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Preparation and characterization of porous polyacrylonitrile membranes for lithium-ion polymer batteries

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Abstract

A porous polyacrylonitrile (PAN) membrane was prepared and characterized. Gel polymer electrolytes were prepared from these porous membranes via soaking in an organic electrolyte solution. They showed high ionic conductivity (2.8×10^{-3} S/cm) at room temperature and sufficient electrochemical stability over 5.0 V that allowed application in lithium-ion polymer batteries.

Keywords: Electrochemical characteristics; Gel polymer electrolyte; Lithium-ion polymer battery; Polyacrylonitrile; Porous membrane

1. Introduction

A large number of studies have been carried out on rechargeable lithium polymer batteries using gel polymer electrolytes in which electrolyte solution has been immobilized by incorporation into a matrix polymer, such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO) [1–5]. While these gel polymer electrolytes exhibit high ionic conductivities exceeding 10^{-3} S/cm, most of them have various deficiencies preventing them from being used in commercial lithium batteries. Most of the processes for preparing the gel polymer electrolytes require a moisture-free environment because of the higher water sensitivity of the lithium salt. Further, their mechanical properties are often very poor, and the films have to be hardened by either chemical or physical curing. To overcome these difficulties, an activation process in which a porous polymer film is soaked in an electrolyte solution has been investigated [6–9]. Compared with the conventional methods such as solution casting and direct dissolution of the polymer in the electrolyte solution, this procedure requires critical moisture control only during the last activation step. Among the various polymers which can be used for this purpose, PVdF and its copolymers have mainly been studied, since the electrolytes prepared using these polymers satisfy most of the properties required for battery applications. However, gel polymer electrolytes based on porous PAN membranes have received little attention, though PAN has been used in preparing gel polymer electrolytes by direct dissolution of the host polymer in the electrolyte.

In this study, we attempt to prepare highly conductive polymer electrolytes by selecting PAN as a matrix polymer for the preparation of porous membranes. PAN is chosen because it is expected that an uptake of the electrolyte solution may result in swelling or gelation of polymer rather than dissolution. It would contribute to the mechanical stability of the membrane after soaking in electrolyte solution. The porous membrane is prepared by a phase-inversion method, which has been shown to be effective for producing a porous structure [10]. Gel polymer electrolytes are prepared by soaking the porous PAN membranes in the different electrolyte solution. The electrochemical characteristics of these gel polymer electrolytes will be reported.

2. Experimental

PAN (Aldrich) was dissolved in dimethylformamide (DMF) with a concentration of 10 wt.% of PAN in DMF. After complete dissolution, the resulting viscous solution was cast with a doctor blade on a glass plate. The cast film was then immersed in a pool of excess de-ionized water for 6 h to induce phase inversion. The resulting membrane was washed with running water and immersed again in a pool of de-ionized water for 24 h. The membrane was then vacuum dried at 80 °C for 24 h. The morphology of the porous

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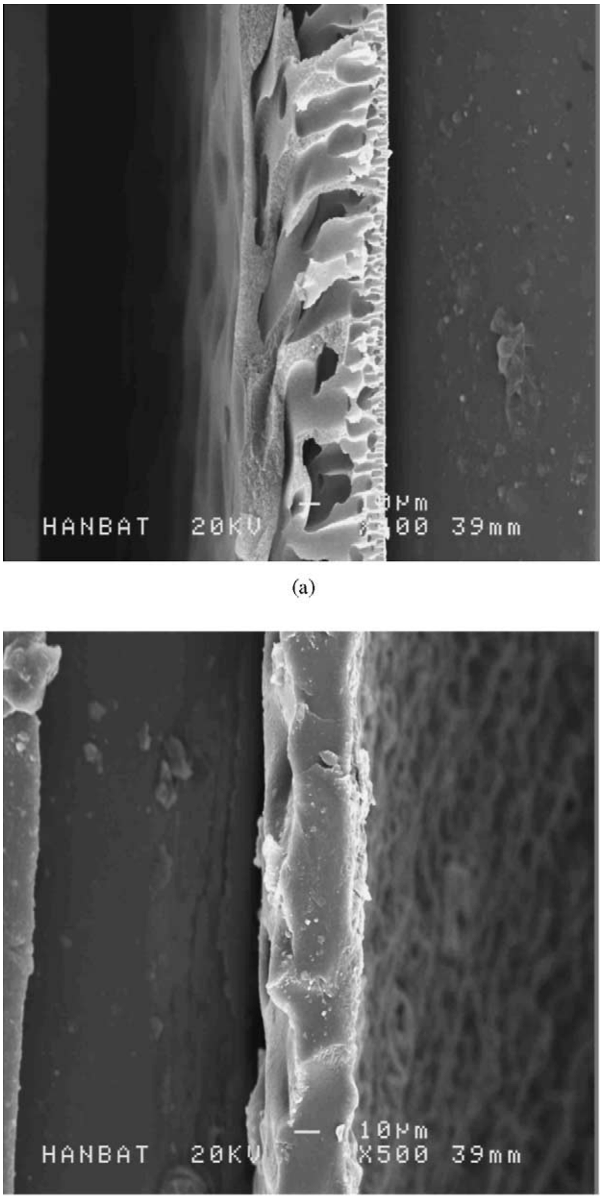
membrane was examined using a scanning electron microscope (JEOL, JSM-6300). Cross-sectional views of the membranes were obtained by breaking them in liquid nitrogen. In order to calculate porosity of the membrane, the density of the porous membrane was measured by a standard pycnometric method. Tensile test of the porous membrane was carried out based on ASTM 882 with a universal tensile meter.

The dried PAN membrane was transferred into a glove box and soaked in the different electrolyte solution for 2 h, to activate the membrane. The organic liquid electrolytes used for soaking the membranes are 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC), 1 M $LiPF_6$ in EC/DMC and 1 M $LiBF_4$ EC/DMC (1:1 by volume, Samsung Cheil Industries, battery grade). The wetted membrane was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The cell was enclosed in an aluminum plastic pouch and sealed in order to permit testing outside of a glove box. The ac impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range 10 Hz to 100 kHz. Linear sweep voltammetry was performed on a SS working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0 mV/s. All cell assemblies were carried out in a dry box filled with argon gas.



(a)

(b)

Fig. 1. Scanning electron micrographs of the cross-section of porous PAN membrane (a) and gelled PAN membrane (b).

3. Results and discussion

Fig. 1 shows the scanning electron micrographs of the cross-section of porous PAN membrane and gelled PAN membrane. An electrolyte solution for soaking the membrane is $LiClO_4$ in EC/DMC. Before soaking in electrolyte solution, the PAN membrane was observed to have the large void and cavities of different size. The pore volume in this membrane was measured to be 68%, and its thickness was in the range of 60–70 μm. From the stress–strain measurements, the dry PAN membrane showed a reasonable mechanical strength (tensile strength: 3.3 MPa) and a rather brittle property (elongation at break: 5%). After soaking the PAN membrane in electrolyte solution, no pores in the membrane could be observed, as shown in Fig. 1(b). This result suggests that an uptake of the electrolyte solution into the porous PAN membrane resulted in complete gelation of the membrane. The gelation of the porous PAN membrane is attributed to its affinity for electrolyte solution, which results from the presence of polar functional groups in PAN.

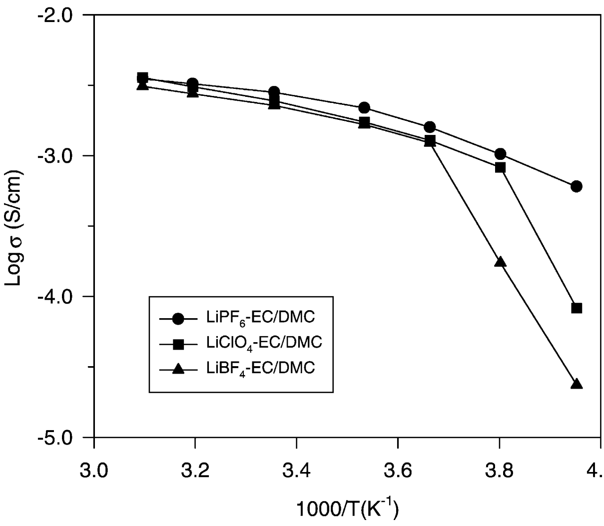


Fig. 2. Temperature dependence of the ionic conductivity for gel polymer electrolytes prepared by soaking the porous PAN membrane in different electrolyte solution.

The amount of electrolyte solution absorbed in the porous PAN membrane is about 8.2 times the weight of the polymer (89% based on the total weight). The thickness of gelled PAN membrane was about 25 μm. A decrease in thickness after soaking in liquid electrolyte solution is due to the fact that the porous membrane is changed to the dense gel film by destruction of pores in the membrane.

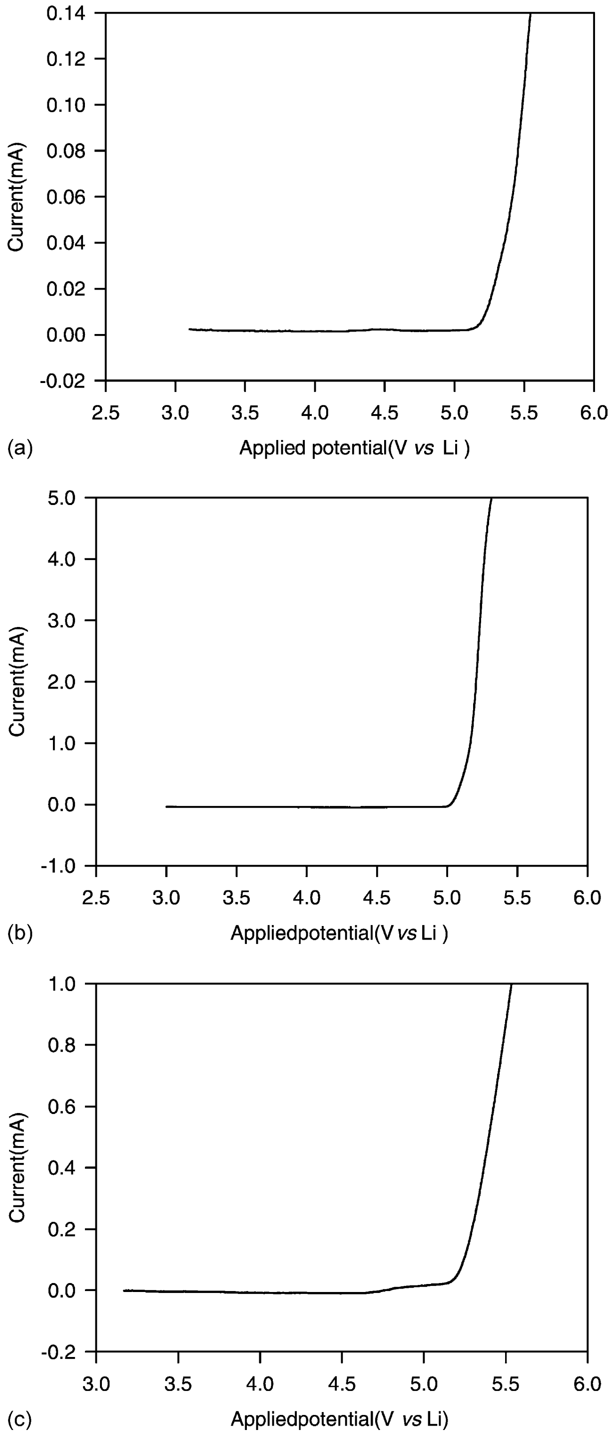


Fig. 3. Linear sweep voltammetry curves of the cells prepared with the porous PAN membrane containing different electrolyte solution (scan rate: 1 mV/s): (a) $LiPF_6$–EC/DMC, (b) $LiClO_4$–EC/DMC, (c) $LiBF_4$–EC/DMC.

Fig. 2 shows an Arrhenius plot of ionic conductivities for gel polymer electrolytes prepared by soaking the porous PAN membrane in different electrolyte solution. It is found that the gel polymer electrolyte soaked by $LiPF_6$–EC/DMC has the highest ionic conductivity among the systems studied over the whole temperature ranges. For the gel polymer electrolyte prepared with $LiBF_4$–EC/DMC or $LiClO_4$–EC/DMC, the ionic conductivity is shown to be decreased abruptly at low temperature. This result is due to the fact that the freezing of solvents in the gel polymer electrolyte occurs on cooling, and so the solvent-rich domains of EC and DMC exist as crystalline solids at low temperature. However, for the gel polymer electrolyte prepared with $LiPF_6$–EC/DMC, the strong interactions that occur in the polymer–solvent–salt mixture hinder the ordering of solvent molecules. These results suggest that the type of salt has a large influence on the melting behavior of incorporated solvents in the gel polymer electrolytes. For the gel polymer electrolyte prepared with $LiPF_6$–EC/DMC, the ionic conductivity reaches 2.8×10^{-3} S/cm at room temperature, and remains at a high value (6×10^{-4} S/cm) even at -20 °C.

The electrochemical stability of the gel polymer electrolytes was evaluated with linear sweep voltammetric measurements. Fig. 3 illustrates linear sweep voltammetry curves of cells prepared with gel polymer electrolytes containing different electrolyte solution. For all systems considered, the current onsets are detected over 5.0 versus Li, which can be assigned to the decomposition voltages of the gel polymer electrolytes. The difference in decomposition potential of three kinds of gel polymer electrolytes arises from the difference in the electrochemical stability of the electrolyte solution. It should be noted that oxidation current for $LiPF_6$-based gel polymer electrolyte is lower than those of any other systems at high voltage region, which means that gel polymer electrolyte prepared by soaking in $LiPF_6$–EC/DMC is the most resistant to oxidation.

4. Conclusions

Porous membrane based on polyacrylonitrile was prepared by phase inversion. With the porous PAN membrane, gel polymer electrolytes were prepared by soaking in different electrolyte solution. Gel polymer electrolytes prepared with PAN membrane of 68% porosity exhibited both high ionic conductivity and good mechanical stability. Ionic conductivity reached 2.8×10^{-3} S/cm in the gel polymer electrolyte containing $LiPF_6$–EC/DMC, and the electrolyte solution was well encapsulated in the porous membrane by physical gelation. In terms of sub-ambient temperature conductivity, gel polymer electrolyte containing $LiPF_6$–EC/DMC exhibited higher ionic conductivity than that containing $LiBF_4$–EC/DMC or $LiClO_4$–EC/DMC. Decomposition voltages exceeding 5.0 V make them suitable for applications in lithium-ion polymer cells.

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