

# The electrochemical activity of polyaniline: An important issue on its use in electrochemical energy storage devices



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## ARTICLE INFO

### Article history:

Received 16 April 2013

Received in revised form 6 October 2013

Accepted 16 October 2013

Available online 14 November 2013

### Keywords:

Electrochemical activity

Polyaniline

Supercapacitor

## ABSTRACT

The efficiency of an energy storage device is closely related to the reversibility and electrochemical activity of the electrode materials. Although polyaniline (PANI) has been used to fabricate various electrochemical devices, its electrochemical activity has not received enough attention. Here, high reversible electrochemical active PANI nanofibers are prepared and mixed with hydroxyethyl cellulose (HEC). Their supercapacitive performance is investigated by cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) techniques on Pt electrodes. The results show that the obtained PANI has reversible electrochemical activity on Pt electrode. But the electrochemical activity decreases gradually with the increase of HEC content and even disappears when the HEC content reaches 30%. It suggests that the content of the inactive materials should be controlled strictly to guarantee the electrochemical activity of the electrode materials in fabricating high performance electrochemical energy storage devices.

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## 1. Introduction

Electrochemical reaction is an important process because of its wide range of applications such as portable or/and moveable power sources, sensors and actuators, corruptions, etc. [1–3]. The reversibility of the electrochemical reaction can be judged by the height of peak current and the variation of peak potentials in a linear sweep voltammogram curve. The nearer the anodic and cathodic peak separation to the theoretical value, the greater the reversibility of the electrochemical reaction, and the higher the symmetry of the shape of the peaks, the greater the reversibility of the electrochemical reaction [4,5]. It is anticipated that under the same operating conditions, the reversible process is more efficient than the irreversible one.

Supercapacitor and secondary battery are two important kinds of energy storage systems of which the former one is characterized mainly by high power density and high capacitance values in the Farad ranges, and the latter one is characterized mainly by low power density while high energy density [6–8]. For both electrochemical supercapacitor and secondary battery, the cathodes

are oxidized while the anodes are reduced in the charge process and the opposite reactions occur in the discharge process. The charge/discharge process is closely related to the redox reaction of electrode materials [9–11]. So the electrochemical activity of the electrode materials is significantly important to their energy storage capacities [12]. Unfortunately, to our best knowledge, there has been no detailed report on the effect of the electrochemical activity of electrode materials on the performance of supercapacitors or secondary batteries.

PANI has a great promising application in supercapacitors or secondary batteries based on the electrochemical activity of PANI which can improve the devices' energy storage capacities substantially [13–17]. PANI may exist in forms of three oxidation states that can convert to each other reversibly when applied with proper potentials, producing two pairs of symmetrical redox peaks in the CV curves [18–20]. The intensities and symmetry of these peaks can provide the criterion to decide whether the PANI remains electrochemical active or not [21,22]. Practically, the poor mechanical strength and stability of PANI films obtained by depositing PANI nanofibres restrain its commercial application. In order to address the problem, various framework materials have been combined with PANI to obtain robust electrodes. Unfortunately, under certain circumvent, high electrochemical active PANI hybrids were not obtained, especially for those PANI composites with inactive materials [23–31]. The adding of the inactive framework materials has adverse effect on the electrochemical activity of the overall hybrid

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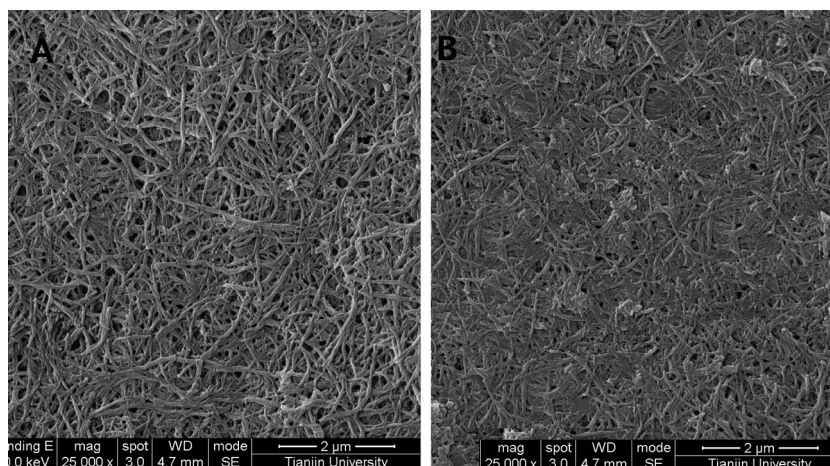


Fig. 1. FE-SEM images of (A) PANI and (B) PANI/HEC.

materials. As discussed above, the high electrochemical activity of PANI can contribute a lot to get large specific capacitances for PANI-based supercapacitors or secondary batteries [32–36], so the influence of those framework materials on the electrochemical activity of PANI should be investigated in detail.

Hydrophilic materials are usually used to improve the dispersibility and film formation of PANI. Hydroxyethyl cellulose (HEC), a hydrophilic material with multiple hydroxyl and hydroxyethyl groups along its molecular chain, has a wide range of applications such as biodegradation materials, gel formation, water conservation, film formation and colloid stabilization [37–39]. The hydroxyl groups along HEC molecular chains can form hydrogen bond with PANI which will improve the stability and strength of the hybrid films. So, mixing HEC with polyaniline (PANI) is helpful for preparing robust PANI films. Furthermore, the conservation of acidic water can help improve the protonic acid doping/dedoping of PANI during charge/discharge process. So, HEC used for assembling PANI film might be superior to other hydrophilic materials, such as polyvinylpyrrolidone.

Here, high electrochemical active PANI nanofibers were prepared and mixed with different contents of hydroxyethyl cellulose (HEC) to study the influence of HEC content on the electrochemical activity of PANI. Cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) techniques were used to characterize the supercapacitive performance of PANI and its hybrids with HEC on Pt electrodes. The experimental results show that the electrochemical activity of PANI decreases gradually with the increase of HEC content and even disappears when the HEC content reaches 30%. It suggests that the content of the inactive materials should be controlled strictly to guarantee the electrochemical activity of the electrode materials in fabricating high performance electrochemical devices.

## 2. Experimental

### 2.1. Materials

Aniline (Aldrich) used for polymerization was distilled under reduced pressure and stored at 4 °C prior to use. Ammonium persulfate (APS), HEC, 37% hydrochloric acid (HCl) solution and 98% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution were purchased from Tianjin Kewei Reagent Co. Distilled water was used for all polymerization and testing experiments.

### 2.2. Preparation of PANI and its hybrids with HEC

PANI was prepared by rapid polymerization [40] of aniline with APS as the oxidant. Solution A was prepared by dissolving 8.0 mmol aniline in 50 ml 1.0 M HCl aqueous solution and solution B was prepared by dissolving 2.0 mmol APS in 50 ml 1.0 M HCl aqueous solution. Then these two solutions were fast mixed together and immediately shaken to ensure sufficient mixing before polymerization begins. The products were filtrated with membrane (pore diameter 0.22 μm) and washed with deionized water until the filter liquor was colorless to collect PANI. After drying in vacuum, the PANI was dispersed in distilled water with the content of PANI being 2.0% (w/w). The PANI solution was mixed with different quantities of aqueous solution of HEC (2.0%, w/w) to regulate the ratio of PANI and HEC. A certain amount of this mixture was deposited on Pt sheets and dried in vacuum to be tested.

### 2.3. Characterization of PANI and its hybrids with HEC

The morphologies of PANI and its hybrids were characterized by FEI, Nanosem 430 Field Emission Gun Scanning Electron Microscope (FE-SEM).

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were operated in a three-electrode

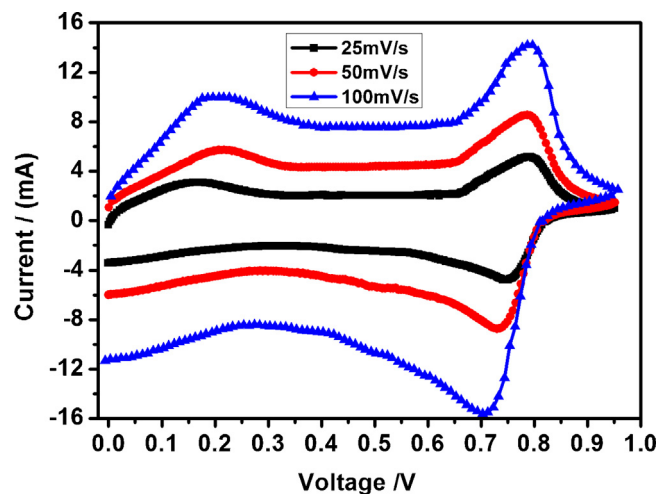


Fig. 2. CV curves of pure PANI tested at different scanning rates.

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