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Short communication

# A general approach toward enhancement of pseudocapacitive performance of conducting polymers by redox-active electrolytes

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## HIGHLIGHTS

- A general approach toward enhancement of conducting polymer pseudocapacitance by redox-active electrolytes is presented.
- The capacitance of the conducting polymer pseudocapacitors increase significantly by the redox-active electrolytes.
- The ionic conductivity of the redox-active electrolytes improved remarkably.

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## ABSTRACT

A general approach is demonstrated where the pseudocapacitive performance of different conducting polymers is enhanced in redox-active electrolytes. The concept is demonstrated using several electroactive conducting polymers, including polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene). As compared to conventional electrolytes, the redox-active electrolytes, prepared by simply adding a redox mediator to the conventional electrolyte, can significantly improve the energy storage capacity of pseudocapacitors with different conducting polymers. The results show that the specific capacitance of conducting polymer based pseudocapacitors can be increased by a factor of two by utilization of the redox-active electrolytes. In fact, this approach gives some of the highest reported specific capacitance values for electroactive conducting polymers. Moreover, our findings present a general and effective approach for the enhancement of energy storage performance of pseudocapacitors using a variety of polymeric electrode materials.

## 1. Introduction

Electrochemical supercapacitors are considered excellent energy storage devices that can be found in many practical applications from consumer electronics and backup power systems to hybrid vehicles. [1–4] Supercapacitors can be basically divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors according to their different energy storage mechanisms. [5,6] Pseudocapacitive materials (such as metal oxides and conducting polymers) showed much higher capacitance than that of carbon based materials for EDLC due to their fast and reversible redox reactions. [7,8] Among them, conducting polymers are very promising materials for pseudocapacitors due to their low-cost, good electrochemical response, and high theoretical capacitances. [9–11] However, the obtained capacitance of conducting polymers is strictly limited by the available reactions between the electrode materials and electrolytes. [12] Different approaches have been adopted to improve the capacitance by electrode materials optimization. [13–15] However, further improvement of the capacitance has been extremely difficult due to the intrinsic limitation of the electrode materials that used in the supercapacitors. Therefore, attention should be paid to other components that make up the pseudocapacitors such as the electrolyte. Recently, Roldan et al. showed the greatly increased capacitance of carbon based supercapacitors by using a redox-active electrolyte. [16] However, the capacitance is still limited by the dominant double layer energy storage mechanism in the carbon based supercapacitors. To the best of our knowledge, there is no study of redox electrolyte being used in pseudocapacitors based on different conducting polymers.

In this study, we report for the first time the significant improvement of the pseudocapacitance through the application of redox-active electrolytes in pseudocapacitors employing various types of polymeric electrodes, including polyaniline (PAni), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT).

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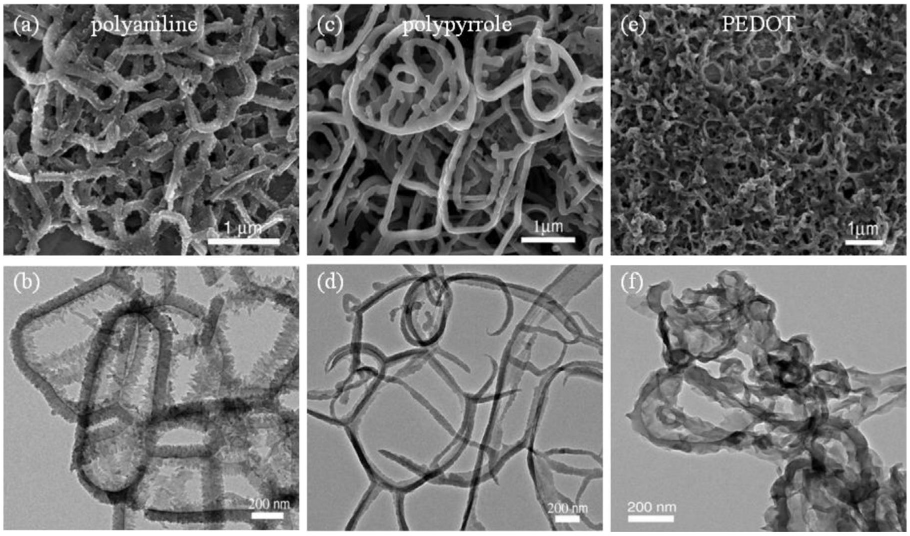

**Fig. 1.** SEM and TEM images of the three different conducting polymer nanofibers (a, b) polyaniline, (c, d) polypyrrole and (e, f) poly(3,4-ethylenedioxythiophene).

## 2. Experimental

### 2.1. Synthesis of conducting polymer nanofibers

The preparation of the three conducting polymer nanofibers (PAni, PPy and PEDOT) was followed by a modified oxidative template method that reported elsewhere. [17] Specifically, 0.01 M cetrimonium bromide (CTAB) was dispersed in 300 mL of 1 M HCl under stirring for 10 min in ice bath, followed by adding 0.03 M ammonium peroxydisulfate (APS) and stirring for another 10 min. 0.1 M conducting monomers (aniline, pyrrole and EDOT) were added separately into the prepared solution and the reactions were allowed to last for 24 h. The resulting products were washed with 1 M HCl, followed by water and ethanol repeatedly and freeze dried for 24 h.

### 2.2. Material characterization

The materials were characterized by scanning electron microscopy (SEM, Nova Nano 630, FEI), and transmission electron microscopy (TEM, Titan 80–300 kV (CT), FEI).

### 2.3. Electrochemical measurement

All electrochemical tests were conducted at room temperature in a classical two-electrode configuration. Conducting polymers acting as active materials were each mixed with acetylene black and polytetrafluoroethylene binder with a ratio of 80:10:10 in ethanol to form homogenous slurry. The electrodes were prepared by drop casting of the slurry onto graphitized carbon papers. Then the electrodes were vacuum dried at 60 °C for 12 h. The mass of the materials on the electrode was determined by a microbalance (Mettler Toledo XP26, resolution of 1 μg). The typical mass loading of the active materials is 3–4 mg cm$^{-2}$. The electrolytes used in this study are 1 M $H_2SO_4$ and 1 M $H_2SO_4$ with addition of different amount of hydroquinone (HQ). The electrochemical performance was measured in a VMP3 multi-channel electrochemical workstation (Bio-Logic) by the techniques of electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge–discharge (CD). The EIS was measured in the frequency range between 100 kHz and 100 mHz. The CV tests were performed from 5 mV s$^{-1}$ to 100 mV s$^{-1}$, and the CD tests from 1 A g$^{-1}$ to 30 A g$^{-1}$ with voltage range between 0 and 0.7 V.

## 3. Results and discussion

Three different conducting polymer nanofibers (*i.e.* PAni, PPy and PEDOT) were prepared by a facile oxidative template based on a chemical polymerization process. [17] These three conducting polymers are among the most heavily investigated polymers for supercapacitor energy storage application due to their relatively high capacity, good electrical conductivity and excellent electrochemical behaviors. [10,18–20] As shown in Fig. 1, the as-obtained conducting polymers have a fiber-like morphology with different features. Specifically, the PAni nanofibers formed interconnected networks (Fig. 1a) and each nanofiber is found to be rough on its surface, making highly porous, caterpillar-like nanofibers (Fig. 1b). The average diameter of the PAni nanofibers is about 150 nm. In contrast, the PPy nanofibers have rather smooth surface and their diameters are between 60 nm and 120 nm (Fig. 1c and d). In the case of PEDOT, a porous film with inter-tangled nanofibers is formed (Fig. 1e). The curled worm-like nanofibers have an average diameter of 80 nm (Fig. 1f). The conducting polymer nanofibers with porous network features are believed to contribute to the high conductivity and easy access of electrolyte for high performance pseudocapacitors.

Fig. 2 shows the electrochemical performance of PAni nanofibers as pseudocapacitor electrode materials in conventional $H_2SO_4$ and redox-active electrolytes ($H_2SO_4$ + HQ) with different concentrations of HQ. It is shown that the PAni nanofibers in $H_2SO_4$ electrolyte exhibits the typical electrochemical behavior of PAni with a pair of redox peaks appears in the CV curve, corresponding to the Faradaic transformation of the emeraldine-pernigranilin form of PAni (Fig. 2a). [21] Once a small amount of HQ was added to the $H_2SO_4$ electrolyte ($H_2SO_4$ + 0.1 M HQ), the CV curve of PAni nanofibers deviates from quasi-rectangular shape and the redox peaks become shaper, indicating that extensive redox reactions are taking place in the pseudocapacitors that are caused by the redox electrolyte. The intensity of the redox peaks in CV curves at the same scan rate of 10 mV s$^{-1}$ becomes larger with increasing HQ concentration in the redox electrolytes (Fig. 2a), resulting in the increased areas of the CV curves and thus the improved energy storage capacity. The CD curves show longer charge–discharge