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# Rechargeable Lithium Batteries Using Polypyrrole–Poly(styrenesulfonate) Composite as the Cathode-Active Material

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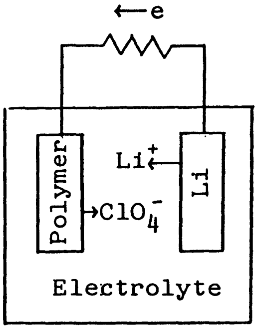
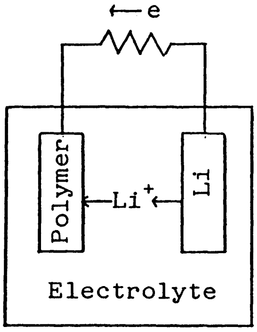
Polypyrrole-polyelectrolyte composite, obtained by electrochemical polymerization on a vapor-grown carbon fiber (VGCF) electrode, was used as a cathode-active material for a rechargeable lithium battery. Poly(styrensulfonate) ion was suitable as a dopant in terms of rechargeability of the battery. The VGCF, which has a fibrous structure, was effective as a current collector for the polymer electrode. The content of the dopant calculated by the molar ratio of sulfur and nitrogen was ca. 30%. The open-circuit voltage was 3.55 V at the time. A charge-discharge, accompanied by an $Li^+$ deinsertion-insertion of the composite, was observed. The charge-discharge mechanism is similar to that of inorganic cathode-active materials that show $Li^+$ intercalation. The battery was cycled stably beyond 30 times between 3.66 and 1.50 V at a constant current of 0.889 $mA\,cm^{-2}$. An experimental capacity of 57 $Ah\,kg^{-1}$ was obtained at the largest value on the basis of the weight of the active material. There is a possibility of developing a light-weight rechargeable battery using the polypyrrole-poly(styrenesulfonate) composite.

A conductive polymer can be used as a cathode-active material for a lithium rechargeable battery.[1-11] A capacity has been reported of more than 100 $Ah\,kg^{-1}$, based on the weight of the active material.[2-4,8] The discharge mechanism of a battery using a p-type conductive polymer is shown in Scheme 1. The following problem, however, must be considered for a practical use of the batteries. For instance, 1.0 g of polypyrrole, which has 0.47 g of $ClO_4^-$ (30% doping), needs ca. 5.2 g of propylene carbonate at a minimum to dissolve $ClO_4^-$ at 1.0 $mol\,dm^{-3}$. A lot of solvent, which is 5 to 10 times the weight of the active material, is usually necessary to assemble a p-type conductive polymer into a lithium battery. The total weight of the battery will inevitably be heavy, even if the cathode-active material is light. This problem might be solved if an n-type conductive polymer was used, since it could accept $Li^+$ as the dopant and the electrolyte is only a path for $Li^+$. The discharge mechanism of a battery using an n-type conductive polymer is shown in Scheme 2. The n-type conductive polymers, however, are usually unstable.[12]

A polypyrrole-polyelectrolyte (PPY-PE) composite that has a charge-discharge property accompanied by $Li^+$ deinsertion-insertion, despite a p-type conductive polymer, has recently been reported.[13-15] There is a possibility to construct a light-weight rechargeable lithium battery when a PPY-PE composite is used as the cathode-active material. The performance of such a battery ($Li|LiClO_4|$PPY-PE) has been investigated in this study.



Scheme 1. Discharge mechanism of secondary battery using p-type polymer cathode.



Scheme 2. Discharge mechanism of secondary battery using n-type polymer cathode.

## Experimental

**Preparation of Polymer Cathode of Rechargeable Batteries.** The cathode consisted of a polypyrrole-polyelectrolyte (PPY-PE) composite and a current collector, which is a piece of vapor-grown carbon fiber (VGCF) electrode or a platinum plate. The PPY-PE was prepared by electrochemical polymerization on the current collector from an aqueous solution containing polyanion and pyrrole monomer with a constant-current system (PAB-1A, Kikusui). Reactions were carried out at a constant current density in a 30 ml cell having a VGCF electrode or a Pt electrode, with a working of 15 mm×15 mm, and titanium mesh as the cathode. Pyrrole monomer was dissolved at 6 wt% in 10 wt% of sodium poly(styrenesulfonate) (NaPSS) or sodium poly(ethylenesulfonate) (NaPES) solutions prepared from concentrated solutions of NaPSS or NaPES (Aldrich Chemical). All PPY-PE electrodes were dried in a vacuum oven at 80 °C for 2 h and weighed. All reaction conditions are summarized in Table 1.

Table 1. Conditions of Polymerization Reactions

| Run No. | Polymer | Current collector/mg | Reaction conditions | | | Weight of polymer /mg |
|---|---|---|---|---|---|---|
| | | | Current/mA | Time/h | Temp/°C | |
| 1 | PPY-PSS | Pt plate | 0.05—1.0V[a] | 5 min | r.t. | — |
| 2 | PPY-PSS | Pt plate | 10 | ca. 2 | r.t. | 33.9 |
| 3 | PPY-PSS | VGCF[b] 10.3 | 10 | ca. 3 | r.t. | 60.8 |
| 4 | | VGCF 33.5 | | | | |
| 5 | PPY-PSS | VGCF 10.2 | 10 | 4 | r.t. | 79.6 |
| 6 | PPY-PSS | VGCF 10.0 | 10 | 4 | r.t. | 75.9 |
| 7 | PPY-PSS | VGCF 10.0 | 20 | 2 | r.t. | 81.3 |
| 8 | PPY-PSS | VGCF 10.0 | 5 | 8 | r.t. | 76.2 |
| 9 | PPY-PSS | VGCF 10.4 | 20 | 2 | 56 | 60.9 |
| 10 | PPY-PSS | VGCF 10.0 | 20 | 2 | 15 | 75.9 |
| 11 | PPY-PSS | VGCF 10.6 | 20 | 2 | 1 | 89.8 |
| 12 | PPY-PSS | VGCF 9.6 | 20 | 2 | −15 | 71.0 |
| 13 | PPY-PES | VGCF 9.6 | 20 | 2 | r.t. | 71.1 |
| 14 | PPY-PSS | VGCF 13.0 | 10 | 4 | r.t. | 76.0 |

a) Polymerization potential vs. Ag/AgCl. b) VGCF electrode was not shaped into a square.

The VGCF electrode was prepared as follows. 0.05 g of VGCF (Asahi Chemical), which was 0.05—0.1 μm in diameter and 50 μm in length, was suspended in 100 ml of methanol. The suspension was unfolded onto filter paper, which was 35 mm in diameter, through vacuum filtration. After drying, the VGCF felt was cut to a size of 15 mmX20 mm. A platinum plate terminal was bound to the edge of the VGCF felt with a conductive binding agent (Electrodug 504, Acheson Japan). The VGCF electrode was washed with methanol and then with water to become hydrophilic before the polymerization reaction.

**The Formation of the Cells and Evaluation of the Batteries.** All cells have a PPY-PE cathode, a lithium anode, and a lithium reference electrode. The lithium anode was made by squashing lithium wire on an SUS net. The anode and the cathode were set up at a clearance of 10 mm, and the tip of the reference electrode was set up between the two electrodes in a cylindrical cell. The solvent was propylene carbonate containing 1.0 mol dm$^{-3}$ of $LiClO_4$. This propylene carbonate (exclusive grade for batteries, Mitsubishi Uka) was stored with Molecular Sieves (4Å) and then used. The support electrolyte was dried in a vacuum oven at 50 °C for one day. The amount of solution was 60 ml. Argon gas was filled into the cell, which was made a vacuum in advance. All cells were galvanostatically cycled between two preset voltage limits by a charge-discharge system (HJ-201B, Hokuto Denko). The upper limit was 3.6 or 3.7 V, and the lower limit was 1.5 V.

**The Pressing Electrode.** Dried PPY-PSS-VGCF electrode was soaked in 6% of a poly(tetrafluoroethylene) dispersion prepared by diluting a 60% dispersion (Polyflon D-2, Daikin), and it was dried for 2 h in a vacuum oven at 80 °C. This material, which was 1 mm thick, was pressed at 50 kg cm$^{-2}$, and a 0.5 mm thick electrode was obtained.

## Results and Discussion

A cyclicvoltamogram of PPY-PSS film on Pt plate (Run 1) showed good reversibility of the redox reaction in an aqueous solution containing 1 mol dm$^{-3}$ of $LiClO_4$, as shown in Fig. 1. A three-volt grade of rechargeable battery was expected in combination with a lithium anode. A cell using a PPY-PSS film and a lithium anode was investigated in Run 2. Figure 2-A shows the charge-discharge cycles of this cell at a constant current of 1.0 mA (0.27 mA cm$^{-2}$). This cell initially showed a 2.80 V of open-circuit voltage, though the cell voltage decreased rapidly during discharge. The capacity was about 1 Ah kg$^{-1}$. The cause of this low performance was presumed to be the high internal resistance of the active material or the small amount of dopant in the active material. Elemental analysis showed that a $SO_3$ unit existed at a rate of 1/4—1/5 unit per polypyrrole unit. (Found: C, 55.7; H, 4.3; N, 8.2; S, 4.3%). If the charge had been able to be completely used, the capacity should have been 57 Ah kg$^{-1}$. It was presumed that an electrode having a fibrous structure, like VGCF felt, would reduce the resistance, since the dense morphology of PPY film probably caused the high $Li^+$ diffusion resistance.[13] The combination of PPY-PSS and VGCF in Run 3 improved the charge-discharge curve, as shown in Fig. 2-B, according to expectation. The cell had 3.55 V of open-circuit voltage and a flat charge-discharge curve.

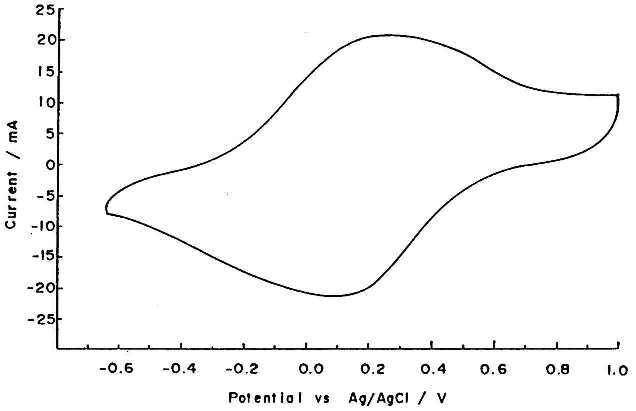


Fig. 1. Cyclic voltamogram of a PPY-PSS film on Pt plate (Run 1). Scan rate: 10 s V$^{-1}$. Counter electrode: Pt. Reference electrode: Ag/AgCl. Electrolyte: 1 mol dm$^{-3}$ $LiClO_4$ in $H_2O$.

The capacity was 42 Ah $kg^{-1}$, based on the polymer weight. The surface structure of PPY-PSS caused by VGCF surely improved the charge-discharge curve, since VGCF alone did not had a good charge-discharge curve as shown in Fig. 2-C (Run 4). Lithium insertion and deinsertion was confirmed as a result of an elemental analysis after 10 cycles of charge-discharge. (Charged state. Found: C, 58.4; H, 3.2; N, 8.9; S, 6.0; Li, 0.3%. Discharged state. Found: C, 57.0; H, 3.2; N, 8.3; S, 6.0; Li, 1.0%). An energy density of about 40 Ah $kg^{-1}$ was calculated from the lithium content in the charged state. The experimental capacity was in good accordance with the calculated capacity. The cathode reaction is shown as follows:

$$(PPY)(PSS)^- Li^+ \rightleftarrows (PPY)^+(PSS)^- + Li^+ + e. \qquad (1)$$

This mechanism is similar to that of inorganic cathode-active materials that show $Li^+$ intercalation.[16,17] The mechanism is very important in terms of setting up a light-weight battery, since the solvent between two electrodes is only a path for lithium ions (Scheme 2) and does not have to exist in large quantities. The degradation of the inorganic active material is accelerated by an excessive discharge, since excessive lithium intercalation causes a destruction of the crystal structure of the active material.[18] The polymer material, which has the mechanism shown by Eq. 1, on the other hand, may have less degradation caused by an excessive discharge, since $Li^+$ cannot insert beyond the limit determined by the content of the $SO_3$ unit.

The battery in Run 5 could be galvanostatically cycled stably over 30 times. The cycles were stopped due to considerable lithium dendrite. Figure 3-A shows the charge-discharge curve. The capacities were about 40 Ah$kg^{-1}$ (including VGCF weight), and the coulombic efficiencies were 100% in each cycle, as shown in Fig. 4. A quick charge seemed possible, since the cell showed a very low overpotential of 0.1 V at the end of the charge. A low overpotential is an important performance factor for practical rechargeable batteries, since it restrains the degradation of both the electrolyte and active material. When the cell was charged under 4 mA (1.78 mA$cm^{-2}$) in Run 5, it was also cycled stably with 100% coulombic efficiencies and with 42 Ah$kg^{-1}$ of capacity, as shown in Fig. 3-B. The capacities were almost constant under various different discharge currents in Run 6. The results are shown in Fig. 5. The highest capacity was 57 Ah$kg^{-1}$ under 1.0 mA (0.44

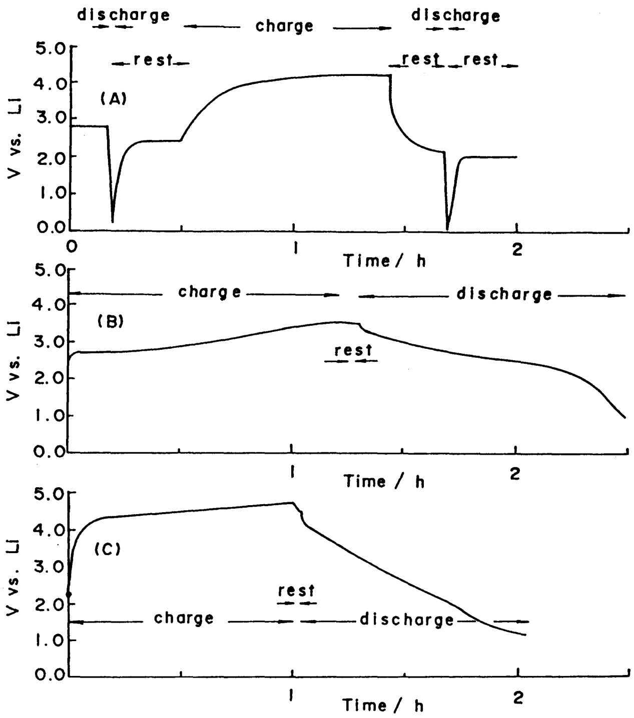


Fig. 2. Charge-discharge curves.
A: PPY-PSS film on Pt, current=1 mA, polymer weight =33.9 mg. B: PPY-PSS-VGCF, current=2 mA, polymer weight=60.8 mg, VGCF weight=10.3 mg. C: VGCF, current=2 mA, VGCF weight=33.5 mg.

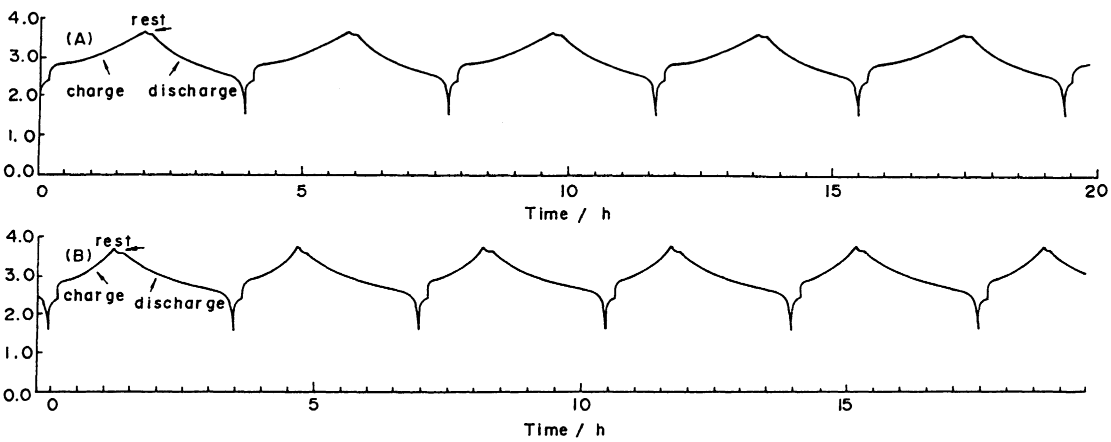
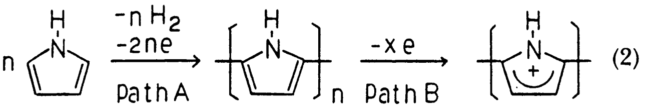


Fig. 3. Charge-discharge cycles.
A: upper limit voltage=3.6 V, lower limit voltage=1.5 V, charge current=2 mA, discharge current=2 mA. B: upper limit voltage=3.7 V. lower limit voltage=1.5 V, charge current=4 mA, discharge current=2 mA.

mA cm$^{-2}$) of discharge.

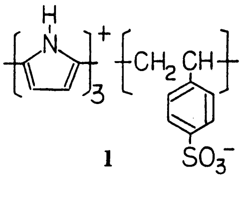
The polymerization current of PPY-PSS affected such performances of the cell as the initial cell voltage (just after setting up the cell), the capacity of the cell, the weight of the polymer, and the overpotential at the end of the charge. All results of Runs 6, 7, and 8 are summarized in Fig. 6. The polymerization and oxidation reaction proceeds as follows:



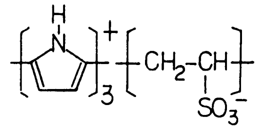
A large oxidation current probably encouraged path A oxidation, followed by a lack of the charged polymer by path B, from the fact that a large oxidation current caused a lower initial cell voltage just after setting up the cell, as well as a large amount of polymer. A small oxidation current probably made the dense structure of polymer followed by the large diffusion resistance of lithium ions, from the fact that a small oxidation current caused a high overpotential, and a small amount of polymer. The medium-range (10 mA) oxidation reaction probably resulted in the largest capacity of the cell, as a result of these facts.

The effects of temperature at polymerization on the capacities of cells were investigated in Runs 9—12. The charge-discharge properties of these cells are shown in Fig. 7. Polymerization at room temperature afforded the largest capacity.

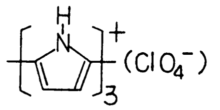
How are the weight increase and volume increase of PPY-PE, itself, compared with polypyrrole such an incorporating monomer dopant as ClO$_4^-$ ? When polypyrrole is doped with the poly(styrenesulfonate) ion, the poly(ethylenesulfonate) ion, and ClO$_4^-$ at ca. 33.3%, unit structures per one electron are exhibited as follows:



**1**



**2**



**3**

The molecular weights of these units are 378, 302, 294.5, respectively. Although a light-weight unit is

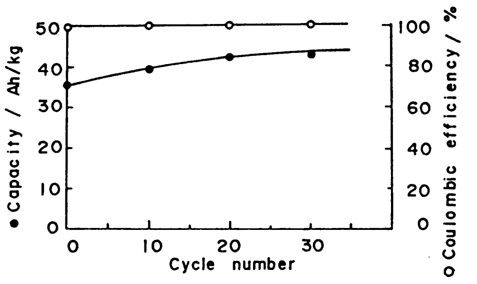


Fig. 4. Capacity vs. cycle number and coulombic efficiency vs. cycle number.

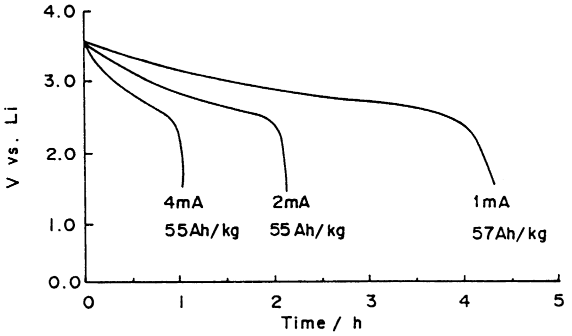


Fig. 5. Discharge curves under 4, 2, and 1 mA discharge current. Capacity were calculated based on PPY-PSS weight.

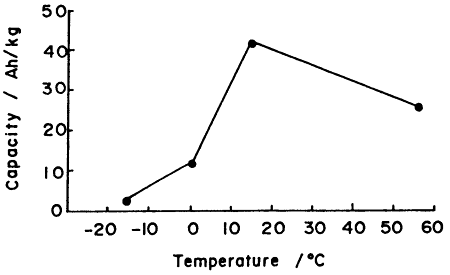


Fig. 7. Effect of polymerization temperature on capacity.

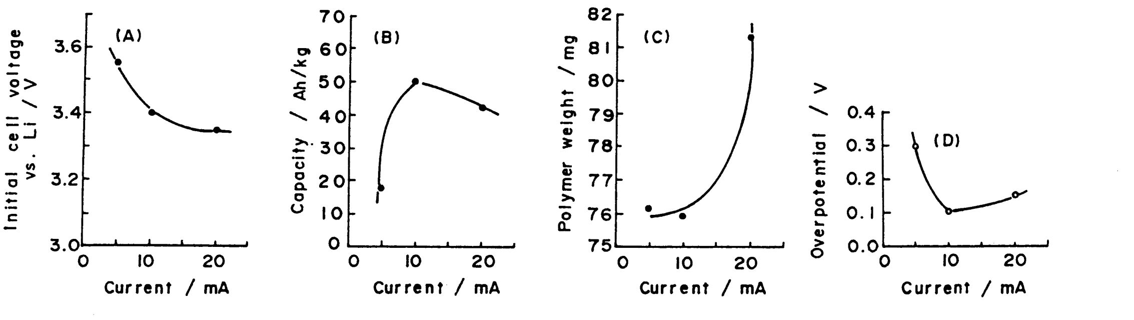


Fig. 6. Polymerization current effects on initial cell voltage, capacity, polymer weight, and overpotential.

desirable for a light-weight battery, a 28% weight excess of unit **1**, compared with unit **3**, is allowable, since the total weight of the battery is not determined only by the cathode active material. The volume of polypyrrole varies with the dopant, and it is not always in direct proportion to the dopant size. It was reported that polypyrrole film incorporating $PSS^-$ had about half the thickness of polypyrrole film incorporating $ClO_4^-$.[15)] This is a suitable performance factor for a compact battery.

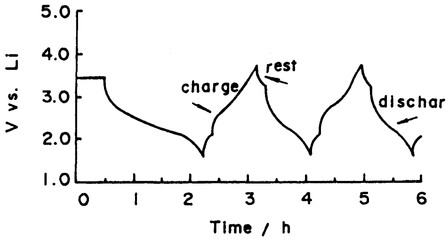


Fig. 8. Charge-discharge curve of PPY-PSS-VGCF cell. Charge current=2 mA. Discharge current=2 mA.

If poly(ethylenesulfonate) ions (**2**) had been capable of being used as a dopant, a very light, active material could have been obtained. However, the performance of the cell using poly(ethylenesulfonate) ions in Run 13 was not very good. Figure 8 shows the charge-discharge curve of the battery. The initial capacity was relatively large (43 Ah $kg^{-1}$), but the capacity could not be repeated by charging up to 3.7 V.

A pressed cathode was investigated in Run 14, since the capacity of a battery per unit volume is an important performance factor of a battery, as well as the capacity per unit weight. The result of the charge-discharge property is shown in Fig. 9. This approach was useful since the capacity rose to 40 Ah $l^{-1}$ form 20 Ah $l^{-1}$. On the other hand, an overpotential at the end of the charge increased and the flatness of the curve became reduced. There is room for an improvement in the pressing technique, such as the kinds of binder and the intensities of pressure.

Figures 10-A,B,C, and D are SEM photographs of

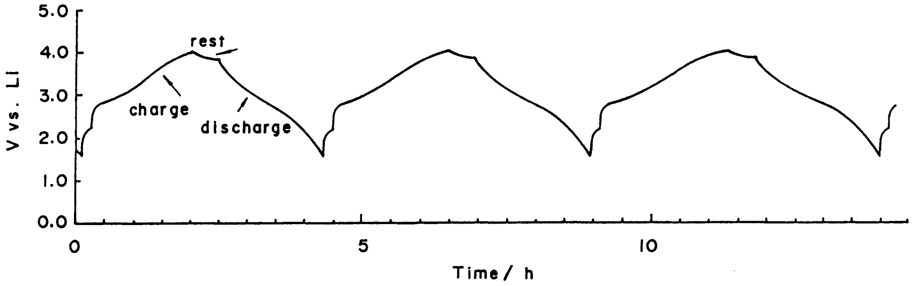
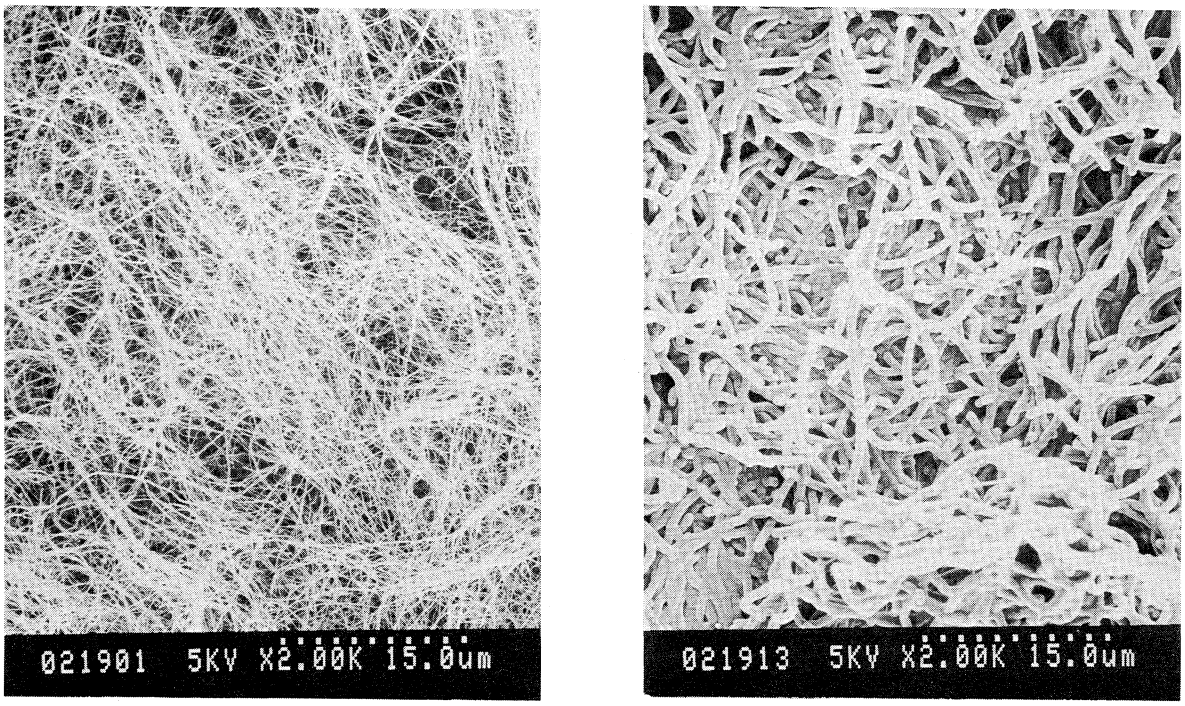
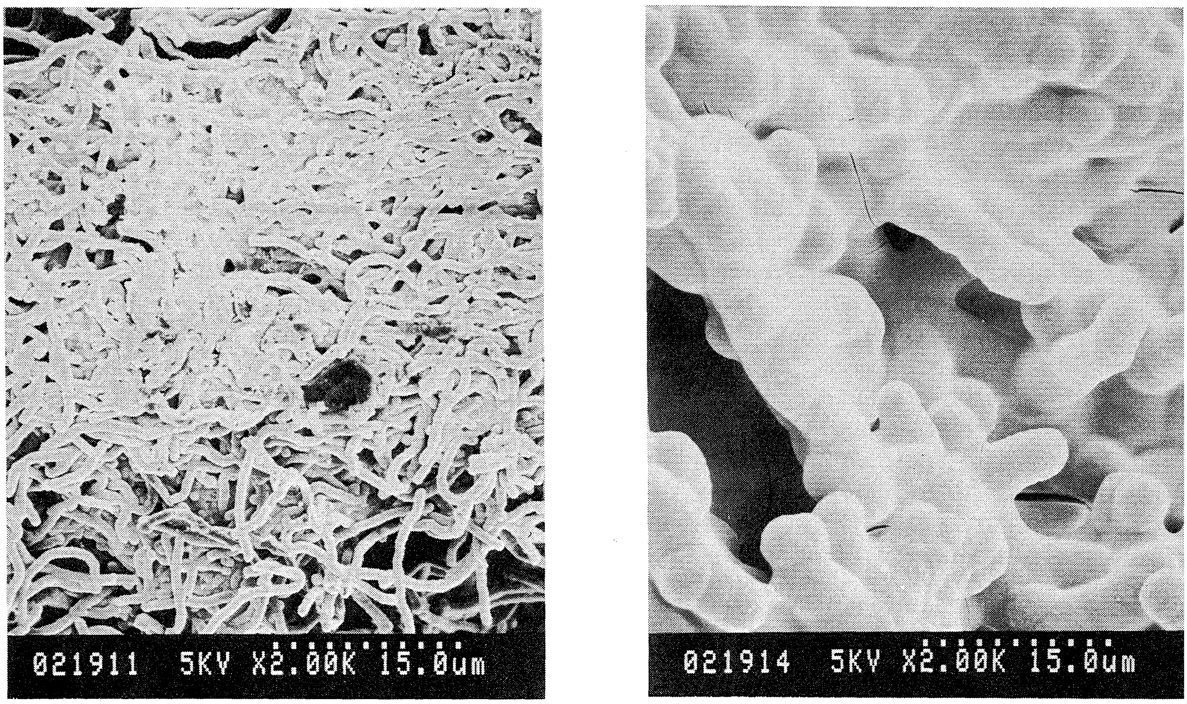


Fig. 9. Charge-discharge curve of pressed electrode. Charge current=2 mA. Discharge current=2 mA.



(A) (B)



(C) (D)

Fig. 10. SEM photographs of the cathode.
A: VGCF, B: PPY-PSS-VGCF, C: PPY-PSS-VGCF, D: pressed PPY-PSS-VGCF.

the VGCF electrode and the PPY-PSS-VGCF electrode. Samples of the PPY-PSS-VGCF composite maintained a fibrous structure as well as the VGCF current collector. This structure must have encouraged the good charge-discharge property, compared with the PPY-PSS film. There were many fibrils of different diameters. Some were about 0.5 μm (Fig. 10-B), but some were about 5 μm (Fig. 10-D). The samples after pressing were slightly crushed and some fibrils were broken (Fig. 10-C). The lower charge-discharge property compared with the non-pressed sample may be due to this structure.

We conclude that the PPY-PSS-VGCF having a lithium insertion-deinsertion mechanism can be used for a light-weight secondary battery, and that the fibrous structure of PPY-PPS-VGCF is essential for a good performance of the battery. This polymer battery is characterized by a low overpotential at the end of the charge, a stable capacity independent of the charge-discharge current, and a 100% coulombic capacity. These are desirable for a practical secondary battery.

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