Electrochimica Acta 127 (2014) 167–172

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrospun Trilayer Polymeric Membranes as Separator for Lithium–ion Batteries

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ARTICLE INFO

Article history:
Received 4 November 2013
Received in revised form 21 January 2014
Accepted 28 January 2014
Available online 12 February 2014

Keywords:
Electrospinning
Porous membrane
Electrolyte uptake
Thermal stability
Charge-discharge studies.

ABSTRACT

Poly(vinylidene fluoride- hexafluoropropylene) (PVdF-HFP)/poly (vinyl chloride) (PVC)/(PVdF-HFP) based- trilayer porous polymeric membrane (PM) was prepared by electrospinning for lithium batteries. The formation of beads was significantly reduced by increasing the concentration and by reducing the surface tension of the polymer solutions. Although, single layer PVdF-HFP membrane exhibited high porosity and uptake of electrolyte, its mechanical integrity was found to be poor (not free-standing). On the other hand, electrospinning of PVC over PVdF-HFP enhanced the mechanical integrity of the membrane. The prepared membranes were subjected to SEM, ionic conductivity, electrolyte uptake and shrinkage analyses. A 2032-type coin cell composed of Li/PM/$LiFePO_4$ has been assembled and its cycling profile was examined at different C-rates. The (PVdF-HFP)/PVC/(PVdF-HFP) trilayer membrane can be a strong contender for lithium battery applications.

1. Introduction

Lithium batteries are identified as the ultimate choice of power to energize portable electronic devices such as laptop computers, digital cameras, cellular phones etc.,[1]. They are the technology of choice for future hybrid electric vehicles, which are urgently needed for addressing energy and environmental issues [2]. The state-of-art lithium-ion battery comprises a graphitic electrode (anode) and a positive electrode (cathode) obtained from layered/olivine lithium transition metal oxides separated by a poly (olifine) separator soaked in a non- aqueous liquid electrolyte [3,4].The key role of a separator is to prevent electrical short circuits between the electrodes with a rapid admission of ionic charge carriers [5].

The ionic conductivity of the porous membranes mainly depends on the conductivity of liquid electrolyte, membrane's porosity, tortuosity of the pores, thickness and its wettability [6,7]. Microporous polyolefin membranes which are made up of poly ethylene (PE) or poly (propylene) (PP) are commonly used for lithium-ion battery applications. Although, these membranes provide excellent chemical and mechanical properties, the low porosity (about 40%) and poor wettability, remain a problem area [8]. Consequently, these factors restrict the performance of the batteries [9,10]. Therefore, in order to circumvent these problems numerous attempts are being made to develop porous polymeric separators for lithium-ion batteries.

The commercially available Celgard (2325) membrane is composed of poly (propylene) (PP)/poly(ethylene) (PE)/poly (propylene)(PP) trilayer structure. The low melting point of PE enables its use as a thermal fuse. When the temperature approaches (due to unexpected chemical reactions in a battery system) the melting point of the polymer 135 °C, for PE and 165 °C for PP, the shutdown process takes by losing its porosity [5]. However, these membranes possess only 50% porosity and the wettability of the membranes is also low.

Very recently, the electrospinning method has drawn attention due to its versatility and simple preparative methods [11,12]. These are made up of thin fibres from micron to submicron diameters. Another advantage is the inter-laying fibres generate large porosity (>90%) with fully interconnected pore structure and large surface area to volume ratio facilitating high electrolyte uptake and easy transport of ions [13]. PVdF-HFP has slightly lower critical surface tension value 'γ_c' (25 mN m^{-2}) than commercially available poly (propylene) separator (29 mNm^{-2}) which facilitates for better wettability of the non-aqueous electrolytes [14]. On the other hand, PVC is mechanically robust, inexpensive and compatible with a large number of carbonate plasticizers, and has been reported for lithium-ion battery applications [15,16].

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http://dx.doi.org/10.1016/j.electacta.2014.01.162
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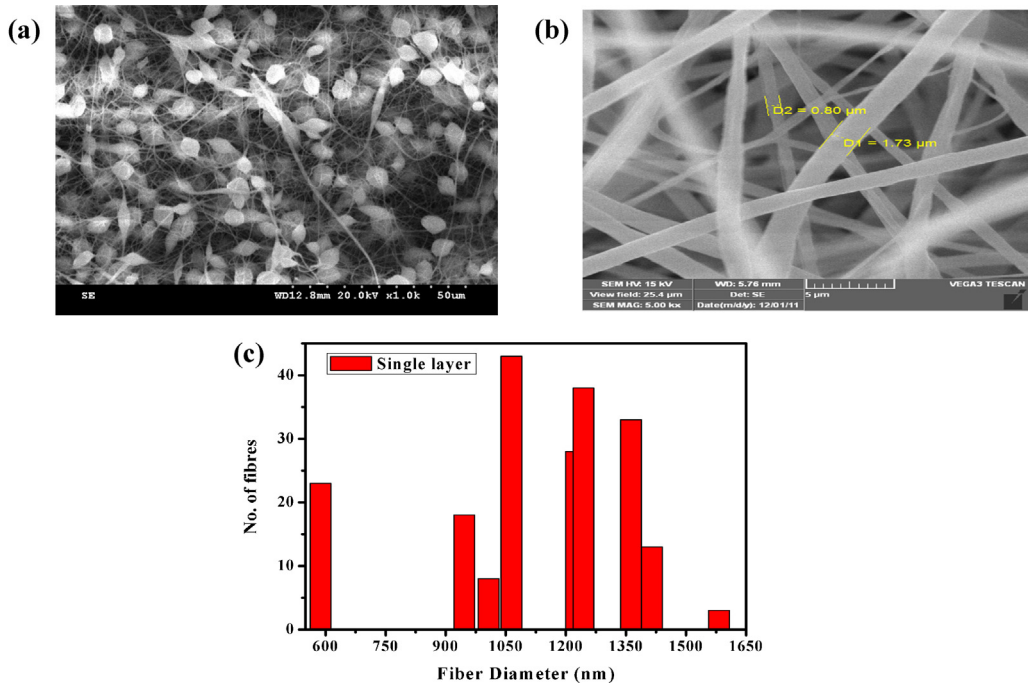

Fig. 1. SEM image of PVdF-HFP (a) membranes with beads (b) membranes without beads (c) Histogram of the electrospun membrane.

In the present work, an attempt has been made to prepare a trilayer polymeric membrane by electrospinning in order to enhance the uptake of electrolyte solution and to improve the mechanical integrity and thermal stability of the polymeric membrane. The cycling performance of the trilayer membrane was analysed by assembling a 2032-type coin cell with Li/$LiFePO_4$ configuration and the obtained results are compared with the commercially available Celgard membrane.

2. Experimental setup

The electrospinning equipment (Plastomek, India) consists of a high voltage supplier (25 kV), and a syringe pump with a plastic syringe equipped with a 22 gauge stainless steel needle. Aluminum foil was used to collect the membrane. PVdF-HFP (88:12) (Kynar 2801, Alf Chem, Japan), poly (vinyl chloride) (Aldrich, USA) were used as received. The distance between the orifice and the aluminum collector was 10 cm and the applied voltage was 12 kV. The solution feeding speed was fixed as 1 ml/h at 25 °C. The polymer solution composed of PVdF-HFP and acetone was electrospun on an aluminum collector. Then PVC was electrospun over PVdF-HFP. The same procedure was adopted to coat PVdF-HFP over PVC in order to get a trilayer configuration. The overall thickness of the membrane was 70 microns. In order to maintain the adhesiveness among the membranes, the coating process was completed within 30mins. Morphological examination of the films was made by a scanning electron microscope (FE-SEM, S-4700, Hitachi) under a vacuum condition (10^{-1} Pa) after sputtering gold on one side of the films. The histogram of the electrospun membranes were generated from the SEM images using the Image J software. **TG measurements were performed at a rate of 10 °C min^{-1} between temperature ranges from 20 to 300 °C in a nitrogen atmosphere.** The ionic conductivity of the membranes sandwiched between two stainless steel blocking electrodes (1 cm^2 diameter) was measured using an electrochemical impedance analyzer (IM6-Bio Analytical Systems) between 50 mHz and 100 kHz frequency range at ambient temperature. **The mechanical strength of the electrospun membrane was determined using a tensile machine (Tinius Olsen, Germany) according to ASTM D882-09 standards with a constant cross-head speed of 10 mm min^{-1}. The stretching of Celgard membrane was in machine direction (MD).** The composite cathode was prepared by blending $LiFePO_4$ as active material with acetylene black carbon as electronic conductor and poly(vinylidene fluoride) as binder in the 70:20:10 *wt.%* ratio respectively as reported earlier[17,18].The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate(DMC) with a 1:2 volume ratio (Merk, Germany). **The lithium metal foil (Aldrich, USA) was used as anode.**

3. Results and discussions

Fig. 1 shows the SEM image of PVdF-HFP electrospun single layer membrane. The SEM image appears with lot of beads (Fig. 1a) with an average fibre diameter of less than 200 nm. The formation of beads along with the nanofibers is an undesirable property. The exact reason for the formation of beads is yet to be understood. According to Shui and James[19] the bead formation is a complex process which competes with solidification. The formation of beads can be avoided by increasing the viscosity of the solution (higher polymer concentration) and increasing the charge density or reducing the surface tension. In the present study, the formation of beads was avoided by increasing the polymer concentration and also reducing the surface tension by adding dimethyl formamide as an additional solvent (Fig. 1b). Fong et al. [20] eliminated the formation of beads in poly (ethylene oxide), PEO system by reducing its surface tension with the addition of ethanol in water. Similarly, Lin et al. [21] formed a beads-free poly (styrene) membrane by adding a small amount of carbon surfactants during electrospinning. It is also observed from the histogram of the electrospun membrane (Fig. 1c) that the average fibre diameter varies from 600 nm to 1.6 microns.

Fig. 2 (a) depicts the surface morphology of PVdF-HFP/PVC/PVdF-HFP trilayer membrane. The cross-sectional SEM image of the PVdF-HFP/PVC/PVdF-HFP trilayer membrane is shown in Fig. 2(b) which implies a hairy rod structure with lot of pores which may facilitate to entrap huge amount of liquid electrolyte and thereby lithium ion conduction. The histogram