

폴리피롤/설펜화 폴리(2,6-디메틸-1,4-페닐렌 옥사이드) 복합전극의 제조 및 특성

허양일 · 정홍련 · 이완진^{*,†}

전남대학교 응용화학공학부, *전남대학교 기능성나노신화학소재사업단
(2006년 10월 23일 접수, 2007년 1월 10일 채택)

Preparation and Characteristics of Polypyrrole/Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) Composite Electrode

Yang-Il Huh, Hong-Ryun Jung, and Wan-Jin Lee^{*,†}

Faculty of Applied Chemical Engineering, Chonnam National University,

*Center for Functional Nano Fine Chemicals, Chonnam National University,

300 Yongbong-dong, Buk-gu, Gwangju 500-757, Korea

(Received October 23, 2006; accepted January 10, 2007)

초록 : PPy^+DBS^- 복합체는 유화중합에 의해 제조되었고 이때 iron(III) chloride(FeCl_3)는 개시제로, dodecyl benzene sulfonic acid(DBSA)는 계면활성제 및 도판트로 사용되었다. Poly(2,6-dimethyl-1,4-phenylene oxide)(PPO)는 chlorosulfonic acid(CSA)를 사용하여 설펜화되었고 양극은 PPy^+DBS^- 복합체, 도전제 그리고 바인더로 구성되며 이때 바인더로 PPO와 설펜화된 poly(2,6-dimethyl-1,4-phenylene oxide)(SPPO)를 사용하였다. $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ 양극은 $\text{PPy}^+\text{DBS}^-/\text{PPO}$ 에 비해 약 50% 높은 충·방전 성능을 나타내었는데 이는 SPPO가 바인더뿐만 아니라 도판트로 작용했기 때문이다. 더욱이 바인더로 사용된 고분자의 설펜화는 전도성 고분자와의 coulombic attraction을 유발시켜 두 상간의 혼화성을 증가시켰을 뿐만 아니라 양극과 전해질 사이의 접촉면적을 증가시켜 전기화학적으로 우수한 성능을 나타나게 했다.

Abstract : Polypyrrole (PPy) was made by an emulsion polymerization using iron(III) chloride (FeCl_3) as an initiator and dodecyl benzene sulfuric acid (DBSA) as an emulsifier and dopant. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was sulfonated by chlorosulfonic acid (CSA). The cathode was composed of PPy^+DBS^- complex, conductor powder, and PPO or sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) as a binder or dopant. The charge-discharge performance of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ cathode was increased as the extent of about 50% than $\text{PPy}^+\text{DBS}^-/\text{PPO}$. This is because SPPO played a role as a binder as well as a dopant. In addition, sulfonation brings out the increase of miscibility between PPy and SPPO, and the increase of contact area between cathode and electrolyte.

Keywords : polypyrrole, sulfonation, poly(2,6-dimethyl-1,4-phenylene oxide), electrochemical property.

Introduction

Electronically π -conjugated conducting polymer has received a lot of attention as the promising electrode materials for polymer battery,¹⁻⁴ electrochemical capacitor⁵⁻⁹ and fuel cell,¹⁰⁻¹² and so on. In particular, the conducting polymers such as polyaniline, polypyrrole, and polythiophene are mainly focused as a cathode by p-doping. The cathode based on lithium-conducting polymer is composed of an active material like conducting polymer, an electronic conducting agent like carbon powder, and a polymer binder like poly-

(vinylidene fluoride) (PVDF). The use of polymer binders is intensively concerned with the electrochemical performance of electrodes, the adherence of the electrode and current collector, and the electrical conductivity. The electrochemical redox process of the electrode concerning conducting polymer greatly depends on the dopant as an anion,^{13,14} electrode morphology, polymer binder, and the electrical conductivity. Especially, polymer binder using about 10 wt% is deeply related to the electrical conductivity affecting the electrochemical performance. The use of the hydrophobic polymer binder to the electrode results in the decrease of the electrical conductivity, the increase of the interfacial resistance between the electrode and electrolyte, and the decrease of the elec-

[†]To whom correspondence should be addressed.
E-mail: wjlee@chonnam.chonnam.ac.kr

trochemical performance to hinder free movement of electrons. The hydrophobic polymer binder like PVDF¹⁵⁻¹⁷ lessens the compatibility of conducting polymer composite and the active material of electrode, and then the occurrence of phase separation lowers the electrical conductivity. Finally this leads to the decrease of electrochemical performance. Recently, the method to improve the electrical conductivity of conducting polymer composite has been attempted by blending the sulfonated polymer to the conducting polymer.¹⁸⁻²⁰ This leads to the increase of the electrical conductivity due to the increase of the compatibility to minimize the phase separation. The study on the effect of sulfonated polymer binder on the electrochemical performance has seldom been reported.

In this study, the effect of PVDF, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and sulfonated PPO (SPPO) as binders was compared. We, mainly, focus on the effect of SPPO as a polymer binder in a PPy/SPPO composite system. PPy was prepared by an emulsion polymerization using dodecyl benzene sulfuric acid (DBSA), and then became p -doping as the type of PPy^+DBS^- . The SPPO in a $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ system was used as a polymer binder and a dopant.

Experimental

Materials. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (M_w : 244000, M_n : 32000, T_g : 11, T_m : 268) purchased from Aldrich Co. Pyrrole monomer purchased from Across Chemical Co. was used with distillation. The iron (III) chloride was purchased from Aldrich Co. Chlorosulfonic acid (CSA) was used as sulfonic agent, which was purchased Kanto Chemical Co. The chloroform (Junsei Chemical Co.) and tetrahydrofuran (THF, Aldrich Co.) were used as solvents. DBSA used as both protonating and emulsifying agent were purchased from Aldrich Co. Carbon black (Super-P, MMM Carbon Co.) was used as a conducting agent, and Li metal was used as electrode materials. The electrolyte was used the mixture of 1:1 vol% propylene carbonate (PC)/dimethylcarbonate (DMC) and LiClO_4 salt.

Sulfonation of SPPO. 10 wt% PPO was completely dissolved in chloroform by mechanical mixing in a three-neck flask at room temperature. Then, chlorosulfonic acid was dropped slowly with vigorous stirring in a nitrogen atmosphere. The reaction was completed in 1 h. The product was precipitated by boiling water and washed several times using boiling water. The sulfonated PPO (SPPO) was obtained as a powder sample after it was dried for 12 h in a vacuum oven. The degree of sulfonation of PPO was reported to the previous study.¹⁸ SPPO of 35% sulfonation degree was used in this study, and the other information such as NMR and TGA

spectra is provided.

10 wt% SPPO was completely dissolved in chloroform by mechanical mixing, and then a LiOH aqueous solution was added to substitute the lithium atom for the protons of the sulfuric group of SPPO through vigorous stirring. The product was precipitated by deionized water and washed several times using water and methanol. Finally, lithiated SPPO was obtained as a powder sample after it was dried for 12 h in a vacuum oven. In this study, SPPO was used Li-substituted SPPO. Hence, lithiated SPPO is denoted as SPPO.

Preparation of Composite Electrode. PPy^+DBS^- complex is prepared by a chemical polymerization. At first, 34 g of DBSA, acting as an emulsifying agent and dopant, was vigorously stirred in water in a 50 mL three-neck flask, and then an aqueous solution of 40 g of FeCl_3 in 80 mL water, acting as an oxidant, was added with vigorous stirring. The molar ratio of DBSA and FeCl_3 to pyrrole was 1 : 2.2.²¹ After that, the solution of 5 g pyrrole in 20 mL chloroform was added at room temperature with stirring. The polymerization was allowed to proceed for about 12 h. The product solution was filtered and washed with methanol. The conducting polymer powder was dried in a vacuum oven at 50 °C for one day.

The cathode was composed with PPy^+DBS^- complex and carbon black as a conducting agent and PVDF, PPO, or SPPO as binders. At first, PPy^+DBS^- and carbon black were dissolved in THF, and then added polymer solution such as PVDF, PPO, and SPPO as binders in THF. The completely dissolved slurry was cast on Al mesh and pressed during 10 sec at 70 °C, 500 psi. Finally, the cathode was dried at 50 °C in vacuum oven. In this study, the content of polymer binder was fixed as 10 wt%. The ratio of PPy^+DBS^- complex, carbon black and binder was 80:10:10, 75:10:15, and 70:10:20 by wt%. The anode was prepared by pressing Li metal on Ni Mesh. Sandwich-type cells were constructed with cathode, anode and porous propylene film as a separator. The liquid electrolyte was used 1M LiClO_4 +PC/DMC (1:1 vol%). The redox reaction of various cathodes was investigated by cyclic voltammetry. The half cell was composed as WE, CE (Li), and RE (Li) to get cyclic voltammogram. Lithium electrodes were used as a reference and a counter electrode. Cyclic voltammetric measurements were performed in a potential range of 0 to 3.5 V to use 1 M LiClO_4 in PC/DMC (1:1 vol%) as an electrolyte solution. The scan rate was from 5 to 20 mV/sec. The charge-discharge test was performed to measure the performance of the $\text{Li}/\text{PPy}^+\text{DBS}^-/\text{SPPO}$ (or PPO) battery in the range of 0 to 3.5 V. In order to test charge-discharge properties, two electrodes were assembled as a sandwich type and enveloped in a

laminated-aluminum pouch in glove box. Typical galvanostatic charge-discharge measurement used Potentiostat/Galvanostat (Won A Tech. Korea). The impedance spectroscopy test was measured from 1 Hz to 100 MHz using an ac impedance analyzer (Zahner Elektrik IM6e). The electrical conductivity was determined by a standard four-probe method to make conducting polymer composite film by compression molding at 50 °C in 500 psi. Also, scanning electron microscopy (SEM) of the electrically conductive composite film were obtained with a Hitachi S-4700 (Japan) instrument. Infrared studies of composite films were carried out on a Mattson 1000 FTIR spectrometer.

Results and Discussion

Figure 1 represents the ^1H NMR spectra of PPO and SPPO. In case of PPO, the symmetric peak of benzene rings shows at about 6.4 ppm. The peak of CH_3 is shown in the vicinity of 2.1 ppm. In case of SPPO, two peaks appeared in the range of 2.0–2.2 ppm. One peak indicates CH_3 of the portion of PPO not to be sulfonated, the other peak points out CH_3 of the portion of PPO to be sulfonated. In other word, a new peak of CH_3 at about 2.2 ppm comes into view by disappearing the symmetric structure to introduce SO_3H group to PPO. This means that PPO is partially sulfonated. The reactive substitution position is situated meta to the aryl ether linkage in the dimethyl phenylene oxide unit. This position is the most favorable site because it is electrophilicity activated by hydrogen rather than methyl group.

Figure 2 shows that the result of FTIR of the original PPO was compared with that of SPPO. The typical peaks of SO_3H absorption are shown at 1250–1150, 1060–1030, and 600–700 cm^{-1} . The strong band at 1250–1150 cm^{-1} can be ascribed to a stretch vibration for $\text{S}=\text{O}$, and the absorption band at the 1060–1030 cm^{-1} is assigned to the symmetric stretching band. The weak peak by the effect of sulfonation is assigned to the frequency of 600–700 cm^{-1} . In addition, the absorption band at 3500–3200 cm^{-1} is assigned to the stretching band because of hydrogen

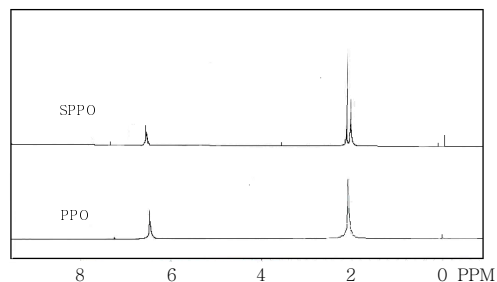


Figure 1. NMR spectra of PPO and SPPO.

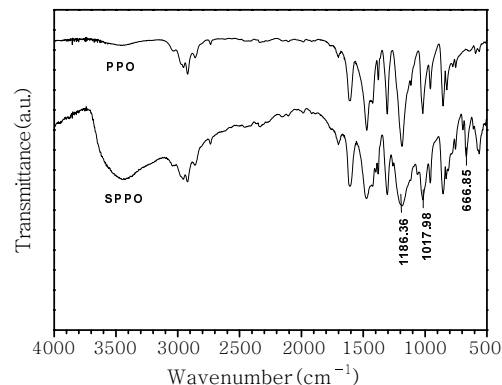


Figure 2. FTIR spectra of PPO and SPPO.

Table 1. Electrical Conductivities of PPy/PPO, PPy/PVDF, and PPy/SPPO

Polypyrrole	Binder contents	Carbon black	Electrical
80 wt%	10 wt% PVDF	10 wt%	0.23
80 wt%	10 wt% PPO	10 wt%	0.33
80 wt%	10 wt% SPPO	10 wt%	0.58

bonding.

The electrical conductivities of $\text{PPy}^+\text{DBS}^-/\text{PPO}$, $\text{PPy}^+\text{DBS}^-/\text{PVDF}$, and $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ were measured by the four probes method. The electrical conductivities of $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ and $\text{PPy}^+\text{DBS}^-/\text{PPO}$ were shown in Table 1. The electrical conductivities of $\text{PPy}^+\text{DBS}^-/10 \text{ wt\% PPO}$, $\text{PPy}^+\text{DBS}^-/10 \text{ wt\% PVDF}$ were 0.33 and 0.23 S/cm, respectively, while that of $\text{PPy}^+\text{DBS}^-/10 \text{ wt\% SPPO}$ was 0.58 S/cm. The electrical conductivities of $\text{PPy}^+\text{DBS}^-/\text{PPO}$ and $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ have the low values by the existence of phase separation because the PPO used as only a binder is hydrophobic. However, the electrical conductivity of $\text{PPy}^+\text{DBS}^-/\text{PPO}$ was slightly higher than that of $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ because of polarity of oxygen atom in PPO. On the contrary, in the case of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$, the electrical conductivity is increased because SPPO promotes the improvement of wettability and compatibility owing to the effect of coulombic interaction between PPy and SPPO.¹⁸

Figure 3 shows the views of SEM for the surface of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ composite, $\text{PPy}^+\text{DBS}^-/\text{PPO}$ and $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ one. In all composites, the PPy particles are shown as small spherical granules with well-developed micro porosity. However, in Figure 3(a) and (b), the phase separation exists between PPy and PPO or PVDF binder, and this ascribes to the decrease of electrochemical performance due to the decrease of electrical conductivity. On the other hand, in Figure 3(c), the phase separation is minimized between PPy and SPPO owing to the role as a dopant of SPPO. This brings out the enhancement of electrochemical performance.

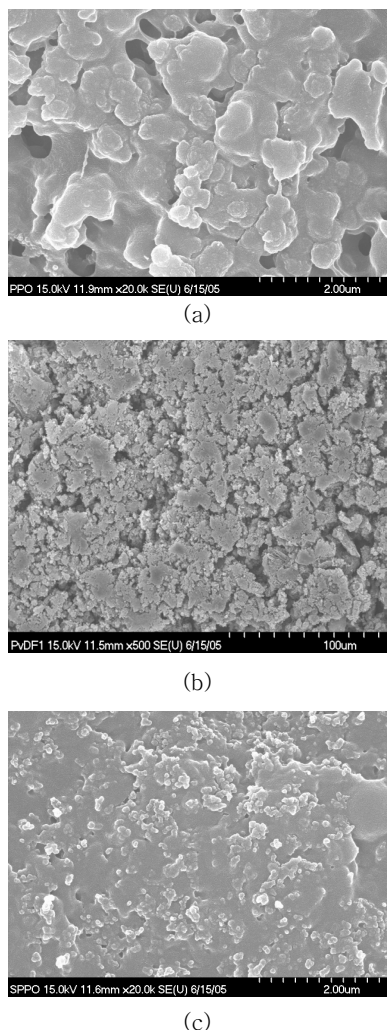


Figure 3. The scanning electron microscopy (SEM) images of (a) PPy/PPO electrode, (b) PPy/PVDF, and (c) PPy/SPPO electrode.

Figure 4 shows the impedance spectra by Nyquist plots with various binders of the cathode in the range of 1 Hz to 1 MHz for $\text{PPy}^+\text{DBS}^-/\text{PVDF}$, $\text{PPy}^+\text{DBS}^-/\text{PPO}$, and $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ electrodes, respectively. The measurement of impedance was carried out under three electrodes to use Li metal as a reference electrode. The interfacial resistances were about 19, 18, 8 Ω with PVDF, PPO, or SPPO binders in the cathode, respectively. The differences of the interfacial impedance are considered to originate from differences in both the role of binders and the electrical conductivity of the composite. For Nyquist plots, generally, the shape of semicircle in the higher frequency region is representing to the charge-transfer process of cathode with doping and de-doping of dopant, and the inclined line in the lower frequency region represents the mass transfer of dopant in cathode. The interfacial resistances of $\text{PPy}^+\text{DBS}^-/\text{PVDF}$, and $\text{PPy}^+\text{DBS}^-/\text{PPO}$

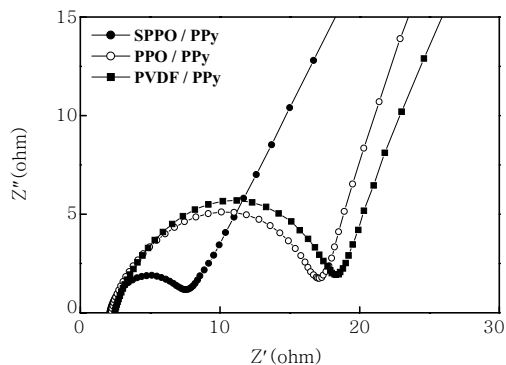


Figure 4. Impedance spectra of the PPy/SPPO electrode, PPy/PPO electrode and PPy/PVDF electrode at the room temperature.

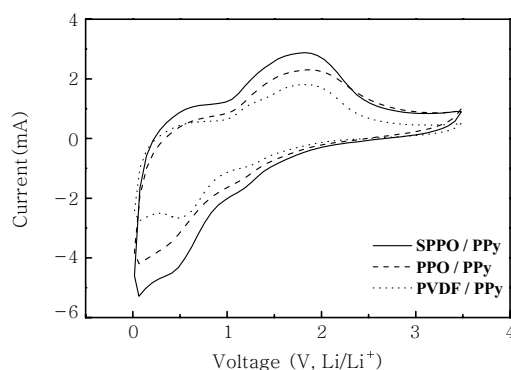


Figure 5. Cyclic voltammogram of the PPy/SPPO electrode, PPy/PPO electrode, and PPy/PVDF electrode at 10 mV/s.

are higher than $\text{PPy}^+\text{DBS}^-/\text{SPPO}$. This is considered to originate from the phase separation between PPy and PPO or PVDF because PPO or PVDF as a binder is the hydrophobic polymer. The interfacial resistance of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ was the lowest among three electrodes. This is because SPPO act as a binder as well as a dopant, and $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ composite is the highest electrical conductivity. In specific, introduction of sulfonation brings out to increase both the miscibility between PPy and binder, and contact area between cathode and electrolyte.

Figure 5 shows the cyclic voltammograms of $\text{PPy}^+\text{DBS}^-/\text{PVDF}$, $\text{PPy}^+\text{DBS}^-/\text{PPO}$, and $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ electrodes in 1 M LiClO_4 + PC/DMC (1:1 vol%) as an organic liquid electrolyte at scan rate of 10 mV/sec in the range of 0 to 3.5 V. In the three electrodes, the oxidation and reduction peak are observed at about 1.8 and 0.5 V, respectively. The current range increases with the classification of dopant. The current of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ electrode is larger than other electrodes. The effect of sulfonation of PPO brings out the increase of the charge capacity and the surface of the electrode by increasing the active sites in redox process.

Figure 6 represents the variation of voltage against specific capacitance for $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PVDF})$, $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PPO})$, and $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{SPPO})$ cell in the fifth discharge test. The amount of binder was 10 wt%. The cycle test was carried out in the range of 0 to 3.5 V with $0.5 \text{ mA}/\text{cm}^2$. The discharge capacities of $\text{PPy}^+\text{DBS}^-/\text{PPO}$ and $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ electrodes show 50 and 41 mAh/g, respectively, while that of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ shows 74 mAh/g. The specific capacitance of $\text{PPy}^+\text{DBS}^-/\text{PPO}$ and $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ was relatively low because PPO and PVDF played a role as only binder. On the other hand, the specific capacitance of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ was very high because SPPO act as both a binder and a dopant.

Figure 7 represents the variation of the specific discharge capacities for $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PVDF})$, $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PPO})$, and $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{SPPO})$ cell with the number of cycles, respectively. As mentioned at Figure 7, the specific capacities of $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PVDF})$, $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PPO})$, and $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{SPPO})$ cell at the fifth cycles represent were 41, 50, and 74 mAh/g, respectively. The specific discharge capacity of $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{SPPO})$ cell was best.

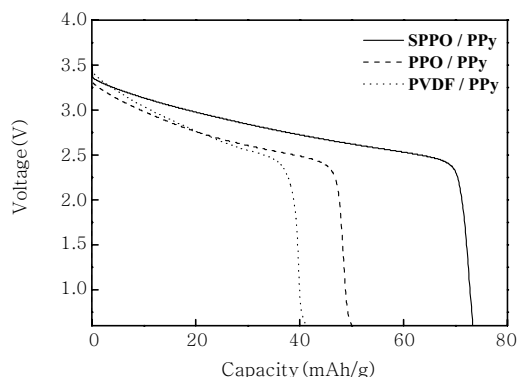


Figure 6. The 5th discharge profile of $\text{Li}/(\text{PPy}/\text{SPPO})$, $\text{Li}/(\text{PPy}/\text{PPO})$, and $\text{Li}/(\text{PPy}/\text{PVDF})$ cell at $0.5 \text{ mA}/\text{cm}^2$ current density.

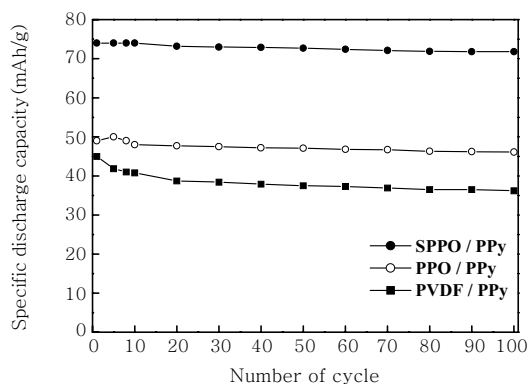


Figure 7. The specific discharge capacities for $\text{Li}/(\text{PPy}/\text{SPPO})$, $\text{Li}/(\text{PPy}/\text{PPO})$, and $\text{Li}/(\text{PPy}/\text{PVDF})$ cell at $0.5 \text{ mA}/\text{cm}^2$ current density.

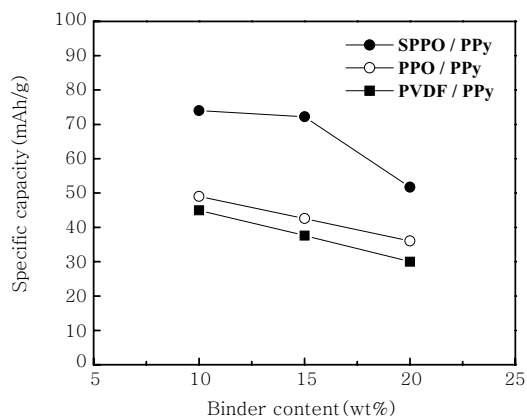


Figure 8. The specific discharge capacities with the binder for $\text{Li}/(\text{PPy}/\text{SPPO})$ and $\text{Li}/(\text{PPy}/\text{PPO})$ cell in 100th.

This is because the SPPO shows the decrease of interfacial resistance to act as an additional dopant. Meanwhile, in three electrodes, the specific discharge capacities decreased gradually with the number of cycles. This ascribed to the degradation of PPy in organic liquid electrolyte. It can be guessed that the degradation of PPy occurred by swelling and shrinking with the number of cycle.

Figure 8 represents the variation of the specific discharge capacities with the contents of binder for $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PPO})$, $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{PVDF})$, and $\text{Li}/(\text{PPy}^+\text{DBS}^-/\text{SPPO})$ cells in 100 cycles. In this study, SPPO, 35% sulfonation degree, was used. The specific capacitance decreases in all cases as the contents of binder increases. In the case using PPO and PVDF, the specific capacitance is proportionally decreased. This is why the electrical conductivity is decreased with increasing the contents of PPO and PVDF. However, the specific capacitance of $\text{PPy}^+\text{DBS}^-/\text{PPO}$ was slightly higher than that of $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ because of polarity of oxygen atom in PPO. In the case using SPPO, even though the specific capacitance is decreased with the contents of SPPO, the case of 10 wt% SPPO is nearly same compared to the case of 15 wt% SPPO, but the case of 20 wt% SPPO is sharply decreased. In the case using 15 wt% SPPO as a binder, SPPO act as both binder and dopant. In the case using 20 wt% SPPO as a binder, although SPPO act as binder as well as dopant, the specific capacitance was sharply decreased because of the decrease of the electrical conductivity with the content of SPPO.

Conclusions

Polypyrrole (PPy) was made by an emulsion polymerization using iron(III) chloride (FeCl_3) and DBSA. DBSA act as an emulsifying agent and dopant. The discharge capacities

of $\text{PPy}^+\text{DBS}^-/\text{PPO}$ and $\text{PPy}^+\text{DBS}^-/\text{PVDF}$ electrodes show 50 and 41 mAh/g at 0.5 mA/cm^2 current density, respectively, while that of $\text{PPy}^+\text{DBS}^-/\text{SPPO}$ shows 74 mAh/g. The specific capacitance using PPO and PVDF was relatively low because PPO and PVDF played a role as only binder. On the other hand, the specific capacitance using SPPO was very high because SPPO act as a binder as well as a dopant.

Acknowledgements : This research was supported in part by BK21 program from the Ministry of Education & Human Resources Development.

References

1. K. Gurunathan, D. P. Amalnerkar, and D. C. Trivedi, *Mater. Lett.*, **57**, 1642 (2003).
2. J. Wang, C.O. Too, D. Zhou, and G.G. Wallace, *J. Power Sources*, **140**, 162 (2005).
3. Y. H. Lee, W. S. Shim, and D. S. Lee, *Polymer(Korea)*, **23**, 587 (1999).
4. J.-M. Kim, H.-W. Lee, S.-H. Song, S.-M. Chang, J.-E. Sohn, H. Muramatsu, and Y.-K. Chang, *Polymer(Korea)*, **22**, 106 (1998).
5. W.-C. Chen and T.-C. Wen, *J. Power Sources*, **117**, 273 (2003).
6. T.-M. Wu, Y.-W. Lin, and C.-S. Liao, *Carbon*, **43**, 734 (2005).
7. V. Khomenko, E. Frackowiak, and F. Béguin, *Electrochimica Acta*, **50**, 2499 (2005).
8. G. Y. Han, J. Y. Yuan, G. Q. Shi, and F. Wei, *Thin Solid Films*, **474**, 64 (2005).
9. K. S. Ryu, Y. G. Lee, K. -S. Han, Y. J. Park, M. G. Kang, N.-G. Park, and S. H. Chang, *Solid State Ionics*, **175**, 765 (2004).
10. F. Xie, Z. Tian, H. Meng, and P. K. Shen, *J. Power Sources*, **141**, 211 (2005).
11. J. -H. Park, J. -H. Kim, H. -K. Lee, T. -H. Lee, and Y. -I. Joe, *Electrochimica Acta*, **50**, 765, (2004).
12. H. K. Lee, J. Y. Kim, J. H. Park, Y. G. Joe, and T. H. Lee, *J. Power Sources*, **131**, 188 (2004).
13. R. C. Patil, S. Radhakrishnan, and K. Ogura, *Polymer Degradation and Stability*, **73**, 7 (2001).
14. T. L. A. Campos, D. F. Kersting, and C. A. Ferreira, *Surf. Coat. Tech.*, **122**, 3 (1999).
15. M. Yoo, C. W. Frank, S. Mori, and S. Yamaguchi, *Polymer*, **44**, 4197 (2003).
16. M. Manickam and M. Takata, *Electrochimica Acta*, **48**, 957 (2003).
17. M. Wachtler, M. R. Wagner, M. Schmied, M. Winter, and J. O. Besenhard, *J. Electroanal. Chem.*, **510**, 12 (2001).
18. W.-J. Lee, H.-R. Jung, C. Kim, M. S. Lee, J.-H. Kim, and K. S. Yang, *Synth. Met.*, **143**, 59 (2004).
19. W.-J. Lee, Y.-J. Kim, M.-O. Jung, D.-H. Kim, D. L. Cho, and S. Y. Kang, *Synth. Met.*, **123**, 327 (2001).
20. R. Scherer, A. M. Bernardes, M. M. C. Forte, J. Z. Ferreira, and C. A. Ferreira, *Mater. Chem. Phys.*, **71**, 131 (2001).
21. S. S. Im and S. W. Byun, *J. Appl. Polym. Sci.*, **51**, 1221 (1994).