharge capacities of 126 and 111 mAh g^{-1}, respectively, obtained for the reference cell with Celgard separator and liquid electrolyte, as shown in Fig. 8(b). Fig. 9 shows the charge/discharge profile of the cell for the first 200 h. It is observed that the cell shows a stable performance on repeated charging and discharging and retained >96% charge–discharge efficiency. The cycle performance was evaluated for 30 cycles at C/20 rate for the cell under study and the reference cell and the discharge capacities obtained are compared in Fig. 10. The cell based on electrospun PAN based gel PE showed stable capacity after a few initial cycles and retained 86% of its initial capacity after 30 cycles. The mid-voltage during the discharge remained stable at 3.7 V throughout cycling indicating the absence of major polarization factors in the cell. This observation indirectly showed that the gel PE could effectively transport lithium ions on repeated cycling of the cell.
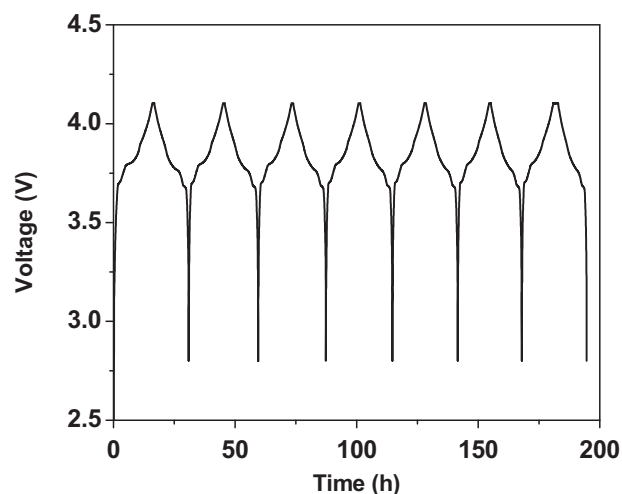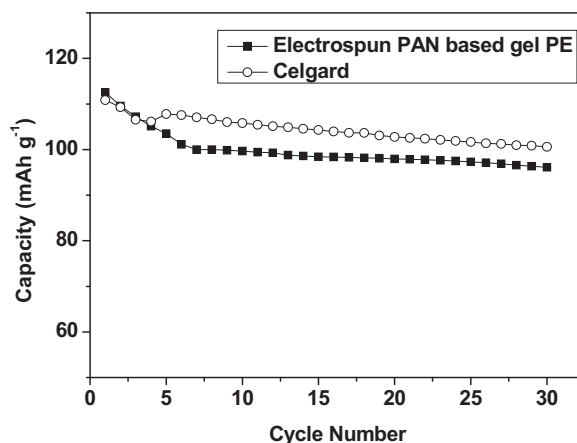
The reference cell exhibited marginally better performance taking lesser number of initial cycles to stabilize and also retained 91% of its initial capacity after 30 cycles. The above comparison demonstrates that the performance of the gel PE is quite encouraging. In addition to the inherent advantages of PAN as an ionic conductor, the good performance of the gel PE can be attributed to the highly porous nature of the electrospun membrane which retains a fairly good amount of the electrolyte enhancing the conductivity of ions through the PE with reduced internal resistance. Post cycling examination of the cell showed that the PE remained intact without any damage. The mechanical stability imparted to the PE by using a high molecular weight PAN as the PE matrix could be another important factor that contributed to the good cycle life achieved for the cell.

4. Summary

The electrospinning technique is used to prepare the fibrous membrane of PAN having a relatively high molecular weight of 4×10^5. The spinning parameters are optimized to get a bead-free membrane with high porosity, uniform fiber distribution and sufficient mechanical strength. The suitability of the membrane as a host matrix for the preparation of gel PE for lithium-ion battery application is explored. The gel PE is prepared by activating the membrane with liquid electrolyte of 1 M $LiPF_6$ in a mixture of organic solvents. The PE exhibits good ionic conductivity at 20 °C, better than

that of Celgard based electrolyte which is attributed to the higher porosity and electrolyte uptake of the electrospun membrane. The gel PE performs with stable charge–discharge characteristics when evaluated as the separator-cum-electrolyte in a lithium-ion cell. This preliminary study demonstrates that the gel PEs based on the electrospun membrane of high molecular weight PAN exhibits good mechanical stability, ionic conductivity and charge–discharge properties when assembled in a lithium-ion cell.

Acknowledgements

References

[1] B. Scrosati, Applications of Electroactive Polymers, Chapman and Hall, London, 1993.
[2] M. Stephan, Eur. Polym. J. 42 (2006) 21.
[3] J.W. Fergus, J. Power Sources 195 (2010) 4554.
[4] S.W. Choi, S.M. Jo, W.S. Lee, Y.R. Kim, Adv. Mater. 15 (2003) 2017.
[5] J.R. Kim, S.W. Choi, S.M. Jo, W.S. Lee, B.C. Kim, ELectrochim. Acta 50 (2004) 69.
[6] J.R. Kim, S.W. Choi, S.M. Jo, W.S. Lee, B.C. Kim, ELectrochim. Acta 152 (2005) A295.
[7] T.H. Cho, T. Sakai, S. Tanase, K. Kimura, Y. Kondo, T. Tarao, M. Tanaka, Electrochem. Solid-State Lett. 10 (7) (2007) A159.
[8] T.H. Cho, M. Tanaka, H. Onishi, Y. Kondo, T. Nakamura, H. Yamazaki, S. Tanase, T. Sakai, J. Power Sources 181 (2008) 155.
[9] 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.
[10] S.S. Choi, Y.S. Lee, C.W. Joo, S.G. Lee, J.K. Park, K.S. Han, ELectrochim. Acta 50 (2004) 339.
[11] K. Gao, X. Hu, C. Dai, T. Yi, Mater. Sci. Eng. B 131 (2006) 100.
[12] F. Croce, S.D. Brown, S.G. Greenbaum, S.M. Slane, M. Salomon, Chem. Mater. 5 (1993) 1268.
[13] B. Huang, Z. Wang, G. Li, H. Huang, R. Xue, L. Chen, F. Wang, Solid State Ionics 85 (1996) 79.
[14] C.R. Yang, J.T. Perng, Y.Y. Wang, C.C. Wan, J. Power Sources 62 (1996) 89.
[15] B. Huang, Z. Wang, L. Chen, R. Xue, F. Wang, Solid State Ionics 91 (1996) 279.
[16] Z. Wang, B. Huang, R. Xue, X. Huang, L. Chen, Solid State Ionics 121 (1999) 141.
[17] Y.W. Chen-Yang, H.C. Chen, F.J. Lin, C.C. Chen, Solid State Ionics 150 (2002) 327.
[18] M.M. Rao, J.S. Liu, W.S. Li, Y. Liang, Y.H. Liao, L.Z. Zhao, J. Power Sources 189 (2009) 711.
[19] P. Raghavan, J.W. Choi, J.H. Ahn, G. Cheruvally, G.S. Chauhan, H.J. Ahn, A. Nah, J. Power Sources 184 (2008) 437.