

Short communication

Supercapacitive properties of polyaniline/Nafion/hydrous RuO₂ composite electrodes

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Abstract

Chemically prepared polyaniline is tested for its supercapacitive behaviour in an aqueous electrolyte of 1.0 M H₂SO₄. In order to improve the cycleability of the polyaniline electrode, it is made into a composite with Nafion. This composite electrode shows improved cycleability and higher specific capacitance compared with a pure polyaniline electrode. It is therefore used as a matrix for the electrochemical deposition of hydrous RuO₂. The resulting ternary composite electrode has a high specific capacitance of 475 F g⁻¹ at 100 mV s⁻¹ and 375 F g⁻¹ at 1000 mV s⁻¹ in the voltage range of -0.2 to 0.8 V versus Ag/AgCl. All three types of electrode are characterized by cyclic voltammetry and impedance analysis.

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1. Introduction

Supercapacitors are battery-complementary devices that are used for the delivery of high power during short pulses of time. One potential application is in electric and hybrid electric vehicles, which are being developed to combat the rapid depletion of fossil fuels and the emissions that arise from combustion of these fuels. Hence, research on the advancement of supercapacitors is being seriously pursued throughout the world.

There are two types of supercapacitor, viz., double-layer and redox supercapacitors. As the names imply, the charge-storage mechanism in double-layer supercapacitors is achieved by the formation of a double-layer on the surface of the electrode material, whereas, in redox supercapacitors, the charge is stored on both the surface of the material through a double-layer mechanism and in the bulk of the material via faradaic reaction. Hence, it is obvious that the charge stored in redox supercapacitors should be higher than that in double-layer counterparts.

Carbon with a high surface area is used as an electrode material in double-layer supercapacitors. By contrast, various conducting polymers such as polyaniline, polypyrrole, PEDOT and polythiophene [1] or metal oxides such as RuO₂, IrO₂ and NiO_x [2–4], are employed as electrode materials in redox supercapacitors. Conducting polymers are relatively cheap, highly redox active materials and are reported to store a charge of up to 815 F g⁻¹ [5–8]. On the other hand, conducting polymers suffer from poor cycleability. This is ascribed to their poor mechanical property [9–13] and the instability of the radical cations for repeated redox processes [14–16]. In addition to these drawbacks, the poor sustainability of conducting polymers towards over-oxidation aggravates the situation and impedes them from commercial use. Among the various metal oxides studied, hydrous RuO₂ has been recognized as one of the most promising electrodes due to its high specific capacitance, highly reversible redox reactions, wide potential window, and very good cycleability [17–20]. On the other hand, the high cost and poor abundance of RuO₂ poses problems for its commercial use. Further, it has been reported that only a very thin layer of RuO₂ participates in the charge-storage process and the rest of material under this thin layer remains inactive and cause low gravimetric

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capacitance [21,22]. Hence, of late, the utility of very low quantities/thin layers of RuO₂ deposited on carbon of high specific area [23], carbon aerogels [24], single- and multi-walled carbon nanotubes (CNTs) [25,26], and conducting polymers [27–29] have been studied for their charge-storage behaviour. By doing so, the quantity of the RuO₂ required has been minimized and at the same time, higher specific capacitance has also been achieved.

Carbon-based materials obviously offer a high dispersion of RuO₂ resulting in relatively higher charge storage and long cycleability. Nevertheless, the lower specific capacitance values of these carbon-based materials (for example, 10–35 F g⁻¹ for CNTs) have a negative impact on gravimetric capacitance when they are used as a matrix for RuO₂ deposition. Moreover, a supporting matrix of single- and multi-walled CNTs is expensive. So, in terms of a cheap matrix and a high charge-storage capability, conducting polymers are considered to be suitable, provided if the cycleability criterion is also met.

In order to improve the cycleability of the conducting polymers, some studies have been made of endowing polymers with a mechanical support by the formation of composites of the polymers with single- or multi-walled CNTs [30,31]. In the present study, an attempt is made to improve the cycleability of polyaniline, by means of stabilizing the radical cations that are formed during the charging process. To achieve this, polyaniline has been made into a composite with Nafion. In addition, the polyaniline/Nafion composite is used as a matrix for the deposition of a thin layer of hydrous RuO₂. Hence, a ternary composite of polyaniline/Nafion/hydrous RuO₂ is prepared and tested for its charge storage and cycleability behaviour.

2. Experimental

All chemicals were purchased from Aldrich. Aniline was vacuum distilled before use. All other chemicals were used as received. Triple-distilled water of 18 MΩ was obtained via an aqua MAX water system (Younglin, Korea) and used to prepare the solutions. Platinum electrodes were cleaned with piranha solution.

Polyaniline was prepared by the conventional chemical polymerization method. In a typical experiment, 20 ml of purified aniline was dissolved in 300 ml of 1.0 M HCl, cooled to 2 °C, and then kept in a polymerization chamber. To this solution, 0.25 M ammonium persulfate oxidant that was dissolved in 200 ml of 1.0 M HCl was added drop-by-drop during 1 h, with magnetic stirring. After the addition was completed, the stirring was continued for at least another 4 h. The resulting polymer precipitate was filtered and washed successively with 1.0 M HCl, water and acetonitrile until the filtrate was colourless. The base form of polyaniline was prepared by stirring the as-prepared polyaniline in 0.5 M NH₄OH for about 10 h.

To prepare the polyaniline-coated electrode, the EB form of the polymer was dissolved in NMP, cast on a Pt foil (1 cm × 1 cm) and dried at 60 °C for 24 h under vacuum. To prepare a polyaniline/Nafion composite electrode, a slurry was made by mixing the salt form of polyaniline (40 wt.%) with Super-P (20 wt.%) and Nafion (5 wt.% in isopropyl alcohol) (40 wt.%). The slurry was cast on a Pt foil (1 cm × 1 cm) and

dried at 60 °C for 24 h under vacuum. In the preparation of a ternary composite, the polyaniline/Nafion composite coated electrode was used as a working electrode and the hydrous RuO₂ was galvanostatically (5.0 mA cm⁻², until 500 mC) deposited on to it from an electrolytic bath that contained 40 mM of RuCl₃·xH₂O, 0.01 M HCl and 0.1 M KCl (pH 2.0) maintained at 50 °C. A Pt foil (2 cm × 2 cm) was used as both a counter and a reference electrode. The resultant polyaniline/Nafion/hydrous RuO₂ composite electrode was dried at 150 °C for 2 h before testing.

Cyclic voltammetry of the polymer-coated electrodes was carried out in a single-compartment cell using an EG&G potentiostat/galvanostat (Model 273A). All potentials mentioned are reported against a Ag/AgCl (3.0 M KCl) reference electrode. Impedance measurements were made for the polymer electrodes using an Auto lab/FRA instrument in the frequency range of 100 kHz–0.01 Hz with an ac perturbation of 5 mV. The polymer materials were weighed using a digital weighing balance (Metler Toledo) that had a sensitivity of 1.0 μg. The morphology of the electrodes was examined by means of a scanning electron microscope (JEOL, JSM-6300).

3. Results and discussion

The electrochemical deposition of hydrous RuO₂ on a polyaniline/Nafion matrix is observed to be highly pH-sensitive. Through trials, an electrolytic bath pH of 2.0 is found to be optimum for the uniform deposition of hydrous RuO₂. Morphological analysis of all the three types of electrodes, namely, polyaniline, polyaniline/Nafion and polyaniline/Nafion/hydrous RuO₂, was performed with a scanning electron microscope; micrographs are shown in Fig. 1. All the three electrodes show distinct differences in morphology. The EB form of pure polyaniline has a very smooth morphology, due to the complete dissolution of the polymer in NMP. On the other hand, the polyaniline/Nafion composite has a rough, granular morphology, which is highly desirable because it can have higher specific surface-area that is helpful to obtain high specific capacitance through high double-layer charging. Further, it is helpful for the effective dispersion of hydrous RuO₂ on the electrode surface. The deposition of hydrous RuO₂ as small globular particles, with a dimension of around 100 nm, is clearly seen in Fig. 1(c).

Cyclic voltammograms recorded for all the three types of electrode in 1.0 M H₂SO₄ solution at various scan rates are presented in Fig. 2. In case of a pure polyaniline electrode, only a broad redox process is observed. With polyaniline/Nafion and polyaniline/Nafion/hydrous RuO₂ composite electrodes, however, both a redox process and a double-layer capacitive region (between 0.5 and 0.8 V) are observable. It is interesting to note that even at a very high scan rate of 1000 mV s⁻¹, there is not any significant change in the shape of the voltammograms in case of composite electrodes. This indicates that the iR loss is insignificant within the studied scan rate, and reveals that composite electrodes have high-power characteristics due to fast faradaic reactions.

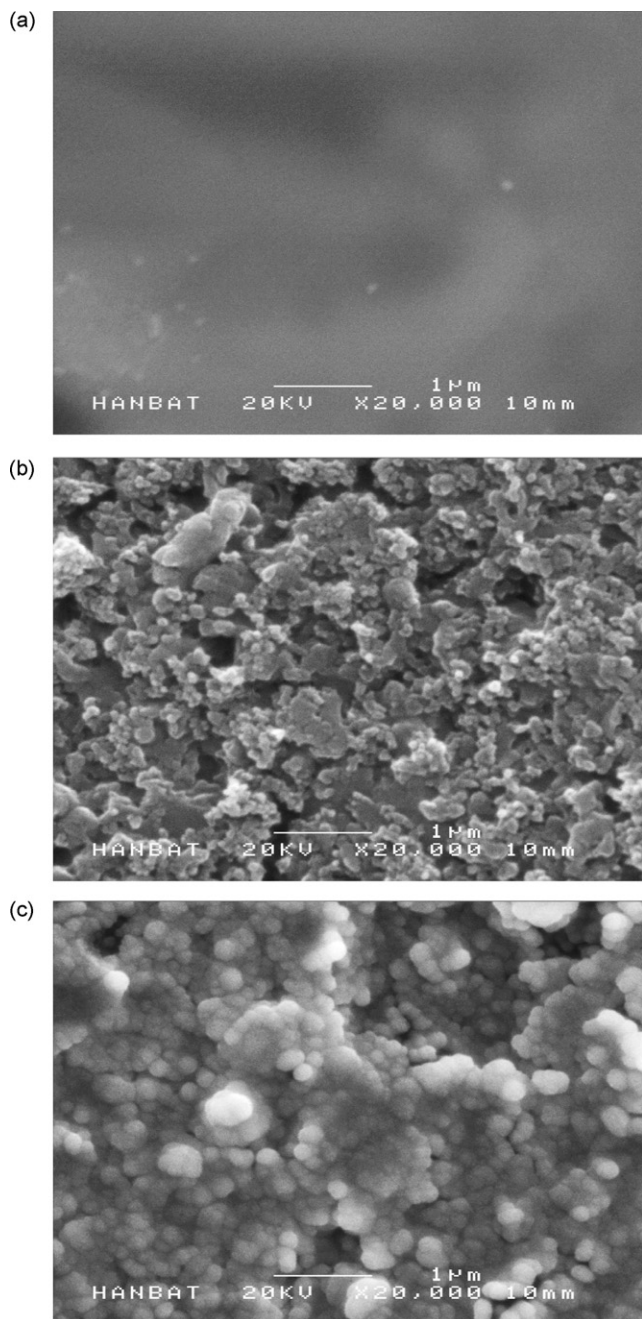


Fig. 1. Scanning electron micrographs of (a) polyaniline, (b) polyaniline/Nafion and (c) polyaniline/Nafion/hydrous RuO₂ electrodes.

The specific capacitance of all three types of electrode were calculated from the cyclic voltammograms according to the equation: $C = (q_a + q_c) / 2m \Delta V$, where q_a , q_c , m and ΔV are the sums of anodic and cathodic voltammetric charges on the anodic and cathodic scans, the mass of the active material and the potential range of the cyclic voltammogram, respectively. The specific capacitance values are plotted as a function of scan rate in Fig. 3. It is interesting to note that the RuO₂-modified electrode shows a very high capacitance of 475 F g⁻¹ at 100 mV s⁻¹. At any one scan rate, the specific capacitance is found to follow the order: polyaniline/Nafion/hydrous RuO₂ > polyaniline/Nafion > polyaniline. All three types of

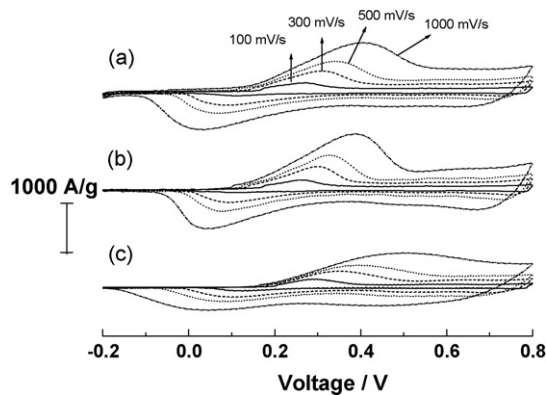


Fig. 2. Cyclic voltammograms of (a) polyaniline/Nafion/hydrous RuO₂, (b) polyaniline/Nafion and (c) polyaniline electrodes recorded at various scan rates in 1.0 M H₂SO₄ solution.

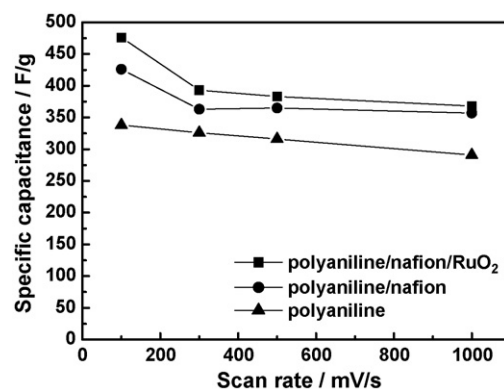


Fig. 3. Specific capacitance of three types of electrode as a function of scan rate recorded in 1.0 M H₂SO₄ solution in voltage range of -0.2 to 0.8 V vs. Ag/AgCl.

electrode are found to show good retention of high-rate capacitance.

Impedance measurements were performed in the frequency range of 100 kHz–0.01 Hz and the resulting spectra are presented in Fig. 4. All the electrodes exhibit typical capacitive behaviour starting from 1.0 to 0.01 Hz. Low-frequency capacitances measured for the electrodes are all ~480 F g⁻¹.

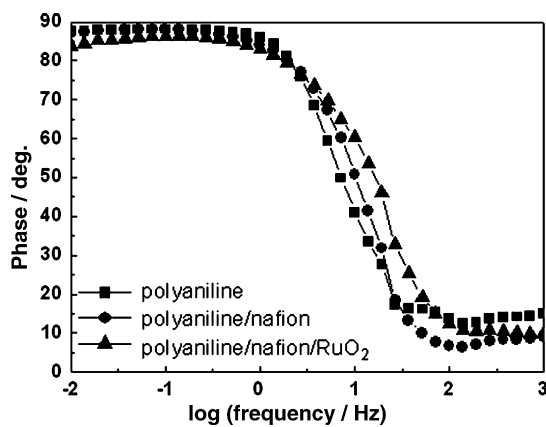


Fig. 4. Impedance spectra for three types of electrode recorded in 1.0 M H₂SO₄ solution under open-circuit conditions. Frequency range: 100 kHz–0.01 Hz; 5 mV ac perturbation.

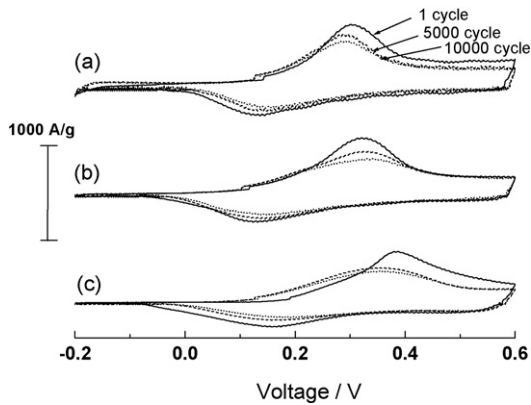


Fig. 5. Representative cyclic voltammograms of (a) polyaniline/Nafion/hydrous RuO₂, (b) polyaniline/Nafion and (c) polyaniline electrodes recorded during cycle-life testing in 1.0 M H₂SO₄ solution. Scan rate: 500 mV s⁻¹.

To evaluate the cycle-life characteristics, the electrodes were cycled back and forth between -0.2 and 0.6 V for 10⁴ times in 1.0 M H₂SO₄ solution at a scan rate of 500 mV s⁻¹. Here, the positive switching potential is restricted to 0.6 V to avoid electrochemical degradation of polyaniline. Representative cyclic voltammograms recorded during this cycle life test are shown in Fig. 5, and the specific capacitance values calculated from these cyclic voltammograms as a function of cycle number are shown in Fig. 6. From these results, it can be observed that the polyaniline/Nafion/hydrous RuO₂ electrode displays the highest initial specific capacitance of 325 F g⁻¹, which is 20 and 50 F g⁻¹ higher than the value exhibited by the polyaniline/Nafion and

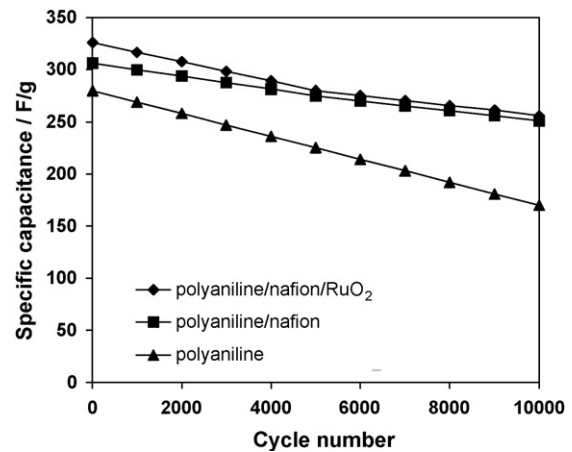
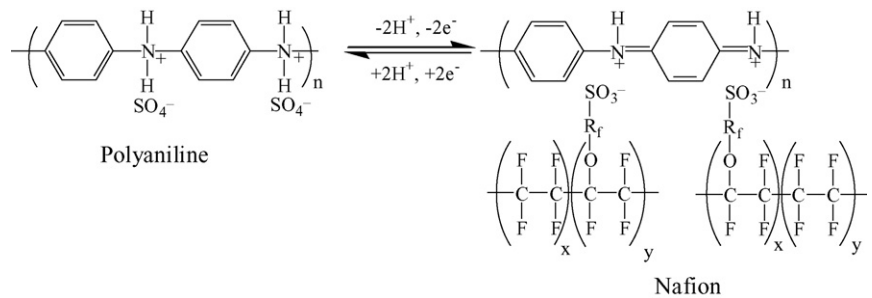


Fig. 6. Specific capacitance of types of electrode recorded as function of cycle number.

After 10⁴ cycles, the capacitance retention of the electrodes is 80%, 84% and 62% for polyaniline/Nafion/hydrous RuO₂, polyaniline/Nafion and pure polyaniline, respectively. The improved cycleability of the composite electrodes in comparison with the pure polyaniline electrode is clearly observed from these data. Polyaniline has been found to have poor cycleability due to the instability of the radical cations formed during the charging (oxidation) process for repeated redox processes [14–16]. In the present case of Nafion-based composite electrodes, Nafion is believed to help improve the cycleability of the polyaniline by means of stabilizing the radical cations formed during the charging process through its negative sulfite ion, as shown below:



pure polyaniline electrodes, respectively. Here, it should be mentioned that the loading of hydrous RuO₂ is equal (50 wt.%) to that of polyaniline in the polyaniline/Nafion/hydrous RuO₂ composite electrode. Both Nafion and Super-P are not considered in the capacitance calculation since Nafion does not participate in the charge-storage process and the contribution by Super-P is less than 5 F g⁻¹. Hence, it can be understood that the charge-storage capacity of hydrous RuO₂ is almost similar to that of polyaniline (300–325 F g⁻¹) under the present experimental conditions. A specific capacitance of 80–250 F g⁻¹ has been reported for hydrous RuO₂ dispersed in various carbon-based matrices such as activated carbon, aerogel and CNT [23,25,32,33]. From the value of 300–325 F g⁻¹ obtained in the present study for hydrous RuO₂, it is obvious that the polyaniline–Nafion serves as a good matrix for dispersion of the hydrous RuO₂.

The charge-storage mechanism for hydrous RuO₂ has been explained in terms of a combined proton–electron transfer mechanism as follows:



This mechanism is quite similar to the charge-storage mechanism operating in polyaniline in acidic medium in the potential window of -0.2 to 0.6 V. Hence, it is concluded that the polyaniline/Nafion composite could be a highly compatible matrix for hydrous RuO₂ dispersion, and due to the similar reaction mechanism between polyaniline and hydrous RuO₂ a synergism might prevail between these two materials in the charge-storage process. Among the composites, despite the fact that the RuO₂-modified electrode has a initial higher capacitance than the polyaniline/Nafion electrode, its capacity retention (80%) is found to be slightly lower than the latter (84%) after 10⁴ cycles.

This is considered to be due to the dissolution of a small quantity of hydrous RuO₂ from the matrix polymer during repetitive cycling of the electrode.

It has been reported [18,34–37] that the specific capacitance value of hydrous RuO₂ is highly dependent on the structural water content [18,34–37]. So, by optimizing the quantity of structural water content by adopting a suitable annealing condition, it is expected that the specific capacitance of the polyaniline/Nafion/hydrous RuO₂ electrode can be enhanced significantly. In addition, by suitably varying the loading of RuO₂ and polyaniline in the composite electrode, an additional improvement in specific capacitance could also be possible. Such possibilities are currently being investigated in our laboratory.

4. Conclusions

An improvement in the cycleability of the polyaniline electrode in an aqueous electrolyte of 1.0 M H₂SO₄ has been realized by making polyaniline into a composite with Nafion. Both the polyaniline and the polyaniline/Nafion composite electrodes have been subjected to 10⁴ cycles in the voltage range of –0.2 to 0.6 V at 500 mV s^{–1}. After this period of cycling, the capacitance retention of the polyaniline/Nafion electrode is 84%, but only 62% for pure polyaniline. The composite electrode is found to be a compatible matrix for the dispersion of hydrous RuO₂. The resultant ternary composite electrode of polyaniline/Nafion/hydrous RuO₂ also displays good cycleability in aqueous 1.0 M H₂SO₄ electrolyte and delivers an initial specific capacitance value of 325 F g^{–1} and 260 F g^{–1} after 10⁴ cycles (80% capacitance retention) for a loading of 50 wt.% hydrous RuO₂. Such a good cycleability and high specific capacitance values indicate that the polyaniline/Nafion composite is a potential matrix for the dispersion of hydrous RuO₂. By adopting suitable annealing conditions and optimizing the loadings of hydrous RuO₂ and polyaniline, a substantial improvement in specific capacitance of the polyaniline/Nafion/hydrous RuO₂ composite electrode is expected.

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