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ScienceDirect
Electrochemistry Communications 9 (2007) 1700–1703
electrochemistry communications
www.elsevier.com/locate/elecom

A novel sandwiched membrane as polymer electrolyte for lithium ion battery

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Received 15 February 2007; received in revised form 16 March 2007; accepted 19 March 2007
Available online 28 March 2007

Abstract

A novel kind of sandwiched polymer membrane was prepared by coating three layers of poly(vinyl difluoride) (PVDF), poly(methyl methacrylate) (PMMA) and PVDF, separately. Its characteristics were investigated by scanning electron microscopy, FT-IR, X-ray diffraction, and differential thermal analysis. It consists of two phases. The outer PVDF layers are porous, and the inner PMMA layer is solid. Since the PMMA has a good compatibility with the carbonate-based liquid electrolyte, the membrane can easily absorb the electrolyte to form a gelled polymer electrolyte (GPE). As a result, the evaporation peak of the liquid electrolyte is increased to 160 °C. Due to very low evaporation of the liquid electrolyte, $LiCoO_2$ shows good cycling behavior in the range of 4.4–3.0 V when this GPE is used as the separator and polymer electrolyte, and lithium as the counter and reference electrode. This unique sandwiched membrane is promising for application in scale-up lithium ion batteries with high safety and high energy density.

Keywords: Lithium ion battery; Polymer electrolyte; Sandwiched membrane; PVDF; PMMA

1. Introduction

In the case of lithium ion battery, a lot of studies have been made to improve its safety performance since the scale-up one has promising application in electric vehicles. One main challenge is the electrolytes because they will react with the active electrode materials. As a result, polymer electrolyte is one good candidate [1].

Since 1973 [2], a lot of studies on solid polymer electrolytes have been carried out such as blending, copolymerizing, cross-linking and adding nanofillers to modify the polymer host to increase the ionic conductivity [1,3–6]. However, the main obstacle is still the ionic conductivity, which is generally below 10^{-3} S/cm and not enough for practical application. As a result, gelled polymer electrolytes (GPEs) came into birth [1,7,8]. The main products are not based on the concept of Bellcore but prepared by coating a layer of a polymer on the surface of porous polyethylene (PE) separator [1,8–12]. Consequently, the shut-down performance of the porous polyethylene due to its melting behavior [13] is still retained. In the case of other linear polymers from radical polymerization such as poly(-methyl acrylate) (PMMA) and poly(ethylene oxide), there is no report about their shut-down performance to our knowledge. Since the melting points of these polymers are different from that of PE, the heat durability of the polymer lithium ion batteries can be adjusted according to requirements if these polymers are used. PMMA, whose melting point is at about 180 °C and higher than that of PE (about 120 °C), has been well studied as a host of GPEs. It has good compatibility with the liquid electrolytes, leading to good absorbing ability of the carbonate-based liquid electrolytes [1,14]. However, its practical application is still not realized due to its poor mechanical stability.

Here we reported a novel sandwiched membrane, which consists of poly(vinyl difluoroethylene) (PVDF) as the outer layers and poly(methyl acrylate) (PMMA) as the

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doi:10.1016/j.elecom.2007.03.021

inner layer. It is similar to the widely used commercial porous separator of Celgard Co. Ltd., PP/PE/PP of three-layered structure. Primary results showed that this kind of sandwiched polymer membrane was promising as GPE for scale-up lithium ion batteries.

2. Experimental

PMMA was prepared by thermal polymerization of methyl methacrylate (MMA) (Aldrich) initiated by benzyl peroxide (BPO). PVDF (SAFT 761) and *N*-1-methyl-2-pyrrolidone (NMP, Wulian Chem. Co. Ltd., China) were used as received. $LiPF_6$ solution (1 M) in ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) (1:1:1, v/v/v) was supplied by Guotai–Huarong Co. Ltd., and used without further treatment as the liquid electrolyte.

Eight grams of PMMA and PVDF were dissolved in the solvent NMP (100 ml), respectively. The PVDF solution was at first coated on a piece of glass. After the solvent NMP was vaporized at 80 °C, a thin layer of PVDF was obtained. Then, the PMMA solution was coated on the surface of the PVDF layer, and the solvent was also vaporized at 80 °C. Later, another layer of PVDF was coated on the PMMA layer in the same way. After vaporizing the solvent, a sandwiched membrane PVDF/PMMA/PVDF with controlled weight ratio (0.5:1:0.5) was obtained. The membrane was further dried under vacuum at 60 °C.

For comparison, a blend composite of PVDF and PMMA (weight ratio = 1:1) was prepared by mixing the solution of PVDF and PMMA following evaporation of the solvent NMP. GPEs based on the blend composite of PVDF and PMMA were prepared by adding 200 wt.% the liquid electrolyte into the polymer hosts.

The morphology of the membrane was examined by means of scanning electron microscope (SEM, Philip XL30). X-ray diffraction (XRD, Bruker D8) was used to identify the crystal structure. FT-IR measurement was carried out on a BRUKER VECTOR-22 spectrometer. Differential thermal analysis (DTA: Perkin Elmer Thermogravimetric Analyzer, TGA7) was used to evaluate the evaporation of solvents in the blend and the sandwiched GPEs.

Electrochemical performance of the sandwiched membrane gelled by the liquid electrolyte was evaluated by coin-type model cells, where lithium foil was used as the counter and reference electrode, and the coated mixture of $LiCoO_2$ (Ruixiang Co. Ltd., China), carbon black and PVDF (weight ratio = 87:5:8) as the cathode. The sandwiched membrane was placed between the Li reference electrode and $LiCoO_2$ cathode. After adding 200 wt.% (based on the weight of the polymer membrane) 1 mol/l $LiPF_6$ solution of EC/DMC/DEC, the inner PMMA layer was moisturized by the liquid electrolyte. The cycling performance of the model cells was carried out by a Land battery tester with a constant charge current density 0.25 mA/cm^2 (0.073 mA, about 0.2 C) between 4.4 and 3.0 V.

3. Results and discussion

SEM micrograph of the cross-section of the sandwiched membrane of PVDF/PMMA/PVDF is shown in Fig. 1. It is very clear that the membrane consists of three layers. After elemental analysis, it was found that the top and bottom layers consist of PVDF and the inner layer of PMMA, which is consistent with our tailored design.

SEM micrographs of the surfaces of the outer PVDF layers and the inner PMMA layer in the sandwiched PVDF/PMMA/PVDF membrane are shown in Fig. 2. It is clear that the deposited PVDF presents porous structure (Fig. 2a), which is good for liquid electrolytes to pass through. The porosity and porous structure are different from those reported in [1], which is evident due to different processes. In contrast, PMMA is a solid film without evidence of pores (Fig. 2b). As mentioned above, it has a good compatibility with the carbonate-based electrolytes. Consequently, it can still form gels easily by absorbing the liquid electrolytes through porous PVDF layer.

FT-IR spectra of (a) PMMA, (b) PVDF and (c) the sandwiched membrane of PVDF/PMMA/PVDF are shown in Fig. 3. The characteristic absorption peaks of PMMA are clearly identified, i.e. 1730 cm^{-1} (stretching band of C=O) and 1443 cm^{-1} (stretching band of $-CH_3$). The typical peaks of PVDF are 1400 (deformation vibration band of $-CH_2-$), 1072 (stretching band of C–C in the β-phase) and 882 cm^{-1} (band for amorphous phase) [15]. In the case of the sandwiched membrane of PVDF/PMMA/PVDF, the characteristic absorption peaks of PMMA (1730 and 1443 cm^{-1}) and PVDF (1400, 1072 and 882 cm^{-1}) are present clearly and there is no shift of absorption bands, indicating that the membrane consists of two compounds: PMMA and PVDF and both compounds do not present much interaction.

XRD patterns of (a) PVDF, (b) PMMA, (c) the blend of PVDF and PMMA (weight ratio = 1:1) and (d) the sandwiched PVDF/PMMA/PVDF are shown in Fig. 4. In the case of PVDF, it is a semi-crystalline polymer, and there

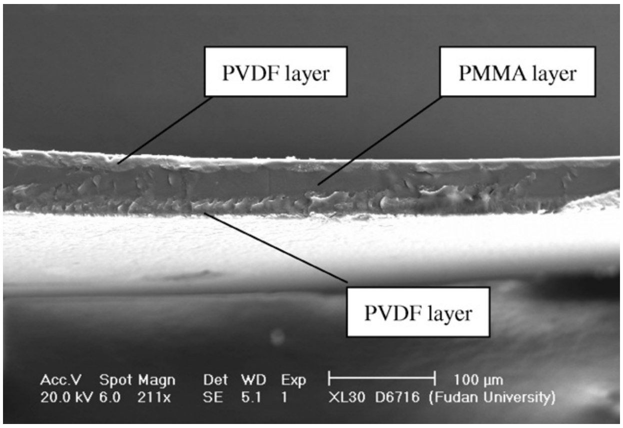

Fig. 1. SEM micrograph of the cross-section of the sandwiched membrane of PVDF/PMMA/PVDF.