Electrochemical Properties of Polyaniline Electrodes Prepared by Chemical Synthesis and Electrodeposition: Revisited with High-Scan-Rate Behaviors

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ABSTRACT :

The polyaniline (PANI) electrodes are prepared by chemical synthesis and electrodeposition methods and their supercapacitive properties are characterized and compared by morphology observation, cyclic voltammetry as a function of scan rate, and impedance spectra analysis. In particular, the supercapacitive properties obtained in the range of higher potential scan rates (e.g., over 200 mV s⁻¹) are emphasized to be capable of utilizing adequately the high power capability of supercapacitor. As a result, the PANI electrode by the electrodeposition shows superior specific capacitance (max. 474 F g⁻¹ at 10 mV s⁻¹ and about 390 F g⁻¹ at 500 mV s⁻¹) than those by the chemical synthesis method. This is mainly due to highly porous structure obtained by the electrodeposition to yield higher specific surface area.

Keywords: Polyaniline, Chemical synthesis, Electrodeposition, Supercapacitive property

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1. Introduction

Polyaniline (PANI) is one of most commonly used conducting polymers as an electrode of supercapacitors,¹⁻⁵⁾ due to its high conductivity, stable redox behavior, environmental friendliness, and even good processability. In early stage for supercapacitor application, chemically synthesized PANI electrodes with different routes achieved comparatively low specific capacitances, e.g., 237 or 335 F g⁻¹ at 100 mV s⁻¹,^{5,6)} due to compact granular morphology which is similar to previous reports.^{7,8)} However, the specific capacitance of PANI electrode could be improved by adopting various synthesis techniques. For instance, the

nanograined PANI prepared by a chemical bath deposition showed a specific capacitance of 503 F g⁻¹ at 10 mV s⁻¹.⁹⁾ The PANI thin film by a microwave-assisted chemical deposition exhibited 753 F g⁻¹ at 5 mV s⁻¹.¹⁰⁾ The electrochemical deposition of PANI yielding the shapes of nanorod,¹¹⁾ nanowire,¹²⁾ and nanowire networks^{13,14)} greatly improved the specific capacitance up to 839 F g⁻¹ at the low scan rate of 10 mV s⁻¹.

However, such the higher capacitance values were obtained in the range of comparatively low scan rates, e.g., 5-200 mV s⁻¹, as summarized in Fig. 3. This figure is introduced in advance for comparison of the previously reported capacitance results as a function of potential scan rate. The nanostructured PANI electrodes obtained by chemical and electrochemical depositions showed very steeply decreasing pattern of capacitance in the range of low scan rates. Meanwhile,

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the bulk PANI electrodes obtained by chemical synthesis exhibited a monotonously decreasing pattern of capacitance in the range of high scan rates. It is thus curious that the steeply decreasing pattern may be relaxed to a monotonous curve with high capacitance values in the range of high scan rates.

In this study, we simply test the supercapacitive properties in a wide scan rate region, covering both the low and high scan rate regions, for PANI electrodes obtained by a chemical synthesis and an electrodeposition method. The PANI electrode by the chemical synthesis is prepared as two samples with and without adopting carbon black to examine the effect of conductive agent. The readers should bear in mind that this study just compares the supercapacitive properties of bulk PANI electrodes, not nanostructured PANIs, obtained by simple chemical synthesis and electrodeposition technique.

2. Experimental

The PANI powder by chemical synthesis was obtained by following procedures: 7 g of aniline monomer (Junsei) was added to the 300 mL of 1 M HClO₄ solution and sonicated to achieve good dispersion. After sonication, the solution was cooled down to 1°C. About 200 mL of 1 M HClO₄ solution containing ammonium persulfate oxidant was then added to the monomer solution drop by drop for 1 h with mechanically stirring at 300 rpm. The stirring was continued overnight after the temperature increased to 15°C. The resultant solid was then filtered, washed, and dried at 40°C to yield the PANI powder. The Brunauer-Emmett-Teller (BET) surface area was measured using a Smartsorb-92/93 and then resulted in 82 m² g⁻¹. The morphology of the PANI powder was examined using a scanning electron microscope (Jeol, JSM-6300). Two kinds of PANI electrode were prepared from the PANI powder obtained by chemical synthesis: (i) the electrode consisting of PANI powder (90 wt%) mixed with poly(vinylidene fluoride) (Aldrich) (10 wt%) [designated as cPANI (no Super P)], and (ii) the electrode consisting of PANI powder (90 wt%) mixed with carbon black (Super P, Timcal) (5 wt%) and poly(vinylidene fluoride) (Aldrich) (5 wt%) [designated as cPANI (Super P)]. The loading density of PANI as an active material in the chemically synthesized PANI electrodes was determined as 1.10 mg cm⁻².

The electrodeposition of PANI on a Pt substrate was carried out potentiodynamically using an Autolab instrument (PGstat 100, Eco-Chemie) by subjecting the working electrode to potential cycling between -0.05 and 0.85 V at a scan rate of 500 mV s⁻¹ in an aqueous electrolyte solution consisting of 0.1 M aniline and 0.2 M H₂SO₄ for 150 cycles under N₂ atmosphere. An electrochemical cell was assembled in a three-electrode configuration in which the working and counter electrodes were Pt (1 × 1 cm²), and the reference electrode was an Ag/AgCl (saturated KCl, 0.222 V vs. SHE). The BET surface area measured was evaluated as 168 m² g⁻¹. The loading density of PANI as an active material in the electrodeposited PANI electrode [designated as ePANI] was determined as 0.11 mg cm⁻². The morphology of the PANI electrodeposited was also examined using a scanning electron microscope (Jeol, JSM-6300).

The supercapacitive properties of the PANI electrodes were mainly obtained by cyclic voltammetry measurement using an Autolab instrument (PGstat 100, Eco-Chemie). An Ag/AgCl (saturated KCl, 0.222 V vs. SHE) reference electrode and Pt counter electrode (2 × 2 cm²) were used to control the potentials of the working electrode between -0.2 and 0.6 V (vs. Ag/AgCl) in 1 M H₂SO₄ aqueous solution at various scan rates (10-500 mV s⁻¹). Complex impedance measurements were also made for the PANI electrodes using an Autolab instrument equipped with a frequency response analyzer in the frequency range of 10⁻²-10⁴ Hz with an alternating current perturbation of 5 mV.

3. Results and Discussion

Fig. 1 shows powder morphologies of PANI prepared by chemical synthesis (cPANI) and electrodeposition (ePANI). The cPANI has slightly elongated particles or particle aggregates with an average diameter and length of about 100 and 400 nm ($L/D \approx 4$), respectively, which are distributed randomly with some distinguishable pores and surface roughness. The morphology of cPANI is very similar to the porous nanorod PANI film obtained by electrochemical deposition,¹⁵⁾ but the cPANI in this study do not contain any nanostructure with interconnected nano-networks. In contrast, the ePANI on Pt substrate has compactly connected particles or particle aggregates (their sizes are below 70 nm), which are to some

Fig. 1. Scanning electron microscopic images of (a) PANI powder synthesized chemically and (b) PANI electrode electrodeposited by potentialdynamic cyclic voltammetry technique.

extent localized with higher specific surface area ($168 \text{ m}^2 \text{ g}^{-1}$) than that of cPANI ($82 \text{ m}^2 \text{ g}^{-1}$). Such the nearly double difference in the specific surface area may be a contributing factor to the capacitive properties of these PANI for supercapacitor electrode application.

Cyclic voltammetry results for the ePANI and cPANI electrodes (with and without Super P) are shown in Fig. 2, obtained in the range of potential scan rate of ($10\text{--}500 \text{ mV s}^{-1}$). As shown in Fig. 2(d), current density response of ePANI is higher than that of cPANI, implying more stable supercapacitive characteristics.¹²⁾ The difference in the redox behaviors between cPANI electrodes (with and without Super P) does not distinguishable, because in this study the powder property (e.g., porosity) seems to suppress efficiently the conductivity enhancing effect by the addition of conductive agent. Also, all the PANI electrodes, irrespective of chemical synthesis and electrodeposition, show that only a broad redox process is observed but shifting the peak potential with increasing the scan rate. The results indicate that the PANI electrode has obvious capacitive performance with a couple of Faradaic peaks relating to the protonation and deprotonation processes.¹⁵⁾ The shift of peak

Fig. 2. Cyclic voltammograms of (a) the cPANI (no Super P), (b) the cPANI (Super P), and (c) the ePANI. Cyclic voltammograms of all the PANI electrodes, recorded at 20 mV s^{-1} , are shown in (d).

Fig. 3. Specific capacitance evolution as a function of scan rate. Data for cPANI and ePANI only were calculated from the cyclic voltammograms in Fig. 2. All other data were quoted from the previous reports.^{5,6,9,12,14)}

potential may be due to growing scan rate where the redox process occurs. It is also interesting to note that the rectangular shape of cyclic voltammograms at higher potential region for the ePANI electrode (see Fig. 2(c)) indicates the presence of pseudocapacitance characteristics, which are distinct from the electrical double layer capacitance.⁹⁾

Specific capacitance values (C) can be calculated from the cyclic voltammogram using an equation of $C = (q_a + q_c)/(2m\Delta V)$, where q_a , q_c , m , and ΔV denote anodic and cathodic charges on each scan, mass of the active material, and the potential window, respectively. Fig. 3 shows specific capacitance of PANI electrodes as a function of scan rate, as well as summarized results from the previous reports.^{5,6,9,12,14)} Comprehensively considering, the supercapacitor should also be viewed at the high-scan-rate region, corresponding to its typical feature of high-rate capability. Some previous reports^{9,12,14)} only concerns at the low-scan rate region that typically exhibits steeply decreasing capacitance with the increase in scan rate. This study extends the scan rate region up to 500 mV s^{-1} and it is expected that the specific capacitance can saturate its value to some extent over the scan rate. As a conclusion, the ePANI reaches a maximum specific capacitance of 474 F g^{-1} at 10 mV s^{-1} and about 390 F g^{-1} at 500 mV s^{-1} (with the capacitance retention ratio of 82.3%), which are higher than those of cPANI electrodes. This is probably why the more porous property and thus the higher surface area of ePANI contribute to the capacitance increase, rather than the conductivity enhancement by, e.g., the addition of conductive agent.

Fig. 4. (a) Nyquist and (b) Bode plots of the cPANI (no Super P), the cPANI (Super P), and the ePANI electrodes.

tion of conductive agent.

The suppression of conductive agent effect can also be evidenced by the Nyquist plot in Fig. 4(a), obtained from complex impedance measurement. As expected, the cPANI electrode with Super P exhibits lower bulk resistance than the cPANI without Super P, due to the conductivity increase to a certain extent. However, the ePANI electrode shows lowest bulk resistance compared to the cPANI electrodes. This can be resulted from the conductivity promoted by the compactly deposited ePANI and the porous property of ePANI surely suppresses the contribution of conductivity increase by the addition of conductive agent to cPANI electrode. Also, Bode plot in Fig. 4(b) indicates response time at the phase angle of 45° . The ePANI electrode gives faster response time than the cPANI electrodes, implying that ionic mobility for charge storage is faster¹⁶⁾ in ePANI than cPANI electrodes.

4. Conclusions

This study is focused mainly on the high-scan-rate

supercapacitive behavior of PANI electrodes, prepared by chemical synthesis and electrodeposition. It is aimed to correspond to real utilization of supercapacitor as typical power storage device with high-power input/output. As a result, the electrodeposited PANI electrode with the compactly connected particles or particle aggregates (their sizes are below 70 nm) can achieve a saturated specific capacitance of 390 F g^{-1} at 500 mV s^{-1} , which promises an adequate electrode material for long-endured high-power supercapacitor application.

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