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Porous Polyacrylonitrile Membrane for Lithium-Ion Cells

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A highly porous polyacrylonitrile (PAN) membrane was prepared and characterized. Polymer electrolyte was prepared by soaking the porous PAN membrane in an electrolyte solution, and its electrochemical characteristics were investigated. Ionic conductivity exceeding 1×10^{-3} S/cm at room temperature was obtained, and the use of this membrane assured an electrochemical stability of at least 4.5 V. A lithium-ion cell employing the porous PAN membrane was assembled, and its charge/discharge cycling performance was evaluated.

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Many studies have been performed on rechargeable lithium-ion polymer batteries using gel polymer electrolytes in which the liquid electrolyte has been immobilized by incorporation into a matrix polymer, such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and poly(ethylene oxide) (PEO).[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 their use 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 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.[8-12] 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. Note that gel polymer electrolytes based on PAN showed high ionic conductivity exceeding 10^{-3} S/cm at room temperature.[1]

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 was chosen because it is expected that an uptake of the electrolyte solution may result in swelling or gelation of polymer rather than dissolution. This would contribute to the mechanical stability of the membrane after soaking in electrolyte solution. To the best of our knowledge, this is the first study that demonstrates the realization of PAN as a porous membrane in lithium-ion cells. The porous membrane is prepared by a phase-inversion method, which has been shown to be effective for producing a porous structure.[13] 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

Preparation of membrane and electrodes.—Porous PAN membranes were prepared according to the procedure shown in Fig. 1. PAN (Aldrich Chemicals) 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 deionized water for 6 h to induce phase inversion. After exchange of organic solvent and water, substantial amounts of pores were formed in the film. The resulting membrane was washed with running water and immersed again in a pool of deionized water for 24 h. The membrane was then vacuum dried at 40°C for 24 h. The morphology of the porous membrane was examined using a scanning electron microscope (SEM, JEOL, JSM-6300). Cross-sectional views of the membranes were obtained by breaking them in liquid nitrogen. 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 (Osaka gas), PVdF, and super-P carbon on a copper foil. The cathode contained the same binder (PVdF) and super-P carbon along with $LiCoO_2$ (Japan Chemical) 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/cm^2.

Electrical measurements.—The dried membrane was transferred

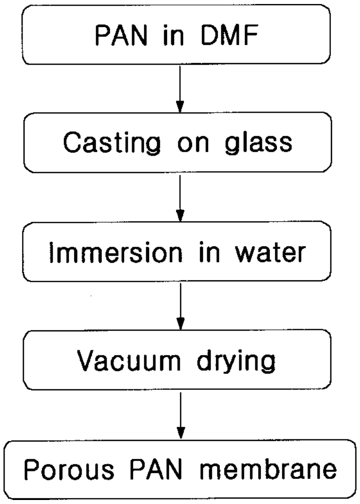

Figure 1. Schematic diagram for preparing the porous PAN membrane.

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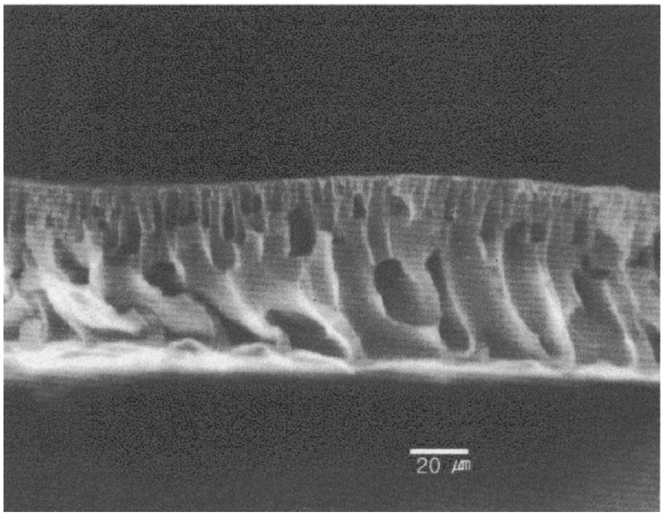

Figure 2. Cross-sectional SEM of the porous PAN membrane.

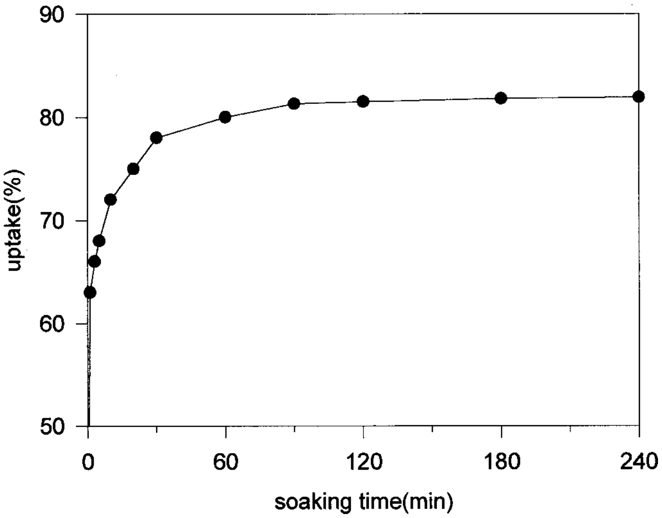

Figure 3. Uptake of electrolyte solution as a function of soaking time.

into a glove box and soaked in 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume, Samsung Cheil Industries, battery grade) for 2 h, to activate the membrane. The wetted membrane was cut into 4 cm^2 squares and sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The cell was enclosed in an aluminum plastic pouch and sealed to permit testing outside of a glove box. 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. A lithium-ion cell was assembled by sandwiching the wetted membrane between a MCMB anode and a $LiCoO_2$ 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

Figure 2 shows a typical SEM image of a cross section of a porous PAN membrane prepared by the phase inversion method. It exhibits a large number of short fingerlike cavities beneath the upper layer. The size of pores is observed to increase from the top to the bottom of the membrane. In the phase inversion process, the membrane is formed by polymer precipitation, which occurs as a consequence of concentration variations following diffusive interchange between the solvent (DMF) and the nonsolvent (water). Because PAN in DMF solution abruptly coagulated and became immobile at the skin layer when the casting solution contacts with water, the dense layer is produced at top of the membrane. The upper skin layer should be formed in very short times, and consequently acts as a barrier against subsequent interdiffusion of solvent and nonsolvent. The retardation of water penetration results in slow phase inversion and, consequently, the large cavities are developed in the bottom of the membrane that is formed in contact with the glass plate during the precipitation step. Porosity (φ) of the membrane was measured to be 0.64 by the equation given in previous studies[10,14]

$$\varphi = 1 - \rho_m/\rho_p \quad [1]$$

where ρ_m and ρ_p are the apparent density of the porous membrane and the density of PAN, respectively.

The porous membrane was soaked in $LiPF_6$-EC/DMC, and uptake of electrolyte solution was measured with soaking time, as shown in Fig. 3. Uptake of electrolyte solution increased with soaking time during the early stage, and eventually reached an equilibrium value. After attaining an equilibrium state, the amount of electrolyte solution absorbed in the porous PAN membrane is about 4.0 times the weight of the polymer (81% based on the total weight), which indicates a high solvent retention ability of the porous PAN membrane. High affinity for electrolyte solution results from the presence of polar functional groups in PAN. Moreover, a large amount of pores in the PAN membrane enlarges the contact areas between polymer and solvent such that the electrolyte solution is well retained in the membrane by the polymer-solvent interactions. However it should be noted that the amount of electrolyte solution to be encapsulated in the porous PAN membrane is lower than that in the conventional PAN gel electrolytes. In previous work, the amount of $LiPF_6$-EC/DMC trapped in the gel-type PAN electrolyte was about 90 wt % based on the total weight of the gel polymer electrolyte composed of $LiPF_6$, EC, DMC, and PAN.[15] For comparison, the microporous polyethylene (PE) separator (Asahi Kasei, thickness 25 μm, porosity 40%) used in a commercial lithium-ion battery was also soaked in the same electrolyte solution. The amount of electrolyte solution absorbed (52%) is lower than that (81%) absorbed by the porous PAN membrane. This result is due to the poor affinity of PE separator for liquid electrolyte.

Ionic conductivity of the polymer electrolyte (PE) prepared by soaking the porous PAN membrane in the electrolyte solution was measured from ac impedance measurements. After soaking in electrolyte solution, the porous PAN membrane showed self-standing film characteristics with excellent mechanical strength. Figure 4a shows a typical ac impedance spectrum of the SS/PE/SS at room temperature. In this figure, the intercept on the real axis gives the electrolyte resistance. The ionic conductivity was calculated to be 1.0×10^{-3} S/cm from the electrolyte resistance with thickness (65 μm) and surface area (4 cm^2) of polymer electrolyte. Here, ionic conductivity of the electrolyte solution ($LiPF_6$-EC/DMC) used in soaking is 1.1×10^{-2} S/cm. Ionic conductivity was measured as a function of storage time in the sealed cell. Figure 4b illustrates the time dependence of the ionic conductivity for the electrolytes prepared with porous PAN membrane and PE separator, respectively. Note that an electrolyte prepared with the porous PAN membrane exhibits a higher ionic conductivity over time periods measured. The difference in ionic conductivity between two systems arises from the difference in the quantity of electrolyte solution encapsulated in them. Ion conduction behavior with time was also different for each parent membrane. A gradual decrease in the ionic conductivity of the PE separator may be related to the solvent exudation upon long

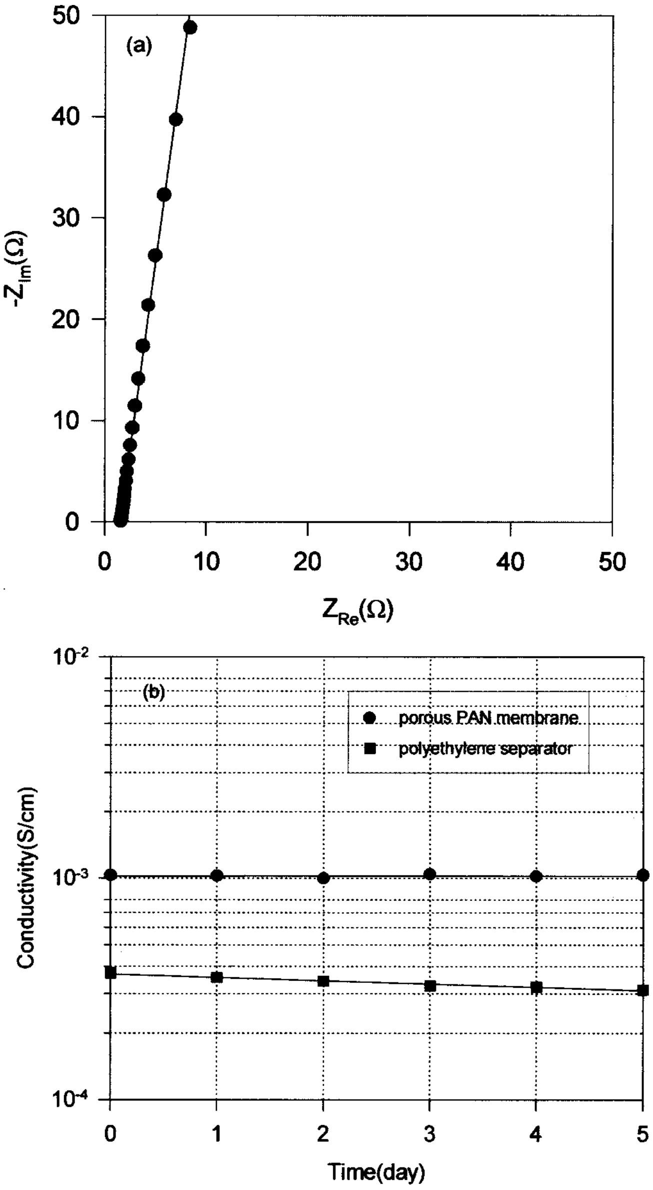

Figure 4. (a) AC impedance spectrum of the SS/PE/SS cell prepared with a porous PAN membrane containing $LiPF_6$-EC/DMC. (b) Time evolution of the room-temperature ionic conductivity of the porous PAN membrane and the PE separator containing $LiPF_6$-EC/DMC.

storage, or it may arise from poor compatibility with the electrolyte solution, as described above. After ac impedance measurements, liquid electrolyte exuding from the PE separator was observed in the cell. A constant value (1.0×10^{-3} S/cm) of ionic conductivity for the porous PAN membrane for a long period of time suggests that the electrolyte solution is well encapsulated in the porous PAN membrane, which gives no solvent exudation in the closed system. However, the porous PAN system also undergoes solvent evaporation upon long storage under open-atmosphere conditions, as observed in gelled PAN electrolytes.

The electrochemical stability of polymer electrolyte was evaluated by linear sweep voltammetric measurements. Voltammograms for cells prepared with a porous PAN membrane that contains an electrolyte solution of $LiPF_6$-EC/DMC are presented in Fig. 5. The decomposition voltage was sufficiently high, which is acceptable for high voltage cathode materials, such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$.

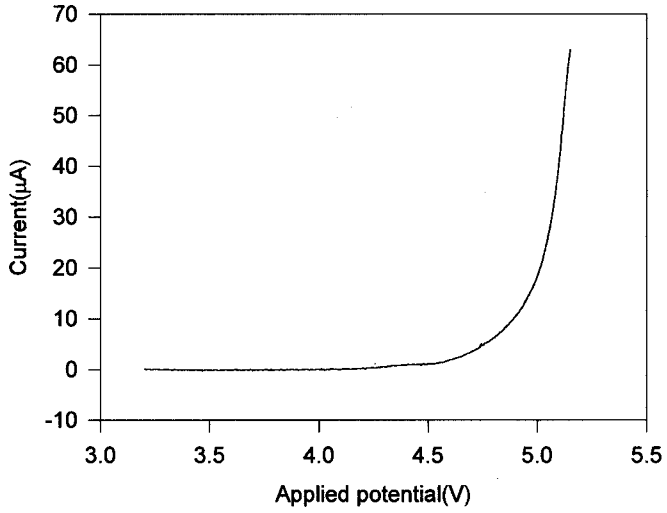

Figure 5. Linear sweep of the cell prepared with a porous PAN membrane containing $LiPF_6$-EC/DMC (scan rate 1 mV/s).

To demonstrate the usefulness of the polymer electrolyte prepared with the porous PAN membrane in lithium-ion cells, we fab-

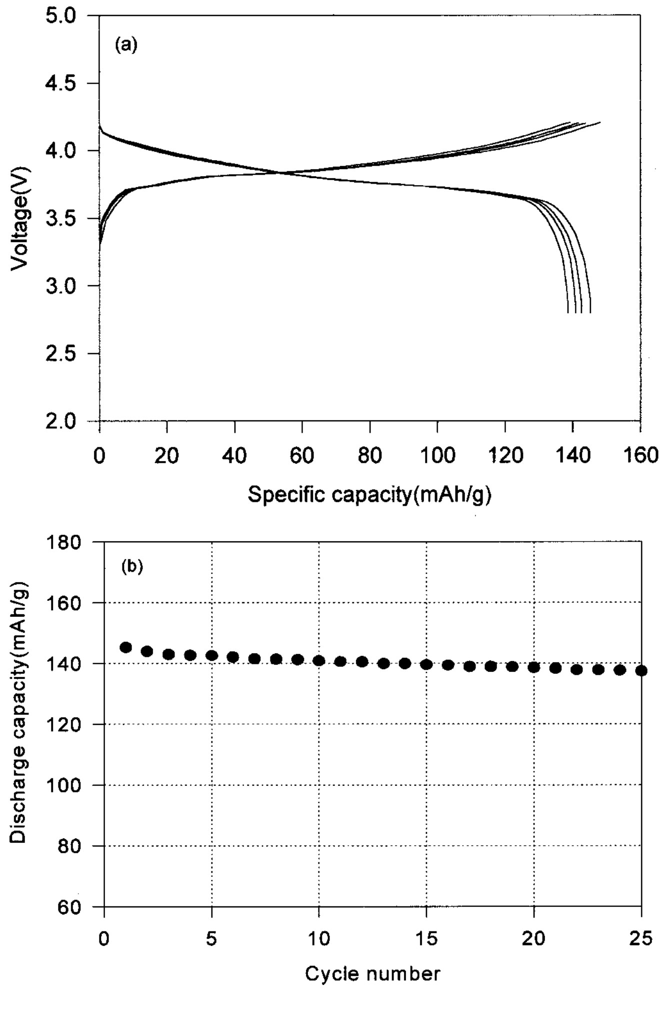

Figure 6. (a) Charge and discharge curves of lithium-ion cell with repeated cycles at C/5 rate (first, fifth, tenth, and twentieth cycle). (b) Discharge capacity of lithium-ion cell as a function of cycle number at C/5 rate.

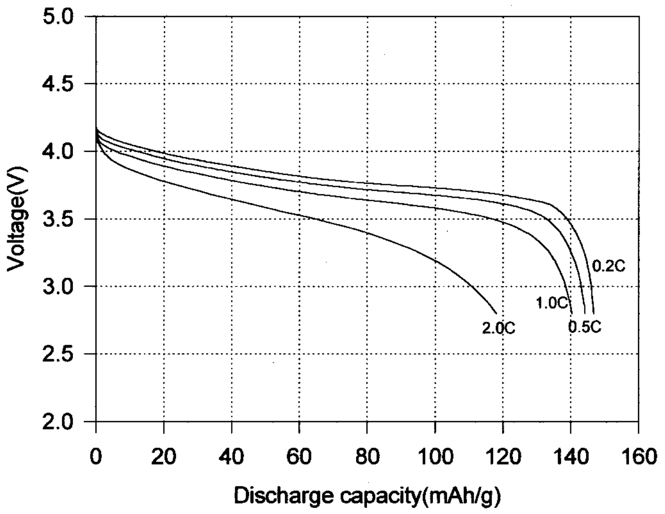

Figure 7. Discharge profiles of a lithium-ion cell. Charge rate is 0.2C with 4.2 V cutoff.

ricated a MCMB/PE/LiCoO$_2$ cell. The assembled cell was subjected to the cycle tests in the following order: preconditioning with cutoff voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at C/10 rate (0.24 mA/cm^2) for the first preconditioning cycle and subsequent C/5 rate (0.48 mA/cm^2) cycles. Figure 6a shows the repeated charge/discharge cycles of the lithium-ion cell at C/5 rate after a preconditioning cycle. It is a plot of the voltage profiles after the first, fifth, tenth, and twentieth cycles. This cell initially delivered a discharge capacity of 145 mAh/g based on LiCoO$_2$ active material in the cathode. The cycling characteristics are regarded as good because the cycling efficiency is high. The discharge capacity *vs.* cycle number for a cell subjected to 25 cycles is shown Fig. 6b. 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 a MCMB/PE/LiCoO$_2$ cell was evaluated. The discharge curves obtained at different current rates are given Fig. 7. The cell delivered a discharge capacity of 143 mAh/g at a 0.5C rate. The discharge capacity slowly decreased with current rate, due to polarization. The discharge capacity dropped to 117 mAh/g at a 2.0C rate, which is 81% of the discharge capacity at a 0.2C rate. This result is not sufficient as a high-rate performance of lithium-ion cell, and must be improved further. However, the preliminary results reported in this work are promising as a basis for further studies. Further research is being conducted in the author's laboratory to improve the cycle life and high-rate performance for the lithium-ion cell using the porous PAN membrane. A soaking of the porous membrane with highly conductive electrolyte solution, an optimization of porosity and pore size in the porous membranes, and a synthesis of PAN-based copolymers for better interfacial contact between electrodes and polymer electrolyte are several approaches to enhance the battery performance.

Conclusions

Highly conductive polymer electrolytes were prepared by soaking porous PAN membranes in an electrolyte solution. High ionic conductivity is attributed to the high volume of pores formed in the porous membrane and its high affinity for an electrolyte solution. The porous membrane encapsulated high amounts of an electrolyte solution, which corresponds to 4.0 times the weight of the polymer. A lithium-ion cell employing the porous PAN membrane was assembled, and its charge/discharge cycling performance was evaluated. The cell showed a high initial discharge capacity of 145 mAh/g based on active LiCoO$_2$ material at a 0.2C rate. At a current rate of 2.0C, the cell retained 81% 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 batteries.

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