



Electrochemical studies of electrospun organic/inorganic hybrid nanocomposite fibrous polymer electrolyte for lithium battery



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ABSTRACT

Poly(vinylidene fluoride-co-hexafluoropropylene) P(VdF-co-HFP)/magnesium aluminate (MgAl₂O₄) hybrid fibrous nanocomposite polymer electrolyte membranes were newly prepared by electrospinning method. The as-prepared electrospun pure and nanocomposite fibrous polymer membranes with various MgAl₂O₄ filler contents were characterized by X ray diffraction, differential scanning calorimetry and scanning electron microscopy techniques. The fibrous nanocomposite polymer electrolytes were prepared by soaking the electrospun membranes in 1 M LiPF₆ in EC:DEC (1:1, v/v). The fibrous nanocomposite polymer electrolyte membrane with 5 wt.% of MgAl₂O₄ show high electrolyte uptake, enhanced ionic conductivity is found to be 2.80×10^{-3} S cm⁻¹ at room temperature and good electrochemical stability window higher than 4.5 V. Electrochemical performance of commercial celgard 2320, fibrous pure and nanocomposite polymer electrolyte (PE, NCPE) membranes with different MgAl₂O₄ filler content is evaluated in Li/celgard 2320, PE, NCPE/LiCoO₂ CR 2032 coin cells at current density 0.1 C-rate. The NCPE with 5 wt.% of MgAl₂O₄ delivers an initial discharge capacity of 158 mAhg⁻¹ and stable cycle performance compared with the other cells containing celgard 2320 separator and pure membrane.

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1. Introduction

Rechargeable Li-ion batteries are the best power sources for the fast growing portable electronic devices, such as laptops, notebooks, cameras, cellular phones, etc [1]. Most of the Li-ion batteries use microporous celgard (2320, 2325, 2340, 2400, 2500 & 2730) separators, which are made up of polyolefin (Polyethylene & Polypropylene) with organic liquid electrolyte [2]. Separators are the critical components, as they play a major role in determining the discharge capacity and cycle performance of the battery [3]. The commercially available celgard separators have several disadvantages, such as low porosity, low thermal stability and poor wettability in organic liquid electrolytes, which restrict the discharge capacity and cycle performance of the battery [4]. In order to overcome these problems, the researchers need to develop the separator-cum electrolyte membrane with excellent properties as well as good medium to conduct the ions between the electrodes.

Recently, gel polymer electrolytes (GPEs) developed by various methods exhibit high ionic conductivity in the order of 10^{-3} S cm⁻¹ at room temperature but their mechanical properties are poor for lithium ion battery applications [5–16]. Now a day's researchers have put effort to develop nanocomposite polymer electrolyte membranes with good thermal, chemical and electrochemical stabilities by incorporating some nano-sized ceramic filler, such as TiO₂, SiO₂, Al₂O₃, ZrO₂, MgAl₂O₄, etc., [17–22]. The polymer electrolytes based on poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), poly(methyl methacrylate) (PMMA) and poly(acrylonitrile) (PAN) were widely used as host polymers [23–29]. Among them, PVdF-co-HFP copolymer was found to be a suitable candidate as it has good electrochemical stability, affinity to electrolyte solution and high dielectric constant ($\epsilon \approx 8.4$) [25,26]. Moreover, P(VdF-co-HFP) is the strongest Lewis basic polymers compared with other polymers. The Lewis acid constant (K_a) of P(VdF-co-HFP) is 0.254, and the base constant (K_b) is 1.199, which may help the formation of complexes with strongest Lewis acid character of fillers [30].

A wide range of synthesis methods, such as solution casting [7], hot press [21,22], plasticizer extraction [12], phase inversion [26], and electrospinning etc., [27–34] have been adopted for the

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development of porous polymer membranes. Among them, electrospinning is a simple and effective technique to develop thin nano-size porous fibrous polymer membranes with highly interconnected porous structure and large surface area, which are very important factors to improve the electrolyte uptake amount, ionic conductivity and electrochemical stability [29–32].

To the best of author's knowledge there are no reports on the development of P(VdF-co-HFP)/MgAl₂O₄/1 M LiPF₆ EC:DEC (1:1, v/v) nanocomposite fibrous polymer electrolyte membranes by electrospinning technique. As we know that, the MgAl₂O₄ ceramic filler has strongest Lewis acid character and also high dielectric constant ($\epsilon = 8.1$ – 8.3) than other fillers, which would compete with the Lewis acid character of Li⁺ ions in LiPF₆ salt for the formation of complexes with the strongest Lewis base P(VdF-co-HFP) polymer chains. The resulting structure provides more easy pathways for Li⁺ ions, which can enhance ionic transport and hence, improves the conductivity [30]. The solvent EC has high dielectric constant ($\epsilon = 89.6$) and high viscosity ($\eta = 1.5$), whereas DEC has low dielectric constant ($\epsilon = 2.82$) and low viscosity ($\eta = 0.748$). Combination of EC and DEC (1:1, v/v) solvent has optimized dielectric constant ($\epsilon = 46.21$) and viscosity ($\eta = 1.124$), which will provide reduced electrostatic attraction between the Li⁺ and PF₆⁻ ions in a LiPF₆ salt. The optimized solvent may separate (dissociate) the Li⁺ ions easily, which in turn improve ionic conductivity at room temperature.

Hence, authors are motivated to develop electrospun fibrous pure [16 wt.% P(VdF-co-HFP)] and nanocomposite polymer membranes with various MgAl₂O₄ (2, 5 & 8 wt.%) fillers content. The as-prepared fibrous pure and nanocomposite polymer membranes were characterized by XRD, DSC and SEM techniques. The fibrous nanocomposite polymer electrolytes (NCPEs) are prepared by soaking the electrospun membranes in 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v). The electrolyte uptake behavior and ionic conductivities of nanocomposite polymer electrolytes are evaluated through electrolyte uptake method and impedance spectroscopy measurements. Electrochemical performance of all the Li/PE, NCPE, celgard 2320/LiCoO₂ CR 2032 coin cells were studied through Battery cycle tester (BCT) at current density 0.1 C-rate.

2. Experimental

2.1. Synthesis of PVdF-co-HFP/MgAl₂O₄ nanocomposite fibrous membranes

Poly(vinylidene difluoride-co-hexafluoropropylene) [P(VdF-co-HFP)] (Aldrich, AM_w = 4×10^5) and MgAl₂O₄ filler prepared by gel-combustion method were used as the starting materials for the preparation of fibrous nanocomposite polymer membranes by electrospinning technique. All the starting materials were dried at 60 °C for 24 h in hot air oven before use. N, N-Dimethylacetamide (DMAc) and acetone were used as mixed solvents. For the preparation of fibrous nanocomposite polymer membranes, first the optimized 16 wt.% of P(VdF-co-HFP) polymer solution was prepared by dissolving it in a mixed solvent of acetone/DMAc (7:3, V/V) under continuous stirring for 3 h at room temperature [31]. Later, 1, 2, 3, 4, 5, 6 & 8 wt.% of MgAl₂O₄ nanoparticle filler (particle size: <100 nm, surface area: 150 m²/g) were added to the above optimized 16 wt.% P(VdF-co-HFP) polymer solution under constant stirring for 3 h at room temperature. The resultant optimized viscous solution was taken into a 10 ml syringe and loaded in a syringe pump to form nanocomposite fibers by setting the electrospinning parameters. The following electrospinning parameters are used for all the compositions: solution feed rate 1 mlh⁻¹, applied voltage between spinneret and collector is 18 kV, distance

between the tip of the spinneret and collector is 12.5 cm, needle bore size 24 G and collector drum rotation speed is 450 rpm. The electrospun fibrous membranes with an average thickness of 80 μm were collected and dried in hot air oven at 60 °C for 24 h to remove the solvent for further use.

2.2. Characterization techniques

X-ray diffraction patterns (XRD) were recorded from 10° to 80° for all the prepared fibrous membranes using PANalytical X-pert PRO diffractometer (Philips) with Cu-Kα radiation ($\lambda = 0.154060$ nm, 30 mA and 40 kV). The DSC curves of the celgard 2320 separator and the prepared electrospun membranes were recorded on DSC Q₂₀ instrument under nitrogen atmosphere. From the analyzed DSC curve, the crystallinity of pure and nanocomposite fibrous membranes was calculated using the following equation [13].

$$X_c = \frac{\Delta H_s}{\Delta H^*} \times 100\% \quad (1)$$

where, $\Delta H^* = 104.7$ J/g, the melting enthalpy of PVdF and ΔH_s J/g is the melting enthalpy of prepared electrospun pure and nanocomposite membranes. The micrographs of prepared electrospun membranes were observed on scanning electron microscopy (SEM, Hitachi S4700). The electrolyte uptake behavior was observed by soaking the membranes in liquid electrolyte [1 M LiPF₆ in EC:DEC (1:1, v/v)] for 1 h. The electrolyte uptake was calculated based on the following equation [13].

$$EU = \frac{W_1 - W_0}{W_0} \times 100\% \quad (2)$$

where, W_1 and W_0 are the weights (g) of the wet and dry membranes respectively. The ionic conductivities of the nanocomposite polymer electrolyte membranes were evaluated at room temperature through impedance spectroscopy measurements. Each polymer electrolyte membrane was placed between stainless steel (SS) electrodes and the impedance spectra were recorded on Alpha high frequency response analyzer (Novocontrol, Germany) in the frequency range of 1 mHz–1 MHz. The ionic conductivities are calculated from the analyzed impedance data and sample dimensions by using the following equation

$$\sigma = \frac{t}{A \times R_b} S/cm \quad (3)$$

where, t is the sample thickness (cm), A is the area (cm) and R_b is the bulk resistance (Ω) of polymer electrolyte membrane.

2.3. Electrochemical studies

The electrochemical stability of the prepared electrospun nanocomposite membrane was studied through cyclic voltametry (Electrochemical test station POT/GAL, Novocontrol, Germany). The measurement (Li/NCPE/SS) was carried out by using stainless steel (SS) as the working electrode and lithium (Li) metal as counter/reference electrode at the scan rate of 1 mV s⁻¹ over the potential range of 2–5 V at room temperature. For electrochemical measurements, the prototype lithium cells were assembled inside an Argon-filled glove box [Vacuum Atmospheres Co. (VAC), USA] by sandwiching the PE, NCPE, celgard 2320 separator between lithium metal anode (380 μm thick, Aldrich) and LiCoO₂ cathode in CR-2032 coin cell. The LiCoO₂ cathode active material was synthesized by combustion method and the cathode electrode was prepared by

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