

# STUDY ON ACTIVATED CARBON /POLYANILINE ELECTRODE MATERIALS FOR SUPERCAPACITORS

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## Abstract

Activated carbon (AC) /polyaniline (PANI) composite electrode materials were synthesized in this article. The effect of preparation such as reaction molar ratio of AC to aniline, BET surface area of AC and surface modification of AC (ammoxidation) on the electrochemical performances of AC/PANI composite material was investigated. The electrochemical performances of the composite are tested with cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectrometry in 6mol/L KOH solution using Hg/HgO as reference electrode. Composite microstructure and surface morphology are examined by X-ray Diffraction and scanning electron microscope (SEM). The result shows that when the ratio of AC to aniline increases, the conversion of aniline and the capacitance value of composite also increase in keeping the ratio of AC to aniline constant. When AC: aniline :  $(\text{NH}_4)_2\text{S}_2\text{O}_8 = 7:1:1$ , the conversion of aniline up to more than 95% and the capacitance value of electrode materials increased from 239F/g(pure AC) to 409F/g., which is 71.1% higher than pure AC. Pore structure of AC also has great effect on electrochemical performances of electrode material. With the increase of proportion of mesoporous, the electrochemical properties of composite are greatly increased.

**Keywords:** supercapacitor; activated carbon; polyaniline; ammoxidation

## Introduction

Supercapacitors are promising energy storage devices, due to their high energy and power densities. Digital communications, electric vehicles and other devices that require electrical energy at high power levels in relatively short pulses have prompted considerable research on supercapacitors [1–3]. According to energy storage mechanisms, supercapacitor can be divided into two types: double-layer capacitor and redox supercapacitors. Activated carbon (AC) which is based on the double-layer capacitance is attractive as an electrode material for supercapacitors due to their high accessibility, good processability, chemical inertness, low cost, and high surface area up to  $2000\text{m}^2/\text{g}$ . but because of its poor conductivity and crystallization, the improvement of capacitance is confined. Polyaniline (PANI) is common and the most attractive p-dopable polymer due to its stability, controllable electrical conductivity, and easy processability. PANI has been considered as a potential candidate for the application of electrochemical supercapacitors [3–11], and it was used as an electrode material for redox supercapacitors, fast faradic charge transfer can lead to high capacitance.

Electrode of carbon material modified by polyaniline can make use of both double-layer capacitance and pseudocapacitance of PANI and the composite can have higher capacitance. Recently, PANI/AC composite materials synthesized by in-situ polymerization of aniline on the surface of activated carbon were studied, but the conversion of aniline and the capacitance of the composite were both not high. In this paper, we investigate the polymerization of aniline on the surface of activated carbon. By choosing preferable special surface area and ratio of activated carbon to aniline, and surface modification of AC (ammoxidation), we optimize the condition of polymerization of aniline on the surface of activated carbon, in order to obtain electrode material with higher capacitance and conversion of aniline.

## Experiment

### *Materials*

Three kinds of activated carbon (AC) material with surface area 936m<sup>2</sup>/g, 1780m<sup>2</sup>/g, and 1880 m<sup>2</sup>/g, respectively, were used for in-situ polymerization of aniline. Other reagent such as ammonium persulphate (APS), hydrochloric acid (HCl) and lithium chloride (LiCl), were used as received without further purification. Distilled and deionized water was used.

### *Ammonoxidation of AC*

The ammonoxidation of AC was carried out as follows: AC material and NH<sub>4</sub>HCO<sub>3</sub> were put in a furnace and then was heated. When the temperature up to 40 °C, keep the reaction system for 1h at this temperature. Then, continue to heat up to 100 °C in 2h. Finally, up to a final temperature of 250 °C in 4h.

### *Synthesis of PANI/AC composite*

The preferred method to prepare the modified carbon particles using in-situ polymerization techniques is briefly presented as follows: First, a certain quantity of activated carbon and aniline and a certain concentration of HCL solution were add into a tri-hole flask. The mixture was subjected to 0.5h exposure to ultrasound, and then was cooled to 20 °C. When the mixture solution was purged with high-purity nitrogen 30 min, APS solution was added gradually to it. The addition of APS was completed about 30min. Then the reaction temperature remained below 40 °C for 8h. The product was separated by centrifugal separation and washed by deionized water. At the end, the composite was extracted in the soxhlet extractor by anhydrous ethanol for 12h and dried at 80 °C.

### *Characterisation of AC and PANI/AC composite*

The specific surface area and pore structure parameters of AC were determined by adsorption isotherm of nitrogen at 77K (ASAP2000, Micromeritic, USA). The BJH method was used to calculate the mesopore distribution. The micropore volume was obtained using the t-plot method.

The morphologies of PANI/AC composite were studied with scanning electron microscope (SEM).

PANI/AC electrodes were prepared by loading the mixture of PANI/AC (80 wt%), carbon black (5 wt%), and poly(vinylidene fluoride) (15 wt%) on the macroporous nickel current collector, and heat-treated at 105 °C to obtain sample electrodes. The electrochemical properties of the PANI/AC composite are estimated by cyclic voltammetry (CV) with a scanning rate of 2mV/s at a potential window of -0.7~0.7V, by galvanostatic charge-discharge with a current density of 300 mA/g in a potential range of 0~0.7V, and by electrochemical impedance spectrometry with a frequency range of 0.1Hz-100KHz in 6mol/L KOH solution using Hg/HgO as reference electrode. The capacitance value of composite was calculated by galvanostatic charge-discharge.

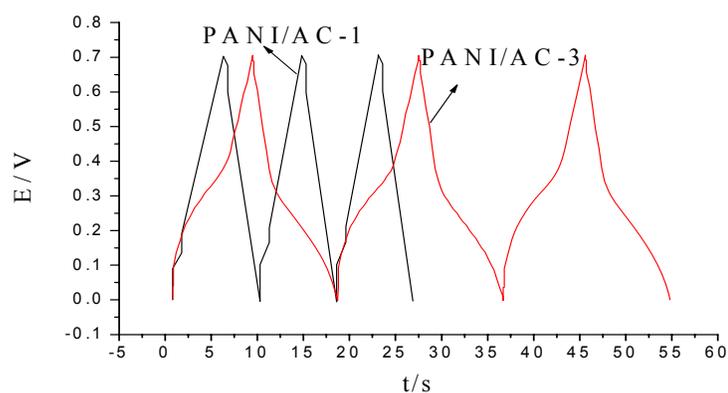
## Results and discussion

The effect of the ratio of AC to PANI on the conversion of aniline and special capacitance of composite were given in Tab.3. The specific capacitance of composites was calculated by galvanostatic charge-discharge. Fig. 1 showed the charge/discharge curves of composites in the range of 0~0.7V. Tab.1 demonstrated that with the increase of the ratio of AC to PANI, not only the conversion of aniline but also the capacitance value of composite highly increased in keeping the ratio of AC to aniline constant. When AC: aniline: APS=7:1:1, the

conversion of aniline up to 96.6% and the capacitance of electrode materials increased from 239F/g(pure AC) to 409F/g, which is 71.1% higher than pure AC.

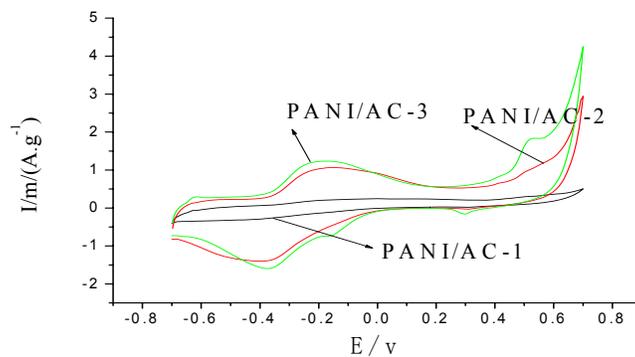
**Tab. 1** The effect of the ratio of AC to PANI on the special capacitance of composite

sample	AC:aniline:APS(molar ratio)	PANI: AC (by weight)	the conversion of aniline/%	capacitance (F·g <sup>-1</sup> )
PANI/AC-1	2:1:1	3.4:1	88.3	80
PANI/AC-2	6:1:1	1.2:1	92.3	362
PANI/AC-3	7:1:1	1.1:1	96.6	408



**Fig.1** Galvanostatic charge and discharge curves of PANI/AC-1 and PANI/AC-3

Cyclic voltammetry is an excellent method to measure the electrochemical activity of electrode material. Cyclic voltammograms of composites of PANI/AC-1, PANI/AC-2, PANI/AC-3 were shown in Fig.2. A pair of redox peaks were observed on the CV curves of all the composites, due to the redox reaction during the charge and discharge process which result to a response current. From Fig.2, we can see that the response current of PANI/AC-3 was much higher than that of PANI/AC-1. It indicated that electrochemical activity of PANI/AC-3 was higher than that of PANI/AC-1 which was one of the reasons for the higher capacitance of PANI/AC-3.

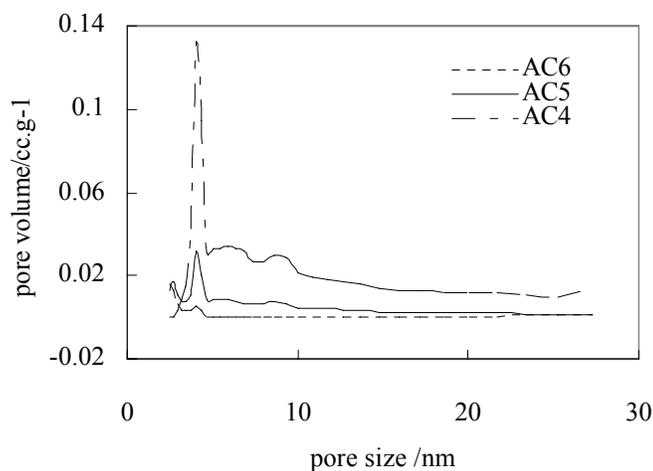


**Fig.2** Cyclic voltammetry of the composite electrode in 6mol/L KOH aqueous solution

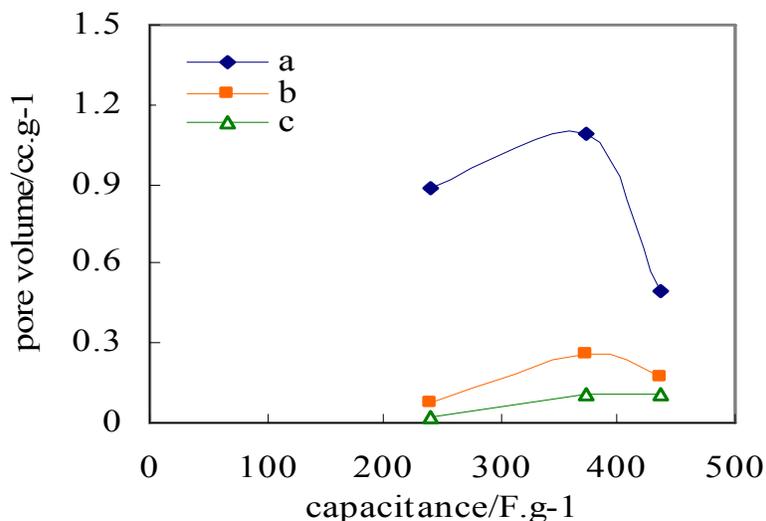
For further investigation of the effect of structure of AC on the PANI/AC composite, we chose three types of AC with different of special surface area for preparing PANI/AC composites. The result showed in Table.2. From the table 2, we can see that with the BET special surface area increases , the conversion of aniline have no obvious change but the special capacitance of composite was significantly decreased. The reason for that is probably the different pore size distribution of AC material. Fig.3 presents the analysis result of pore size distribution of AC by DFT method. The special surface area of AC is not the predominant factor in capacitance of PANI/AC composites. Perhaps the mesopore volume and macropore volume play a more important role. The effects of pore volume of AC on capacitance of PANI/AC composites are given in Fig.4. From Fig4, it can be seen that the capacitance of PANI/AC composites increases with pore volume of pores between 5nm and 300nm.

**Tab.2** The effect of BET Specific surface area of AC on the special capacitance of composite

Sample	BET Special surface area $m^2 \cdot g^{-1}$	AC: aniline: APS (molar ratio)	PANI: AC wt.%	The conversion of aniline wt.%	Special capacitance $F \cdot g^{-1}$
PANI/AC-4	936	6: 2: 1	1.2: 1	46.0	436
PANI/AC-5	1898	6: 2: 1	1.2: 1	44.5	373
PANI/AC-6	1780	6: 2: 1	1.3: 1	49.4	239



**Fig.3** Pore size distribution of AC by DFT



**Fig.4** Capacitance of PANI/AC composites versus pore volume of AC, a: total pore volume; b: pore volume of pores between 2.5nm and 300nm; c: pore volume of pores between 5nm and 300nm

AC material was ammoniated by  $\text{NH}_3$  produced from  $\text{NH}_4\text{HCO}_3$ . The effect of AC modification on the capacitance of PANI/AC composite is showed in table.3. From the above table, we can say that the capacitance of PANI/AC-7 (after ammoniating) has no obviously change compared with PANI/AC-4. To a certain extent, the functional groups on the AC surface were changed because of ammoniation which perhaps have little effect on the electrochemical properties. The detail reason needs further study.

**Tab.3** The effect of ammoxidation of AC on the capacitance of composite

sample	AC:aniline:APS (molar ratio)	PANI: AC (Wt.%)	the conversion of aniline (%)	capacitance ( $\text{F}\cdot\text{g}^{-1}$ )
PANI/AC-4	6:2:1	1.19:1	46.0	436
PANI/AC-7	6:2:1	1.20:1	44.8	403

## Conclusions

In this paper, the PANI/AC composites were synthesized using an in-situ chemical polymerization method. We have investigated the effect of the condition such as reaction molar ratio of AC to aniline, BET surface area and pore size distribution of AC and surface modification of AC (ammoxidation) on the capacitance of PANI/AC composite. When AC: aniline :  $(\text{NH}_4)_2\text{S}_2\text{O}_8 = 7:1:1$ , the conversion of aniline up to 96.6% and the capacitance value of electrode materials increased from 239F/g(pure AC) to 409F/g., which is 71.1% higher than pure AC. Pore structure of AC also has great effect on the performances of electrode material. With the increase of proportion of mesoporous, the capacitance properties of composite are greatly increased.

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