— Note —

Electrochemical Behaviors of Polyaniline/ Poly (aniline-2,5-disulfonic Acid) Composites

Akira KITANI,* Kenji IWAI, and Sotaro ITO

Faculty of Engineering, Hiroshima University (Kagamiyama, Higashi-Hiroshima 739-8527, Japan)

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Polyaniline/anionic-polymer composites are important for battery applications due to the cation-inserting property. Electroactive poly-aniline-2,5-disulfonic acid (poly-ADSA) was used instead of conventional electroinactive sulfonated polymer. Polyaniline/poly-ADSA composite was prepared by electrochemical dopant exchange. The redox charge of resulting composite increased up to 120 % of the initial value. The specific capacity was determined to be 98 Ah/kg in aqueous solution and 70 Ah/kg in propylene carbonate solution.

Key Words : Self-doped Polyaniline, Poly(aniline-2,5-disulfonic acid), Electrochemical Behavior, Specific Capacity

1 Introduction

Polyaniline (PAn) having cation-inserting properties is particularly interesting for battery applications to minimize the volume of electrolyte solution. A convenient method for the preparation of cation-inserting PAn electrode is the modification of PAn surface by anionic polymers as a bulky dopant.¹⁾ However, the use of electroinactive anionic polymers considerably reduces the specific capacity of polymer electrode itself. Utilization of electroactive anionic PAn as a polymeric dopant is promising for battery applications.²⁾ Recently, we succeeded in the preparation of highly sulfonated PAn by electrochemical polymerization of aniline-2,5-disulfonic acid (ADSA).^{3,4)} In this study, electroactive poly-aniline-2,5-disulfonic acid (poly-ADSA) was used instead of conventional electroinactive sulfonated polymer like polystyrene sulfonic acid (PSS). If the composite thus obtained works well, its specific capacity should be the same as that of PAn.

2 Experimental

Poly-ADSA was synthesized by electropolymerization of ADSA under controlled current as described in our previous paper.³⁾ PAn was deposited by controlled potential electrolysis at 0.9 V (vs. SCE) onto Pt plate (2×2 cm) in 0.1 M ($M = \text{mol dm}^{-3}$) H_2SO_4 aqueous solution containing 0.1 M aniline under N_2 atmosphere at 25 °C. PAn deposit was reduced electrochemically in 0.1 M H_2SO_4 , then undoped by treating with 0.1 M NaOH solution for 30 minutes. Undoped PAn was doped in 0.1 M poly-ADSA aqueous solution (molar concentration corresponds to monomeric form) by continuous potential cycling between -0.2 and 1.0 V at 5 mV/s (Potential sweep method) or by repeated constant potential electrolysis at -0.2 V and 1.0 V (Potentiostatic method). Voltammetric

behaviors of PAn/poly-ADSA composite were measured in 0.1 M H_2SO_4 aqueous solution with a sweep rate of 1 mV/s, and compared with those of untreated PAn electrode. Charging-discharging behaviors of PAn composite electrode were measured in propylene carbonate (PC) solution containing 0.1 M LiClO_4 under controlled current density of 0.2 mA/cm² at 25 °C.

3 Results and Discussion

3.1 Electrochemical behaviors of poly-ADSA doped PAn in aqueous solution

Figure 1 shows the cyclic voltammogram of poly-ADSA doped PAn in 0.1 M H_2SO_4 solution. PAn/poly-ADSA composite was obtained after 50 cycles of repeated constant potential electrolysis (1 cycle : oxidized at 1.0 V until the current reached to background level, then reduced at -0.2 V). Unlike untreated PAn, PAn/poly-ADSA composite showed one oxidation peak. Since the oxidation peak potential of poly-ADSA (*ca.* 0.4 V) is in the middle of the first (*ca.* 0.2 V) and the second (*ca.* 0.7 V) oxidation peak of ordinary PAn,³⁾ these three peaks merged into one wave.

The anodic charge of PAn/poly-ADSA composite was compared to that of untreated PAn, and plotted as a function of cycle number of electrochemical dopant exchange (Fig. 2). The oxidation charge increased with successive electrochemical doping-undoping treatment, and reached to the steady value after about 35 cycles regardless of the methods employed (Potential sweep or Potentiostatic).

The redox charge increased up to 120 % of the value of untreated PAn, indicating electroactive poly-ADSA was doped electrochemically. The specific capacity was determined to be 98 Ah/kg, which is almost the same as that of PAn (108 Ah/kg).

Fig. 1 Cyclic voltammogram of poly-ADSA doped PAN in 0.1 M H_2SO_4 aqueous solution at 1 mV/s. Sample was prepared by potentiostatic method (50 cycles).

Fig. 2 Change of redox charge of poly-ADSA doped PAN during electrochemical doping.

Charge ratio = anodic charge of composite / anodic charge of untreated PAN

Empty square : Potential sweep method, Full circle : Potentiostatic method.

3. 2 Redox activity of the resulting composite in non-aqueous solution

It was found that poly-ADSA doped PAN shows high redox activity in aqueous media as expected. The electrochemical behavior of the composite in non-aqueous media is also of interest. Charging-discharging behavior of the resulting composite, obtained by potentiostatic method after 50 cycles, was measured in PC solution containing 0.1 M LiClO_4 .

The composite electrode showed the excellent charging-discharging characteristics with high coulombic efficiency. As shown in Fig. 3, the specific capacity was determined to be 70 Ah/kg. This value is lower than that of PAN, but is still higher than that of PAN/PSS composite electrode (54 Ah/kg).¹⁾ Almost similar results were obtained for the composite prepared by potential sweep method.

Fig. 3 Charging-discharging behavior of PAN/poly-ADSA composite electrode in 0.1 M LiClO_4 /PC solution under controlled current of 0.2 mA/cm². Dotted line indicates 100 % coulombic efficiency.

3. 3 Redox activity of aniline / ADSA copolymer in PC

Since redox activity of poly-ADSA doped PAN was not high enough in PC solution, charging-discharging characteristics of aniline/ADSA copolymer were also studied. The copolymer electrode was prepared by continuous potential cycling in 0.5 M HCl solution containing 10 mM aniline and 190 mM ADSA as described in our previous paper.⁵⁾ The content of ADSA moiety was estimated to be 30 % based on the atomic ratio of sulfur to nitrogen determined by using ESCA measurements. However, the specific capacity of copolymer, determined in 0.1 M LiClO_4 /PC solution, decreased to 55 Ah/kg.

In the present stage, the specific capacities of PAN/poly-ADSA composites are high enough in aqueous solution, but they are not satisfactory in PC solution. Further studies are needed to improve the redox activity in non-aqueous solutions.

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