

Capacitive performance of the composite electrodes consisted of polyaniline and activated carbons powder in a solid-like acid gel electrolyte

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Received 2 June 2003; received in revised form 15 December 2003; accepted 24 February 2004

Available online 28 July 2004

Abstract

Composite electrodes for supercapacitors were fabricated by depositing polyaniline (PAN) on the surface of activated carbon powders (ACP) by using the electrochemical method. Their capacitance values were measured in the 1 M H₂SO₄ aqueous electrolytes containing SiO₂, which showed the conductivity values of 2.6×10^{-1} , 2.3×10^{-1} , and 1.5×10^{-1} S/cm for their liquid, gel, and solid-like gel states, respectively, according to the content of SiO₂. The Pt/ACP/PAN electrodes showed a specific capacitance value of 270 F/g in the 1 M H₂SO₄ solid-like electrolyte, which value was larger than the capacitances of 144 and 209 F/g for the Pt/ACP and the Pt/PAN, respectively. This result suggests that the capacitance performance of the ACP can be improved by compositing with PAN, and the 1 M H₂SO₄ solid-like electrolyte is suitable for the use in the supercapacitor.

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Keywords: Supercapacitor; Gel electrolyte; Polyaniline; Activated carbon; Capacitance

1. Introduction

Supercapacitors have been studied due to the demand of power sources delivering high power [1–2]. They have been recognized as a potential device improving the performance and service life of batteries and fuel cell, which are applicable in several systems such as hybrid electric vehicles, fuel cells, cellular phones, PDAs, etc. [1–5].

Activated carbon powders (ACP) has been considered as a good candidate for the electrode material in a supercapacitor because of its high surface area, long cycle life, wide use in aqueous and nonaqueous solvents, cheap price, etc. But the capacitance performance of ACP is somehow low compared to the redox conducting polymers or metal oxides. Many researchers have tried to improve the charge storage capacitive performance of ACP. On the other hand, polyaniline (PAN) is one of the most important conducting polymers because

of its many advantages, such as an ease of polymerization in aqueous media, good stability in air, simplicity in doping/dedoping, etc. In addition, PAN has been considered as a potential candidate for the application of electrochemical supercapacitors [3–11].

On the other hand, a gel electrolyte has many advantages such as no leakage, high flexibility in a manufacturing process, and an ease in a cell assemble, compared to liquid-based electrolytes. However, to our knowledge, there have been little reports on the capacitance properties searched in the gel electrolyte for supercapacitors. In particular, the aqueous gel electrolytes based on sulfuric acid, which have SiO₂ as a gelating agent, have been known to have high ionic conductivity due to fast H⁺ proton hopping in a solid-like state [8].

In this work, we prepared the composite electrode to deposit PAN on the surface of ACP to improve capacitance performance by using electrochemical technique, and investigated their capacitance properties in the 1 M H₂SO₄ solid-like electrolyte containing a hydrophilic SiO₂.

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2. Experimental

Active carbon powders (MSC-300, Osaka Gas) serving as a main electrode material were used with a specific surface area of $3000 \text{ m}^2/\text{g}$. To fabricate an electrode, the slurry solution which consisted of ACP (90%), polyvinylidene fluoride (PVdF, 5%) as a binder and Super-p (5%) as a conductive agent in *N*-methyl pyrrolidinone (NMP) was made, and its mixture was stirred at ambient temperature. The ACP electrodes were fabricated by coating the slurry on Pt, followed by evaporating the solvent, NMP, with a vacuum oven, and pressed by a roll press.

The aqueous electrolytes were prepared by adding SiO_2 (Degusa) powders with hydrophilic surface into a $1 \text{ M H}_2\text{SO}_4$ solution. According to the amount of SiO_2 as a gelating agent, the prepared electrolyte states were determined. The liquid, gel, and solid-like electrolytes were obtained at 3.85, 10.8, and 13.7% SiO_2 , respectively. Their ionic conductivity values were measured using impedance spectroscopy in the frequency range of 100 MHz to 100 kHz with an amplitude of 5 mV in the three electrode cell.

Reagent grade aniline (Merck) was distilled prior to use. Electrochemical polymerization of PAN was made by using a potentiostat/galvanostat (EG&G 273A). A three-electrode cell assembly was utilized with an Ag/AgCl reference electrode, platinum (Pt) plate with an exposed area of 1 cm^2 as a working and a counter electrode, respectively. To composite the ACP electrode with PAN, the ACP electrode of 1 cm^2 was used as a working electrode. The PAN was electrochemically loaded on the ACP electrode substrates in the $1 \text{ M H}_2\text{SO}_4$ solution containing 20 mM aniline by using cyclic voltammetry (CV) in a sweeping potential range between -0.2 and 1.0 V with the scan rate of 30 mV/s . The PAN polymerization was conducted for 60 cycles.

All electrochemical half-cell measurements were conducted in a three-electrode cell which was equipped with a reference of the Ag/AgCl sat'd with KCl, a counter electrode of Pt, and a working electrode of ACP/PAN. The apparent surface area of the electrodes was kept to be 1.0 cm^2 . The charge capacitance was obtained from an integration of the anodic wave in cyclic voltammograms (CVs) between -0.2 and 0.8 V with a scan rate of 50 mV/s .

3. Results and discussion

To investigate the effect of the polymerization of aniline on different electrode substrates of platinum and ACP, respectively, the CVs were repeatedly recorded when the aniline was polymerized on the ACP electrode and the bare Pt electrode in a $1 \text{ M H}_2\text{SO}_4$ aqueous solution containing 20 mM aniline, as shown in Fig. 1. It is interesting to note that the first oxidation peak of PAN observed at approximately 0.3 V in the Pt electrode shown in Fig. 1(a) is shifted to 0.6 V for the Pt/ACP electrode in Fig. 1(b). This means that the electrical resistance for the electron transfer from the aniline to the

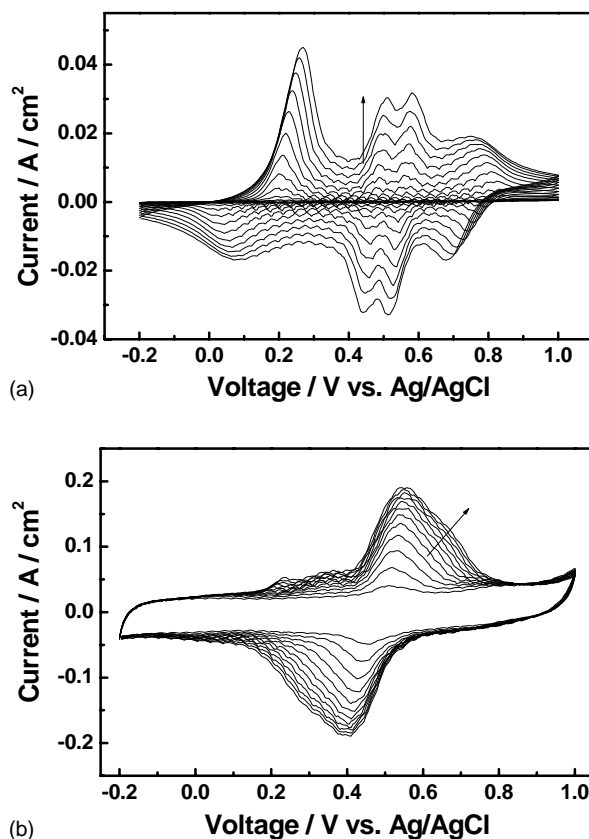


Fig. 1. The CVs were repeatedly recorded when aniline was polymerized on the bare Pt electrode (a) and the Pt/ACP electrode (b) in $1 \text{ M H}_2\text{SO}_4$ aqueous solutions containing 20 mM aniline.

substrate electrode during the oxidation process is larger in the Pt/ACP electrode than the Pt electrode. This phenomenon is easily understandable in the electrical conductivities of Pt and ACP electrodes. In addition, it is noticeable in Fig. 1(b) that there is a large electrical double layer capacitance region in the Pt/ACP electrode that is the result of the charge storage in the ACP electrode, which phenomenon was not observed in the bare Pt electrode as shown in Fig. 1(a).

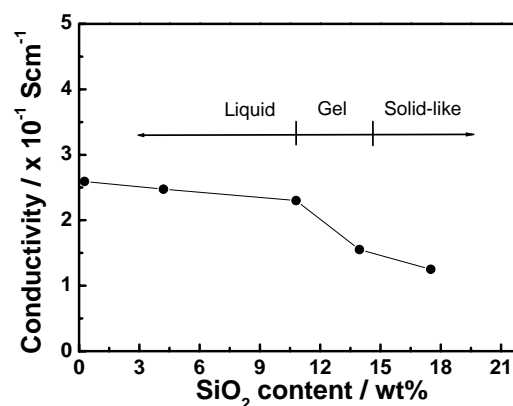


Fig. 2. Ionic conductivities as a function of the content of SiO_2 for the $1 \text{ M H}_2\text{SO}_4$ aqueous electrolytes.

The different state electrolytes were prepared by adding SiO_2 powders with a hydrophilic surface into the 1 M H_2SO_4 aqueous electrolytes. It was observed from Fig. 2 that the ionic conductivities slightly decreased with an increase in the content of SiO_2 , and the prepared electrolyte states were strongly dependent on the amount of SiO_2 as a gelating agent. A liquid, a gel, and a solid-like electrolyte were obtained at 3.85, 10.8, and 13.7% SiO_2 , respectively, as shown in Fig. 2. It is interesting that there is no significant difference in the ionic conductivities between the liquid and the solid-like state

Table 1

A summary of conductivity and capacitance values

States	SiO_2 content in 1 M H_2SO_4	Conductivity (S/cm)	Capacitance value (F/g)		
			ACP	PAn	ACP/PAn
Liquid	1 M H_2SO_4	2.6×10^{-1}	150.0	228.8	283.3
	3.85% SiO_2	2.4×10^{-1}	148.5	220.0	276.6
Gel	10.8% SiO_2	2.3×10^{-1}	148.0	217.5	271.6
Solid-like	13.7% SiO_2	1.5×10^{-1}	144.0	209.4	270.2

electrolytes. This phenomenon can be explained by the proton hopping that occurred along the hydration nanostructure between water and hydrophilic SiO_2 powders [8].

Fig. 3 shows the CVs obtained for the different electrodes of Pt/ACP(a), Pt/PAn(b), and Pt/ACP/PAn(c), respectively, in the electrolytes containing the liquid, the gel, and the solid-like states. In the case of the Pt/ACP electrode, there is no change in the shape of the CVs obtained in different electrolyte states, confirming that the proton ionic movement for charge storage is sufficiently fast even in the solid-like electrolyte state. On the other hand, in the case of Pt/PAn electrode, there is a somehow decrease in the shape in the CVs obtained in the solid-like electrolyte, implying that the redox reaction of PAn is somehow limited by the proton transfer process. In the case of Pt/ACP/PAn electrode, it is also noticeable that the oxidation peak in the backbone of PAn at around 0.5 V is shifted to a higher potential as the electrolyte state is changed from the liquid to the solid-like state, and the area of CVs seem to be larger than those of Pt/ACP and Pt/PAn electrode. This indicates there is a little improvement in capacitive performance as a result of composition of the ACP with the PAn. This phenomenon is confirmed in Table 1, which summarizes the conductivity and capacitance values. It is clearly noticeable that there is a synergistic effect in the increase of the capacitance values by the composition of ACP and PAn. This effect may be originated from the large surface area of the ACP which makes PAn to be rougher and thinner to give the better redox kinetics. Also, this result means that the solid-like sulfuric acid electrolyte is suitable for the supercapacitors.

4. Conclusion

We have prepared the composite electrodes by depositing polyaniline on the surface of an activated carbon powder (ACP) by using the electrochemical method for supercapacitors. Their capacitance values were measured in a 1 M H_2SO_4 aqueous electrolyte containing SiO_2 , which showed the conductivity values of 2.6×10^{-1} , 2.3×10^{-1} , and 1.5×10^{-1} S/cm for a liquid state, a gel state, and a solid-like gel state, respectively, according to the content of SiO_2 . The Pt/ACP/PAn electrodes showed a specific capacitance value of 270 F/g in the 1 M H_2SO_4 solid-like gel electrolytes, which values are larger than the capacitances of 144 and 209 F/g for ACP and PAn, respectively. This result suggests that the

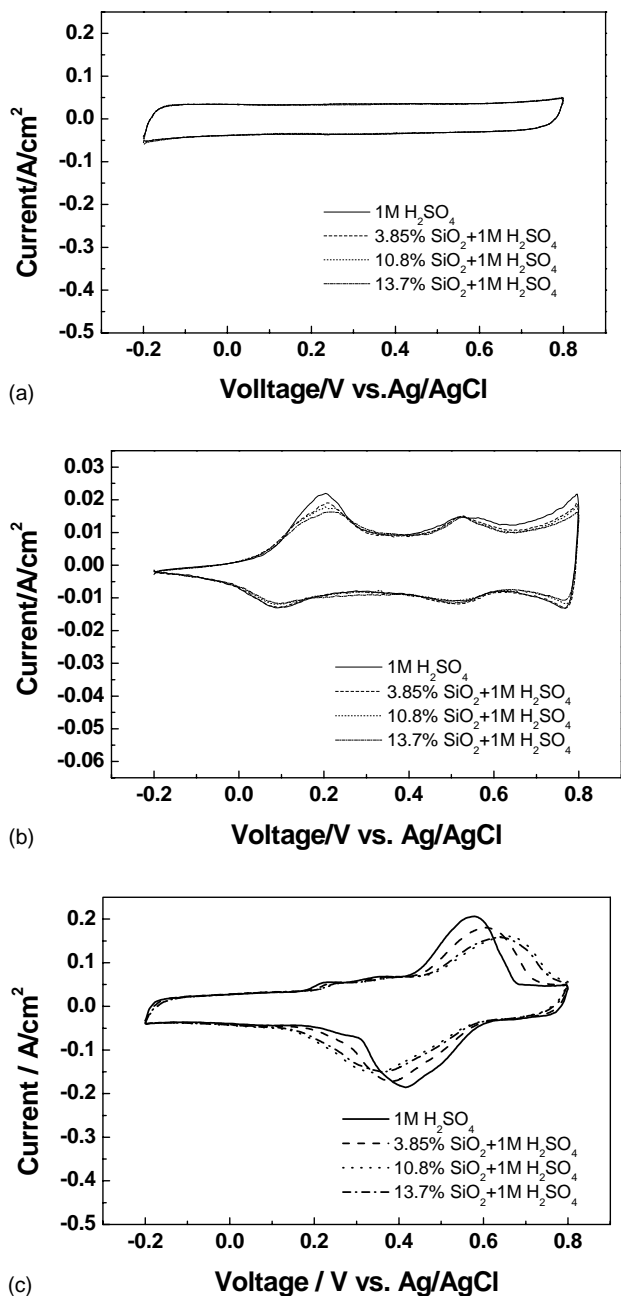


Fig. 3. The CVs obtained for the different electrodes of Pt/ACP (a), Pt/PAn (b), and Pt/ACP/PAn (c), respectively, in the different state electrolytes containing the liquid, the gel, and the solid-like.

capacitance performance of ACP can be improved with the composite of PAN, and the solid-like acid gel electrolytes are suitable for the use in supercapacitors.

Acknowledgements

This work was supported by Korea Research Foundation grant (KRF-2002-041-D00155).

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