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Characteristics of polypyrrole chemically synthesized by various oxidizing reagents

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Polypyrrole was chemically synthesized using various oxidizing reagents and examined as a positive electrode material. Physical properties, morphologies and electrochemical characteristics of polypyrrole were greatly influenced by the oxidizing reagent used for polymerization. In general, polypyrrole with a smaller particle size and a larger specific surface area showed better discharge performance than that with a larger particle size and a smaller specific surface area. Polypyrrole was also synthesized on various conducting and nonconducting substrates using $Fe(ClO_4)_3$ as an oxidizing reagent. By using PP nonwoven fabric as a substrate material, a high discharge capacity of $72\,mA\,h\,g^{-1}$ was obtained. Polypyrrole synthesized on only one side of PP nonwoven fabric was able to be used as an electrode.

1. Introduction

Among various conductive polymers, polypyrrole displays good reversibility in doping and undoping. Polypyrrole is one of the most promising materials for the positive electrode of secondary lithium batteries [1–3], because the chemical stability in electrolyte solution is also good.

The electrochemical properties of polypyrrole are expected to be influenced by the chemical synthesis conditions. With regard to the relationship between polymerization conditions and polypyrrole properties, there have been many reports on electrochemical synthesis [4–10], but fewer on chemical synthesis [11–14]. In this paper the influence of oxidizing reagents for polymerization on the physical properties, morphology and electrochemical characteristics of polypyrrole are described.

One of the advantages of conductive polymer electrodes is their multiple shape capabilities due to the properties of polymers. In particular, the preparation of thin-film electrodes is useful when constructing flexible ultrathin film type batteries. From this viewpoint, the fabrication of polypyrrole thin films by a vapour polymerization method was also investigated.

2. Experimental details

2.1. *Preparation of polypyrrole electrodes*

As oxidizing reagents for polymerization (a) ferric perchlorate [$Fe(ClO_4)_3$], (b) ferric chloride [$FeCl_3$], (c) ferric nitrate [$Fe(NO_3)_3$], (d) ferric ammonium sulfate [$(NH_4)Fe(SO_4)_2$], (e) potassium persulfate [$K_2S_2O_8$], and (f) cupric tetrafluoroborate [$Cu(BF_4)_2$] were examined. In this paper, polypyrrole synthesized by $Fe(ClO_4)_3$, for instance, is written as $Fe(ClO_4)_3$–PPY.

For vapour phase polymerization, carbon paper, carbon cloth, stainless steel (SUS 304) net, and nickel foam were used as conductive substrates, and polypropylene (PP) nonwoven fabric was used as a nonconductive substrate.

These substrates were impregnated with aqueous solution of $Fe(ClO_4)_3$, and exposed to pyrrole vapour for 24 h in a sealed glass vessel to form a polypyrrole film.

2.2. *Measurement of physical and electrochemical properties*

Functional groups of polymers were examined with an FTIR spectrophotometer (Jeol, model JIR-100). The surfaces of these polymers were observed by using a scanning electron microscope (Hitachi, model S-570). Specific surface areas were measured by the BET method using a surface area analyzer (Shimadzu–Micromeritics, model 2200). The conductivity of polypyrrole was measured for pellet electrodes.

Electrochemical measurements were conducted in a beaker-type test cell. Polypyrrole powder was made into a pellet shaped electrode (60 mg, diam. 10 mm, area $0.79\,cm^2$). Polypyrrole film was cut into a sheet with an area of $4\,cm^2$ ($2\,cm \times 2\,cm$) and used as a positive electrode. Lithium metal (area $4\,cm^2$) was used as a negative electrode. An excess volume ($50\,cm^3$) of propylene carbonate (PC) containing $1\,mol\,dm^{-3}$ of $LiBF_4$ was employed as an electrolyte solution.

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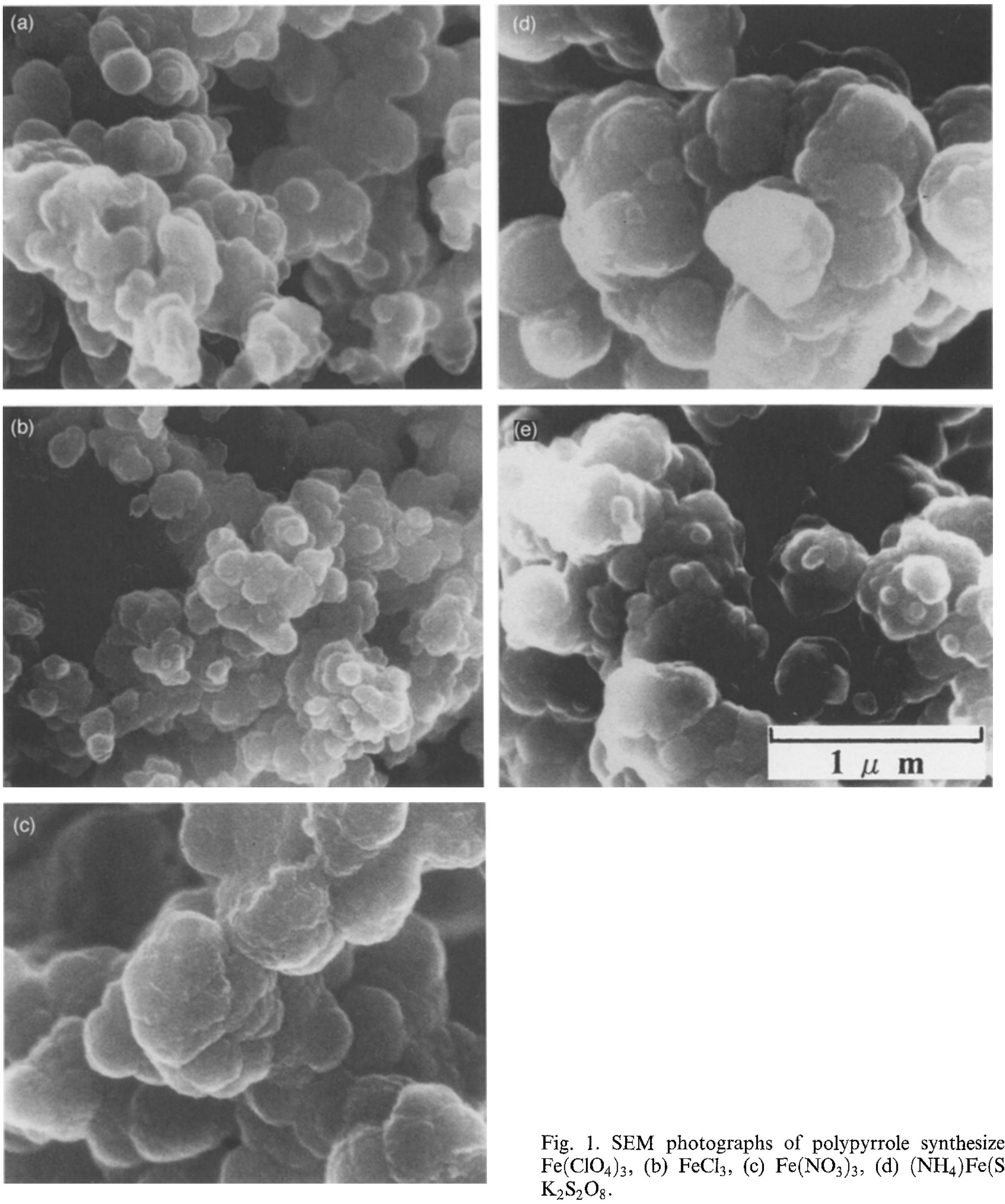

Fig. 1. SEM photographs of polypyrrole synthesized by (a) $Fe(ClO_4)_3$, (b) $FeCl_3$, (c) $Fe(NO_3)_3$, (d) $(NH_4)Fe(SO_4)_2$, (e) $K_2S_2O_8$.

3. Results and discussion

3.1. *Influence of oxidizing reagents on the morphology and physical and electrochemical properties of polypyrrole*

Polypyrrole was synthesized by using $Fe(ClO_4)_3$, $FeCl_3$, $Fe(NO_3)_3$, $(NH_4)Fe(SO_4)_2$, and $K_2S_2O_8$ as oxidizing reagents. Although all of these polypyrroles had a granular morphology, their particle size and specific surface area were different as shown in Fig. 1.

Charge–discharge curves of polypyrrole electrodes at a $17\,mA\,h\,g^{-1}$ charge depth are shown in Fig. 2. $Fe(ClO_4)_3$–PPY has a flat charge–discharge curve and an excellent coulombic efficiency of 100%. $FeCl_3$–PPY and $Fe(NO_3)_3$–PPY also have a high coulombic efficiency. $(NH_4)Fe(SO_4)_2$–PPY, however, shows poor characteristics. It should be noted that a cell using $K_2S_2O_8$–PPY showed an immediate rise in

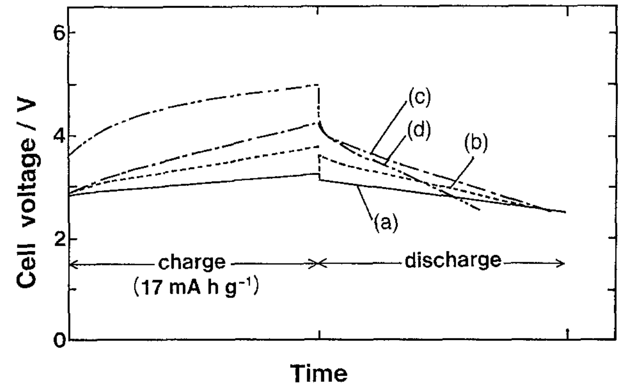

Fig. 2. Charge–discharge curves of polypyrrole/Li test cells. Polypyrrole synthesized using (a) $FeClO_4$, (b) $FeCl_3$, (c) $Fe(NO_3)_3$, (d) $(NH_4)Fe(SO_4)_2$. Electrolyte: $1\,mol\,dm^{-3}$ $LiBF_4$/PC. Charge– discharge current density: $0.64\,mA\,cm^{-2}$.

Table 1. Physical properties and charge–discharge characteristics of polypyrrole synthesized by various oxidizing reagents

Oxidizing reagent	*Specific surface area*/$m^2\,g^{-1}$	*Conductivity* /$S\,cm^{-1}$	*FTIR spectra*	*Coulombic efficiency*/%
(a) $Fe(ClO_4)_3$	21.1	3×10^{-1}	*	100
(b) $FeCl_3$	26.5	1×10^{-4}	*	98
(c) $Fe(NO_3)_3$	14.3	7×10^{-4}	*	98
(d) $(NH_4)Fe(SO_4)_2$	7.6	1×10^{-3}	†	65
(e) $K_2S_2O_8$	6.0	1×10^{-5}	†	‡

* Peaks attributed to polypyrrole.
† Peaks attributed to polypyrrole and carbonyl group (C=O).
‡ Charging was unable.

Table 2. Polypyrrole synthesized by vapour phase polymerization

Substrate	*Thickness*/μm substrate	*product*	Weight of *polypyrrole*/$mg\,cm^{-2}$
(a) Carbon paper	240	295	2.76
(b) Carbon cloth	460	540	7.97
(c) SUS net (400 mesh)	66	68	0.73
(d) Nickel foam	1433	1452	7.40
(e) PP n.w.f.	365	445	1.32
(f) PP n.w.f. (one side)	290	420	2.52

n.w.f.: nonwoven fabric.

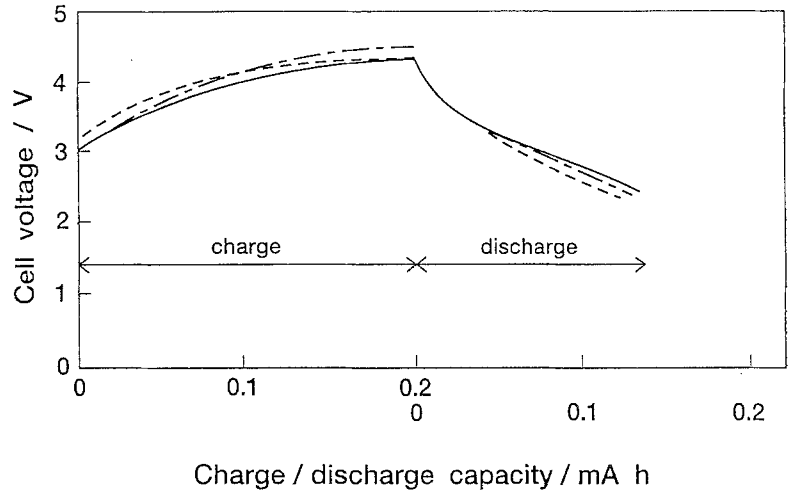

Fig. 3. Charge–discharge characteristics of polypyrrole synthesized by vapour phase polymerization (1). Electrolyte: 1 mol dm^{-3} $LiBF_4$/PC. Charge–discharge current density: 0.025 mA cm^{-2}. Key: (——) carbon paper, (– – –) carbon cloth, and (– · – ·) pp n.w.f. (one side).

cell voltage after the start of charging and was not charged.

Table 1 summarizes the specific surface area, conductivity, results of FTIR spectra, and charge–discharge coulombic efficiency of these polypyrroles.

$Fe(ClO_4)_3$–PPY and $FeCl_3$–PPY, each of which had a comparatively large specific surface area of 21.1 and 26.5 $m^2\,g^{-1}$, respectively, showed good charge–discharge performance. These polypyrroles had smaller particle sizes of 0.1 ~ 0.15 μm. On the contrary, those polypyrroles that had a smaller specific surface area of 6 ~ 13 $m^2\,g^{-1}$ and larger particle sizes of 0.25 ~ 0.35 μm, that is, $Fe(NO_3)_3$–PPY, $(NH_4)Fe(SO_4)_2$–PPY and $K_2S_2O_8$–PPY, showed poor charge–discharge performance. From these results, differences in the performance of polypyrrole electrodes can be attributed mainly to the differences in their real surface areas.

3.2. *Characteristics of polypyrrole synthesized by vapour phase polymerization*

Polypyrrole film electrodes were prepared by a vapour phase polymerization method using $Fe(ClO_4)_3$ as an oxidizing reagent.

The thickness and weight of polypyrrole films synthesized by vapour phase polymerization are summarized in Table 2. It was possible to synthesize polypyrrole on one side of PP nonwoven fabric by treating the other side with a water-repellent agent. The side without polypyrrole was confirmed to be non-conductive. Charge–discharge characteristics of polypyrrole film electrodes are shown in Fig. 3 and Fig. 4.

The results of charge–discharge tests are summarized in Table 3. Among the six tested electrodes, polypyrrole on the stainless steel net substrate could not be

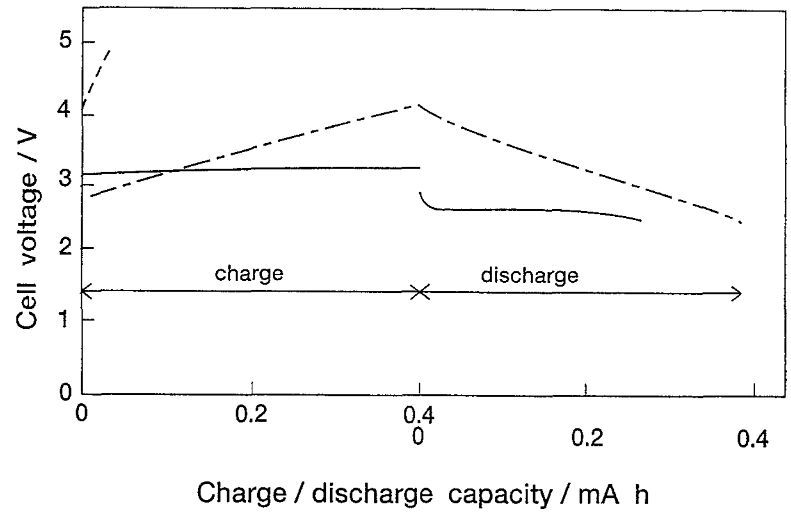

Fig. 4. Charge–discharge characteristics of polypyrrole synthesized by vapour phase polymerization (2). Electrolyte: 1 mol dm^{-3} LiBF$_4$/PC. Charge–discharge current density: 0.05 mA cm^{-2}. Key: (——) foam Ni, (– – –) stainless steel net, and (- - - -) pp n.w.f.

Table 3. Charge–discharge characteristics of polypyrrole film electrodes synthesized by vapour phase polymerization

Substrate	*Capacity* /mA h	*Capacity per unit weight*/mA h g^{-1}	*Coulombic efficiency* /%
(a) Carbon paper	0.12	11	60
(b) Carbon cloth	0.11	3.5	55
(c) SUS net (400 meth)	0 (unable to be charged)		
(d) Nickel foam	0.27	9.1	68
(e) PP n.w.f.	0.38	72	96
(f) PP n.w.f. (one side)	0.12	12	60

charged. Actually, stainless steel net is considered to be unsuitable as a substrate material because of its weak holding of the oxidizing reagent. The other polypyrrole film electrodes could be charged and discharged. In particular, polypyrrole synthesized on just one side of PP nonwoven fabric was able to be utilized as an electrode.

Polypyrrole on the PP substrate (e) shows a high discharge capacity of 72 mA g^{-1} and a coulombic efficiency of 96%. The other polypyrrole film electrodes, in contrast, show very low discharge capacities per unit weight and coulombic efficiencies. The differences in properties are considered to be caused by the differences in shape, roughness, etc., among substrates.

It is well known that electrochemical synthesis gives a film of polypyrrole on an electrode [16, 17]. However, this electrochemical method has a drawback in mass production because the size of a thin film is limited by the area of the electrode used for the electrolysis. On the other hand, polyacetylene can be obtained as a film by polymerizing acetylene on a substrate using a Ziegler–Natta catalyst [18], but application of this method is limited only to polyacetylene. For preparation of thin films of conductive polymers by the oxidative dehydrogenation polymerization of monomers, vapour phase polymerization is considered to be a useful method.

4. Conclusions

Chemically synthesized polypyrrole was examined as a positive electrode material. Through the present investigation on the morphology, physical properties and electrochemical characteristics of polypyrrole synthesized by various oxidizing reagents, the following results were obtained.

The physical properties, morphology and electrochemical characteristics of polypyrrole were greatly influenced by the oxidizing reagent used for polymerization. In general, polypyrrole with a smaller particle size and a larger specific surface area showed better discharge performance than polypyrrole with a larger particle size and a smaller specific surface area.

Polypyrrole synthesized on various conducting and nonconducting substrates, such as carbon paper, carbon cloth, nickel foam, and PP nonwoven fabric, was examined as an electrode material. Most of these electrodes could be charged and discharged. By using PP nonwoven fabric as a substrate material, a high discharge capacity of 72 mA h g^{-1} was obtained. Polypyrrole synthesized on only one side of PP nonwoven fabric was able to be used as an electrode.

References

[1] A. Mohammadi, O. Inganas and I. Lundstrom, *J. Electro-Chem. Soc.* **133** (1986) 947.
[2] P. Novak and W. Vielstich, *ibid.* **137** (1990) 1681.
[3] J. Y. Lee, L. H. Ong and G. K. Chuah, *J. Appl. Electrochem.* **22** (1992) 738.
[4] A. F. Diaz and K. K. Kanazawa, *J. Chem. Soc. Chem. Comm.* (1979) 635.
[5] K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt and G. B. Street, *J. Chem. Soc. Chem. Comm.* (1979) 854.
[6] B. J. Feldman, P. Burgmayer and R. W. Murray, *J. Am. Chem. Soc.* **107** (1985) 872.
[7] K. Naoi, H. Sakai, S. Ogano and T. Osak, *J. Power Sources* **20** (1987) 237.

[8] B. F. Cvetko, M. P. Brungs, R. P. Burford and M. Skyllas-Kazacos, *J. Appl. Electrochem.* **17** (1987) 1198.

[9] M. L. Marcos, I. Rodoriguez and J. Gonzalez-Velasco, *Electrochim. Acta* **32** (1987) 1453.

[10] L. F. Warren and D. P. Anderson, *J Electrochem. Soc.* **134** (1987) 101.

[11] J. P. Travers, P. Audebert and G. Bidan, *Mol. Cryst. Liq. Cryst* **118** (1985) 149.

[12] M. Mermilloid, J. Tanguy and F. Petiot, *J. Electrochem. Soc.* **133** (1986) 1073.

[13] H.-M. Wu, H.-J. Shy and H.-W. Ko, *J. Power Sources* **27** (1989) 59.

[14] K. Nishio, M. Fujimoto, N. Yoshinaga, N. Furukawa, O. Ando, H. Ono and T. Suzuki, *ibid.* **34** (1991) 153.

[15] H.-M. Wu, H.-J. Shy and H.-W. Ko, *ibid.* **27** (1989) 59.

[16] A. F. Diaz and K. K. Kanazawa, *J. Chem. Soc. Chem. Comm.* (1979) 635.

[17] K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini and J. F. Kwak, *Synth. Met.* **1** (1979/80) 329.

[18] H. Shirakawa and S. Ikeda, *Polym. J.* **2** (1971) 231.