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Effect of poly(ethylene oxide) on ionic conductivity and electrochemical properties of poly(vinylidenefluoride) based polymer gel electrolytes prepared by electrospinning for lithium ion batteries

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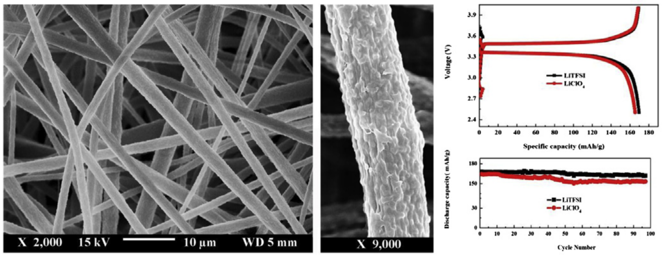
HIGHLIGHTS

- Effect of PEO on electrochemical properties of electrospun PVdF based PEs studied.
- PEs are prepared by activating membrane with lithium salts in carbonate solvents.
- PEs show high ionic conductivity and good compatibility with lithium electrodes.
- Li/LiFePO$_4$ cell using PVdF/PEO delivers significantly higher discharge capacity.
- The cells show stable cycle performance under continuous cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

Effect of poly(ethylene oxide) on the electrochemical properties of polymer electrolyte based on electrospun, non-woven membrane of PVdF is demonstrated. Electrospinning process parameters are controlled to get a fibrous membrane consisting of bead-free, uniformly dispersed thin fibers with diameter in the range of 1.5–1.9 μm. The membrane with good mechanical strength and porosity exhibits high uptake when activated with the liquid electrolyte of lithium salt in a mixture of organic solvents. The polymer gel electrolyte shows ionic conductivity of 4.9×10^{-3} S cm^{-1} at room temperature. Electrochemical performance of the polymer gel electrolyte is evaluated in Li/polymer electrolyte/LiFePO$_4$ coin cell. Good performance with low capacity fading on charge–discharge cycling is demonstrated.

1. Introduction

Polymer electrolytes (PEs) have received considerable attention in recent years for application in lithium ion batteries [1–5]. Poly(ethylene oxide) (PEO)-based electrolyte has been widely studied as solid polymer electrolyte due to its good thermal properties, mechanical properties and interfacial stability with lithium metal. It has ether linkages, with oxygen atoms present at a suitable inter-atomic

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separation to allow segmental motion of the polymeric chain which is beneficial for facile ionic conduction [2]. The prototypical solid PE is PEO-LiX, prepared by blending PEO with lithium salt (LiX) of a large anion [6,7]. The transport of Li^+ ions in these electrolytes has been associated with the local relaxation and segmental motion of the amorphous regions in the PEO chains. Due to the formation of crystallites in PEO systems, these polymers often show high crystallinity and low ionic conductivity (typically $\leq 10^{-5}$ S cm^{-1}) at low temperatures. This necessitates operation at higher temperatures (generally, >70 °C) for their successful utilization in practical battery applications. The most straightforward approach to overcome this problem is to modify the solvating polymer in order to decrease the crystallinity and glass transition temperature of the PE, while retaining the excellent solvating properties of the ethylene oxide chain. Efforts have been made to provide such an environment for increasing the ionic conductivity at low temperatures. Several approaches have been examined, including use of copolymers, blending with other polymers, addition of plasticizers and cross-linking [8]. PEO is soluble in common battery electrolytes like ethylene carbonate (EC) and diethyl carbonate (DEC), which limits its use in dimensionally stable PGEs, so PEO is mostly studied as solid polymer electrolyte. Therefore, the present study aims to develop polymer gel electrolyte (PGE) which utilizes the advantageous electrochemical properties of PEO. For that, PVdF is blended with PEO, and the effect of PEO on ionic conductivity and electrochemical properties of PVdF based PGEs is studied. The presence of PVdF in the polymer blend retains the mechanical properties of the membrane, while the ether linkages with oxygen atoms in PEO help to improve the segmental motion and dissociation of lithium salts.

PVdF is specifically selected to prepare polymer blend with PEO due to its compatibility with PEO, excellent electrochemical stability and affinity to liquid electrolyte. PVdF has a strong electron withdrawing fluorine atom in its back bone and high dielectric constant ($\varepsilon \approx 8.4$). Thus, the polymer blend effectively dissociates lithium salts to generate a large quantity of charge carriers for conduction [9,10]. In the present study, PGEs have been prepared by immobilizing the porous polymeric film prepared by electrospinning with liquid electrolyte. The electrospun membranes appear to be particularly suitable as host matrices in microporous polymer gel electrolytes, because the fully interconnected pores have large surface area that can function as efficient channels for ion conduction [11].

The nature of the liquid electrolyte used to activate the polymer to form PGE affects the properties of the PGE significantly. Different lithium salts have different electrochemical properties which affect ion dissociation, ion diffusion, ion transference number, electrochemical stability etc [1,12,13]. Also they interact differently with polymeric matrices affecting the ionic coupling [13]. In this work, five different lithium salts have been studied to understand their compatibility with the electrospun PVdF/PEO polymer membrane as battery electrolyte cum separator and their electrochemical properties studied to choose the best performing electrolyte for this polymeric system. The suitability of the PGEs based on electrospun PVdF/PEO polymer blend membrane for room temperature lithium metal polymer batteries is also investigated.

2. Experimental

2.1. Preparation of PVdF/PEO blend membrane

PVdF (M*w*, 53,4000, Sigma Aldrich) and PEO (M*v*, 100,000 Sigma Aldrich), were vacuum dried at 60 °C for 6 h before use. Solvents, acetone and *N*,*N*-dimethyl acetamide (DMAc) (HPLC grade, Aldrich) were used as received. Uniform solution of 90% PVdF and 10% PEO in a mixed solvent of acetone/DMAc (7:3, w/w) was prepared by magnetic stirring for 24 h at room temperature. Polymer/solvent (w/w) ratios for all the final solutions were kept at 16 wt.% solid content. The resulting solution was kept for 15 min to get bubble free clear solution in air tight container. Sufficient quantity of the solution was fed to the steel needle using a syringe infusion/withdrawal pump (KD Scientific, Model-210). The tip of the needle was connected to high voltage source and electrospun at ambient atmosphere. The essential electrospinning parameters were as follows: applied voltage 18–20 kV (depends on the viscosity of the solution), working distance from collector to tip of the spinneret ~20 cm, bore size of the needle 0.6 mm, solution feed rate 0.2 ml min^{-1} and collector drum rotation speed 150 rpm. The as spun fibers in the form of free standing nonwoven membrane of average thickness ~150 μm with sufficient mechanical strength was collected on a grounded, aluminum drum wrapped with a thin aluminum foil. Further, the membrane was dried at room temperature on the drum for 6 h to prevent the shrinking of fibers and then removed from the collection drum. Final drying of the membrane was carried out in a vacuum oven at 60 °C for 12 h to remove any traces of solvent. The dried membrane was transferred to a dry box at 25 °C (H_2O level < 20 ppm) for further use.

2.2. Preparation of electrolytes

1 M $LiPF_6$ in EC/DEC (1:1, w/w) (Danvec on Technologies Pvt. Ltd), EC and DEC (Sigma Aldrich) was used as received. LiTFSI, $LiCF_3SO_3$, $LiClO_4$, and $LiBF_4$ (Sigma Aldrich) were vacuum dried and transferred to argon-filled glove box with oxygen and moisture level <0.1 ppm. The electrolytes were prepared by dissolving required amount of lithium salts in EC/DEC (1:1 w/w) to get 1 M solution.

2.3. Characterization of PVdF/PEO blend membranes

Surface morphology of membranes were examined with high resolution field-emission scanning electron microscope (FE-SEM: JEOL JSM7600F) at an accelerating voltage of 15 kV. The samples were mounted on metal stubs using conductive double-sided carbon tape, and a thin layer of platinum was sputtered on the sample using JEOL JFC-1200 prior to scanning. Average fiber diameter (AFD) (~300 fibers) was estimated from the micrograph taken at high magnification. Porosity (*P*) was determined by immersing the dry membrane in *n*-butanol for 1 h. Following relation was used to calculate the porosity:

$$P(\%) = \frac{M_{\mathrm{BuOH}}/\rho_{\mathrm{BuOH}}}{M_{\mathrm{BuOH}}/\rho_{\mathrm{BuOH}} + M_m/\rho_P} \times 100$$

where M_m is the mass of the dry membrane, M_{BuOH} is the mass of *n*-butanol absorbed, ρ_{BuOH} and ρ_P are the densities of *n*-butanol and polymer, respectively [14].

Thermal properties were evaluated by differential scanning calorimetry (DSC: 2950, TA Instruments) at a heating rate of 10 °C min^{-1} from room temperature to 350 °C and thermogravimetric analysis (TGA: Q500 TA Instruments) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C under N_2 atmosphere, respectively. From the DSC data, crystallinity of the samples was calculated according to the following formula.

$$Xc(\%) = \frac{\Delta H_m^{\mathrm{Sample}}}{\Delta H_m^*} \times 100$$

where *Xc* is crystallinity, $\Delta H_m^{\mathrm{Sample}}$ is the apparent enthalpy of fusion per gram of polymer sample which is obtained from the integral area of the base line and each melting curve in DSC, ΔH_m^* is the apparent enthalpy of fusion per gram of totally crystalline polymer. For PVdF, $\Delta H_m^* = 104.7$ J g^{-1} [14].