

Performances of lithium/gel electrolyte/polypyrrole secondary batteries

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Abstract

Poly(methylmethacrylate) (PMMA)- and poly(acrylonitrile) (PAN)-based gel electrolytes were applied to Li/polypyrrole (PPy) battery and its performance was investigated. These batteries showed excellent performance with 3 V output voltage and 90–100% coulombic efficiency. Using chemically more stable PMMA gel electrolyte, long charge/discharge cycle life more than 8000 cycles at 0.1 mA cm⁻² was obtained. © 1997 Elsevier Science S.A.

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1. Introduction

In recent years, there is a strong need of high energy and high power secondary batteries, for portable electric devices, load leveling systems, and electric vehicles.

Lithium secondary battery using lithium metal as the anode is the most attractive candidate for these requirements. For fear of reaction to lithium, an aprotic organic solvent-based electrolyte solution is required for lithium batteries. However, using these liquid electrolytes, there is the possibility that the electrolyte solution leaks out from the cell. Furthermore, a separator must be placed between a cathode and an anode to avoid short-circuit in the cell, which prevents the progress of energy density for the battery.

Solid polymer electrolyte, which consists of an ionic conductive polymer matrix and a supporting electrolyte salt was introduced as a new electrolyte material for lithium batteries by Fenton et al. [1] and Armand et al. [2]. By using solid polymer electrolyte as the battery electrolyte, a separator is needless, and the electrolyte can be fabricated as an ultra-thin film, which enables to construct an all-solid, high energy density lithium battery. In initial studies, poly(ethylene oxide) (PEO)-based electrolytes were investigated [3–6]. However, it had a drawback that PEO-based solid polymer electrolytes showed relatively lower ionic conductivity (about 10⁻⁷ S cm⁻¹) than that of liquid electrolytes (about 10⁻² S cm⁻¹) at room temperature. Improvement in ionic

conductivity is considerably required and many researches have been carried out, e.g., adding plasticizer [7,8], introduction of intermolecular bridge formation to polymer matrix [9]. Especially, the gel electrolyte which consists of polymer matrix, supporting electrolyte and organic solvent shows high ionic conductivity about 10⁻³ S cm⁻¹ at room temperature and has a sufficient mechanical strength [10–12]. Therefore, the application of a gel electrolyte to lithium secondary battery is expected to achieve room temperature operation, all-solid construction, and high energy density. We already applied the PAN-based gel electrolyte to lithium/polymer battery using polypyrrole (PPy) film as the cathode material [13]. However, this battery showed poor shelf life, and the fact may be due to the chemical and/or electrochemical instability of PAN. In this work, we apply a much stable, PMMA-based gel electrolyte to an Li/PPy battery, and investigate characteristics and charge/discharge performance comparing battery systems using the PAN-based and the PMMA-based electrolytes.

2. Experimental

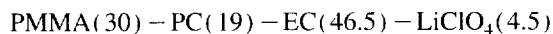
2.1. Preparation of PMMA- and PAN-based gel electrolytes

Both ethylene carbonate (EC) (Fluka, reagent grade) and propylene carbonate (PC) (Fluka, reagent grade) were purified by distillation under the reduced pressure. The pure solid

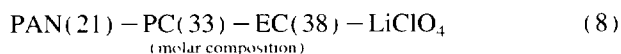
* Corresponding author

EC was added to the distilled PC and the resulting EC–PC liquid mixture was dried by storing it over molecular sieves. Lithium perchlorate (LiClO_4) (Fluka, 99.5%) was dried by heating it at 120 °C under vacuum for 24 h. PAN and PMMA (Aldrich, reagent grade) were dried under vacuum at 100 °C for 10 h. LiClO_4 as a supporting electrolyte and PAN or PMMA powder were dissolved in the EC–PC mixture at temperatures ranging between 40 and 50 °C. Chemical composition of these gel electrolytes were as follows

[PMMA – based gel]



[PAN – based gel]



These solutions were slowly heated to favor gelification up to 100–110 °C for PAN gel and 70–80 °C for PMMA gel, respectively, and finally cast between glass sheets to obtain the desired solid membranes. They had a transparent and elastomeric appearance, whose thicknesses were about 300 μm and ionic conductivities were on the order of $10^{-3} \text{ S cm}^{-1}$ [12].

2.2. Preparation of electrochemical cells

Two types of electropolymerized PPy films were applied to the cell as a cathode material. In our previous study, it is shown that surface morphology of PPy film was controlled by selecting electropolymerization potential [6]. PPy was obtained by potentiostatic oxidative polymerization at potentials of 3.9 or 4.2 V versus Li/Li^+ in PC (Mitsubishi Chemical, reagent grade) containing 0.2 M LiClO_4 (Wako Pure Chemical, 98%) and 0.2 M pyrrole (Wako Pure Chemical, 99%). The film morphologies became flat and dense (hereafter indicated as fPPy) at the former condition, and rough and porous (hereafter indicated as rPPy) at the latter condition, respectively [6]. Fig. 1 shows a schematic diagram of the coin-type cell. The film was deposited on a cathode case, which had been treated by platinum sputtering to prevent peeling the film from the case. The film deposition area was limited to 5 mm in diameter and the amount of PPy was regulated by the passed charge of 0.5 C cm^{-2} . PAN and PMMA gel electrolyte membranes were punched to 15 mm in diameter. A lithium metal disk was applied as the anode material, and its surface area was 1.539 cm^2 (14 mm in

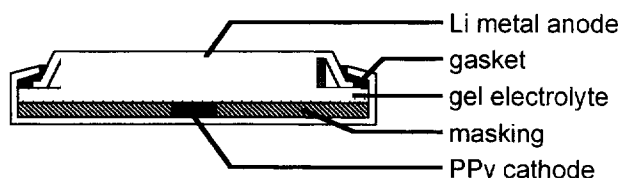


Fig. 1. Schematic diagram of coin-type cell.

diameter) in order, for the battery performance, to be regulated by the cathode reaction. These components of PPy film on cathode case, gel electrolyte disk, and lithium metal disk on the anode case were combined and sealed by pressing. A similar coin-type cell with $\text{Li}/\text{gel electrolyte}/\text{Li}$ symmetrical construction was used to investigate the interfacial stability between lithium and the gel electrolyte.

2.3. Electrochemical measurements

Cyclic voltammetry of the cell was performed from 2.0 to 3.5 V at 5 mV s^{-1} . Charge/discharge battery performance was examined at 0.1 mA cm^{-2} . Cut-off voltages were 3.5 V on charging and 2.0 V on discharging, respectively. A.c. impedance spectroscopy was measured at 3.0 V for the battery and 0 V for the symmetrical cell at frequencies from 20 000 to 0.01 Hz. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Electrochemistry of PPy film in gel electrolyte

In our previous study, it was shown that the redox activity of PPy film in solid polymer electrolyte considerably depended on its surface morphology and condition of the interface between PPy and the electrolyte [6]. The liquid-free, solid polymer electrolyte has poor permeability into polymer electrode owing to its large molecular volume, so the diffusion process of dopant ion in PPy is the rate-determining step for the redox reaction of PPy. In a PEO-based polymer electrolyte, PPy reacts at only the PPy/PEO interface. Therefore, rPPy which has a larger surface area shows extremely higher redox activity than fPPy.

Fig. 2 shows cyclic voltammograms of Li/PPy cells using PMMA gel electrolyte. Intensity of current peaks and revers-

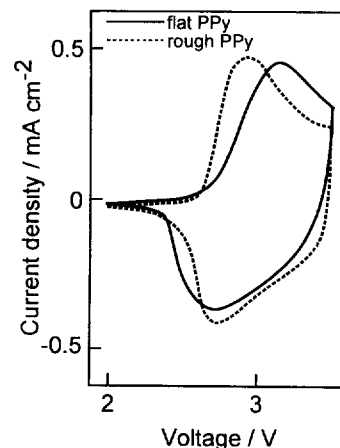


Fig. 2. Cyclic voltammograms of (—) fPPy and (· · ·) rPPy films in PMMA gel electrolyte; scan rate, 5 mV s^{-1} .

ibility of redox reaction are slightly better for rPPy than fPPy. However, it is interesting to note that both of PPy films similarly show satisfyingly high redox activity. These tendency is quite resembling to the behavior of PPy in a conventional organic liquid electrolyte [14]. Liquid components in PMMA gel electrolyte, PC and EC can soak into PPy film and they should enhance ion mobility in the film, thus in the gel electrolyte, both at the inner and at the surface, conditions of PPy are almost equal to in liquid electrolyte. As a result, the ion diffusion process in the film hardly regulates the activity, which does not depend on the surface morphology of the film. Using PAN gel electrolyte, the same results were obtained in our previous report [13]. Results of a.c. impedance measurement for Li/PMMA gel/fPPy cell are represented in Fig. 3. In these Cole–Cole plots, the semicircle in the higher frequency region and the inclined line in the lower frequency region that is the Warburg impedance, correspond to the charge-transfer process of PPy with doping/undoping of ClO_4^- , and the diffusion of ClO_4^- in the film, respectively. In the lower frequency region, the Warburg impedance decreases with storage time, and in the lowest frequency region the linear spectrum, which is vertical to the Z_{real} -axis corresponding to the limiting diffusion impedance, gradually becomes larger. This phenomenon of decreasing in Warburg impedance was observed for about 50 h and finally stopped. Except the diffusion impedance, charge-transfer resistance, double-layer capacitance and electrolyte bulk resistance hardly changed.

When the PPy electrode film and the gel electrolyte film prepared separately are stuck together to fabricate a cell, liquid compounds in gel electrolyte have penetrated into the PPy film. Then the ion mobility in the PPy film comes to be enhanced, which is clearly shown in Fig. 3. The film thickness of rPPy is about 5 times of that of the flat one, hereafter in

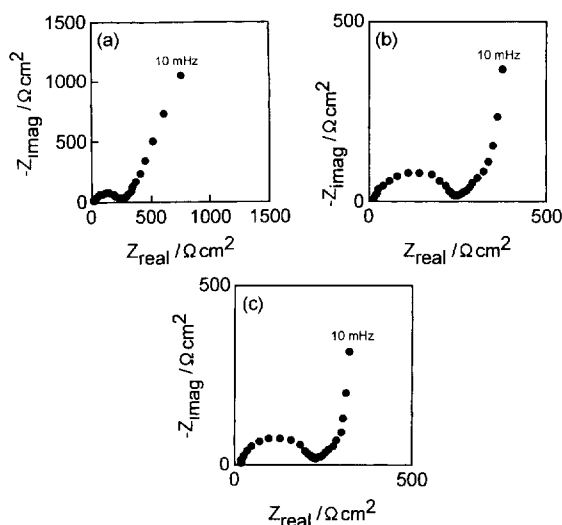


Fig. 3. Cole–Cole plots of Li/PMMA gel/fPPy battery at 3.0 V measured (a) as prepared, (b) after 1 h, and (c) after 23 h

this work, we used fPPy as a cathode, which has higher energy density by volume.

3.2. Charge/discharge performance of Li/gel electrolyte/fPPy battery

Charge/discharge performance of Li/fPPy battery using PMMA gel or PAN gel as a electrolyte was investigated by the galvanostatic battery test at 0.1 mA cm^{-2} . Fig. 4 shows a typical charge/discharge curve of Li/gel electrolyte/fPPy battery. Cut-off voltages were 3.5 V on charging, 2.0 V on discharging, respectively. One slightly inclined plateau is observed in each charge curve and discharge curve, from which the average output voltage of the battery is calculated as 2.9 V. Discharge capacity and coulombic efficiency estimated from these curves are shown in Fig. 5. Both the PMMA and the PAN systems showed about 90 to 100% of coulombic efficiency through all cycles. These results demonstrate that the Li/PMMA gel/PPy and Li/PAN gel/PPy systems have sufficient electrochemical stability and reversibility. Further-

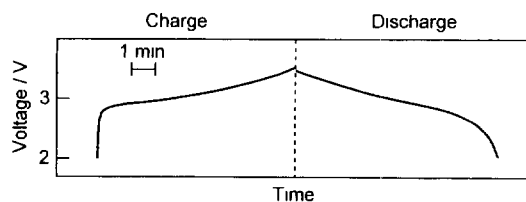


Fig. 4. Typical charge/discharge curve for Li/gel electrolyte/fPPy battery. Charging and discharging current densities are 0.1 mA cm^{-2}

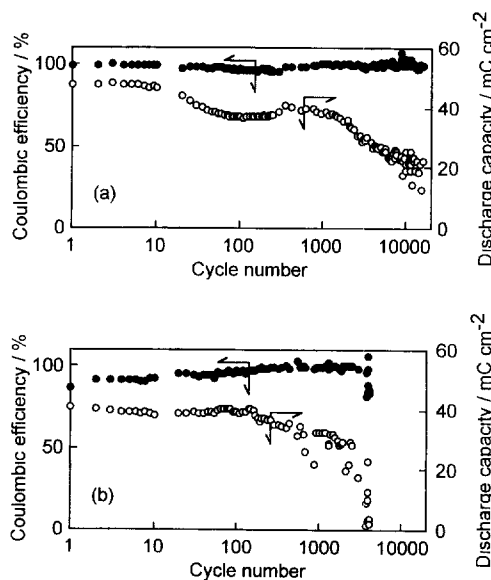


Fig. 5. Dependence of (●) coulombic efficiency and (○) discharge capacity of: (a) Li/PMMA gel/fPPy battery, and (b) Li/PAN gel/fPPy battery on number of cycles, charging and discharging current densities are 0.1 mA cm^{-2}

more, both batteries showed excellent performance with constant discharge capacities about $50\text{--}40\text{ mC cm}^{-2}$ (discharge depth of the PPy cathode was about 90–80% using 53.6 mC cm^{-2} as the maximum capacity of PPy [6]) up to 500 cycles. However, when continuing the measurement, the discharge capacity of both batteries gradually decreased. Especially, in Fig. 5(b) on the PAN system, the capacity became nearly 0 when 4000 cycles were completed, and it could not be operated beyond 4000 cycles. On the contrary, the PMMA system showed no sudden decrease and more than 8000 cycles were obtained (Fig. 5(a)).

The difference in cycle performance between the PMMA and the PAN systems should be due to the difference in the chemical stability of the Li/gel electrolyte interface. The interfacial stability of lithium and the gel electrolyte was investigated by a.c. impedance measurements. Fig. 6 shows the interfacial resistance (R_i) which is estimated from the first semicircle in the Cole–Cole plots of the Li/gel electrolyte/Li symmetrical cell. In this figure, R_i is about $150\text{--}200\ \Omega\text{ cm}^2$ and almost constant in during the first 100 h. After 100 h, R_i suddenly increases with storage time in both the PMMA and the PAN system. We believe that the increase in R_i is due to the chemical side reaction of lithium and the liquid components (PC, EC) in the gel electrolyte, which is generally known at the organic liquid electrolyte systems. The side reaction products, which have poor ionic conductivity, accumulate on the interface of lithium and the gel electrolyte, and the accumulation layer grows with storage time. As a result, the interfacial resistance including the layer resistance also increases.

This increasing tendency of R_i differs between two systems, in Fig. 6. R_i value of the PAN system reaches to $4000\ \Omega\text{ cm}^2$, while the value of the PMMA system remains less than $2500\ \Omega\text{ cm}^2$. These results indicate that the PAN system should be chemically less stable than the PMMA system because of the other side reaction of lithium and the cyano (CN) group in the PAN molecule. This difference of the interfacial stability should be the main cause of the difference in the charge/discharge cycle performance between two batteries.

The increase of the interfacial resistance induces the increase in the total inner resistance of the cell, thus it causes

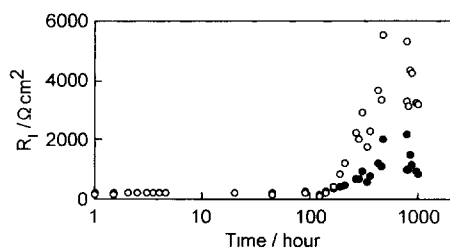


Fig. 6 Time dependence of R_i , which are estimated from the first semicircle (high frequency region) in the Cole–Cole plots of (●) Li/PMMA gel/Li cell and (○) Li/PAN gel/Li cell.

the growth of the iR loss. Increasing the iR loss, the practical operating voltage range becomes narrow. Thus, discharge capacity of the battery decreases with storage time or cycle number.

4. Conclusions

Both rough and flat PPy cathode films showed satisfying high redox activities similarly in PMMA- and PAN-based gel electrolytes. It was observed by an a.c. impedance measurement that liquid components, PC and EC soaked into PPy film, which enhanced the ion diffusion process of the dopant anions in the film. The Li/fPPy battery using these gel electrolytes worked with high output voltage about 3 V and about 100% coulombic efficiency. However, the discharge capacity unlikely decreased with cycle number, and it was due to the chemical side reaction of lithium and the gel electrolyte.

The PMMA gel electrolyte has higher chemical stability versus the lithium anode than that of PAN gel electrolyte, and the stability enables the Li/PMMA gel/PPy battery long cycle life of more than 8000 cycles.

Further investigation, about the mechanism of the side reaction and its control is required to construct a much more stable all-solid system.

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