

겔화 가능한 다공성막을 이용한 리튬이온폴리머전지의 싸이클 특성

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**Cycling Performances of Lithium-Ion Polymer Batteries
Prepared with Gelling Porous Membranes**

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Introduction

A large number of studies have been carried out on rechargeable lithium-ion polymer batteries using gel polymer electrolytes in which the liquid electrolyte has been immobilized by incorporation into a matrix polymer[1-7]. These gel polymer electrolytes are usually prepared by casting a mixture of the electrolyte solution and a matrix polymer in a low boiling point solvent. While many gel polymer electrolytes prepared by the casting method exhibit high ionic conductivities exceeding 10^{-3} S/cm, most of them have various deficiencies preventing them from being used in commercial lithium batteries. The casting process requires a moisture-free environment because of the higher water sensitivity of the lithium salt. In addition 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 electrolyte solution has been investigated[8-9]. Compared with the casting method, 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 been most extensively studied, as the polymer electrolytes prepared with them satisfy most of the properties required for battery applications. However, the polymer electrolytes based on porous PAN membranes have received little attention, though PAN has been used in preparing gel polymer electrolytes by conventional casting methods.

In this study, we attempted 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]. With the PAN membrane, polymer electrolyte is prepared by soaking in electrolyte solution. Its electrochemical characteristics are reported, and the electrochemical performances of lithium-ion cells composed of a mesocarbon microbead(MCMB) anode and a lithium-cobalt oxide cathode are presented.

Experimental

PAN was dissolved in dimethylformamide(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. After exchange of organic solvent and water, substantial amounts of pores are formed in the film. 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 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. The carbon anode was prepared by coating the slurry of MCMB, PVdF and super-P carbon on a copper foil. The cathode contained the same binder and super-P carbon along with LiCoO₂ cathode material, which was cast on aluminum foil. Electrodes were roll pressed to enhance particulate contact and adhesion to foils. The thickness of electrodes ranged from 50 to 65 μm , and their active mass loading corresponded to capacity of about 2.4 mAh/cm². The dried membrane was transferred into a glove box and soaked in electrolyte solution for 2 h to activate the membrane. The wetted membrane was cut into 4 cm² squares and 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/sec. A lithium-ion cell was assembled by sandwiching the wetted membrane between a MCMB anode and a LiCoO₂ cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. All cell assemblies were carried out in a dry box filled with argon gas. The charge and discharge cycling tests of lithium-ion cells were conducted galvanostatically using Toyo battery test equipment(TOSCAT-3000U).

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 LiClO₄ 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 to 70 μm . 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 high affinity for electrolyte solution, which results from the presence of polar functional groups in PAN. 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 25 μm .

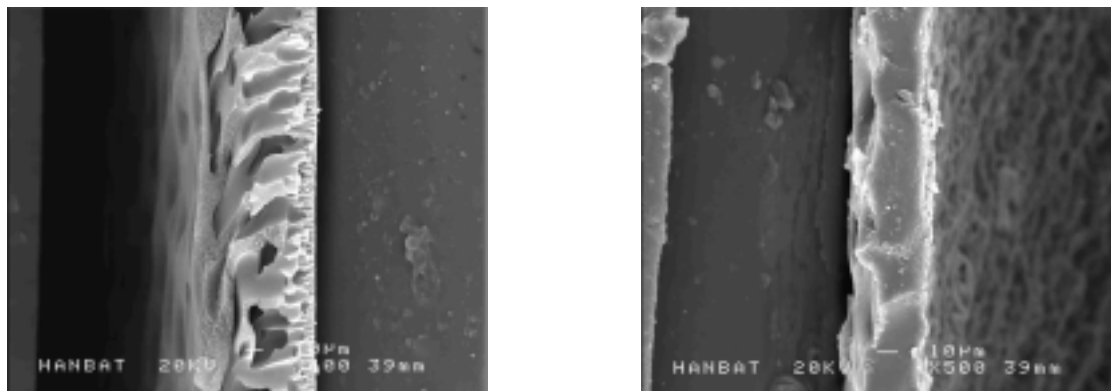


Fig. 1. Scanning electron micrographs of the cross section of (a) porous PAN membrane and (b) gelled PAN membrane.

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 $\text{LiPF}_6\text{-EC/DMC}$ has the highest ionic conductivity among the systems studied over the whole temperature ranges. For the gel polymer electrolyte prepared with $\text{LiBF}_4\text{-EC/DMC}$ or $\text{LiClO}_4\text{-EC/DMC}$, 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 $\text{LiPF}_6\text{-EC/DMC}$, the strong interactions that occur in the polymer-solvent-salt mixture hinder the ordering of solvent molecules. For the gel polymer electrolyte prepared with $\text{LiPF}_6\text{-EC/DMC}$, 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.

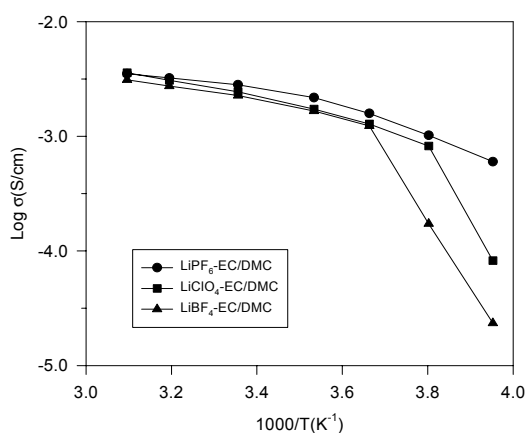


Fig. 2. Temperature dependence of the ionic conductivity for gel polymer electrolytes.

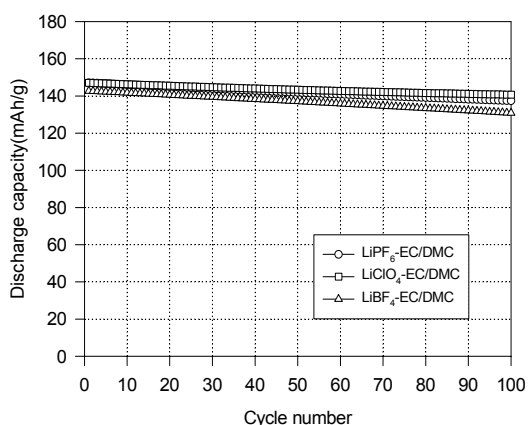


Fig. 3. Discharge capacity of lithium-ion polymer cells as a function of cycle number.

The electrochemical stability of the gel polymer electrolytes was evaluated with linear sweep voltammetric measurements. 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. This result makes these gel polymer electrolytes acceptable for high voltage cathodes such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 . To demonstrate the usefulness of the polymer electrolyte prepared with the porous PAN membrane in lithium-ion cells, we fabricated a MCMB/PE/ LiCoO_2 cell. Fig. 3 shows the discharge capacity of lithium-ion polymer cell as a function of cycle number. The cell initially delivered a discharge capacity of 147 mAh/g based on LiCoO_2 active material in the cathode. Although the discharge capacity displayed slight decay in the course of the cycling, the results suggest that use of porous PAN membrane as a polymer electrolyte allows stable cycling characteristics to be reached. The rate capability of the MCMB/PE/ LiCoO_2 cells was evaluated. The cell delivered a discharge capacity of 146 mAh/g at 0.5C rate. The discharge capacity slowly decreases with current rate, which is due to polarization. However, it showed a good performance at high current rate(2.0C), whose discharge capacity was 139 mAh/g. It corresponds to 95 % compared to that obtained at 0.2C rate.

Conclusions

Gel polymer electrolytes prepared with the porous 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 $\text{LiPF}_6\text{-EC/DMC}$, and the electrolyte solution was well encapsulated in the porous membrane by physical gelation. The lithium-ion cells employing the porous PAN membrane were assembled, and their charge/discharge cycling performance was evaluated. The cell showed a high initial discharge capacity of 147 mAh/g based on active LiCoO_2 material. At a current rate of 2.0C, the cell retained 95 % of its discharge capacity at 0.2C. With further efforts to improve the cell performance, the polymer electrolyte prepared by soaking the porous PAN-based polymer membrane in an electrolyte solution is believed to be a good candidate as an electrolyte material for rechargeable lithium-ion polymer batteries.

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