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Effects of counterions on pseudocapacitance performance of polyaniline in sulfuric acid and p-toluene sulphonic acid electrolyte

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ABSTRACT

In order to research the effects of counterions, the pseudocapacitance performance of polyaniline (PANI) electrodeposited on glassy carbon (GC) substrate was investigated in sulfuric acid (H_2SO_4) and p-toluene sulphonic acid (p-TSA) electrolyte, respectively. It was found that the performance of PANI/GC electrode in p-TSA was inferior to that in H_2SO_4 at a low scan rate, while its superiority was shown gradually with the increase of scan rate, especially at a high scan rate of 100 mV s^{-1} in our work. The results predicted that PANI material had a more suitable heavy load charge–discharge performance in p-TSA electrolyte. Cyclic voltammetric (CV) experiments, electrochemical impedance spectroscopy (EIS) and single potential step studies were carried out to investigate the effects of the counterions. The results revealed that there were such different control processes in these two electrolytes as the diffusion control in H_2SO_4 and the surface electron transfer control in p-TSA. The diffusion coefficient D or D_{app} was calculated and equals 1.57×10^{-7} ($cm^2\ s^{-1}$) in H_2SO_4 compared with 2.97×10^{-8} ($cm^2\ s^{-1}$) in p-TSA.

1. Introduction

Conducting polyaniline (PANI) can be synthesized through chemical polymerization or electropolymerization in aqueous acid solutions [1–3]. A great number of papers about how to improve the physical and chemical properties of PANI have been published [4–11], which reported various influential facets such as solubility, conductivity, morphology, thermal stability and photoelectric characteristics. The effects of counterions have been a hot topic.

In virtue of their larger ionic radius, polarity or non-polarity, the organic acids were employed to perform doping polymerization or secondary doping, particularly with the sulfonic group such as p-toluenesulfonic acid (p-TSA), sulfosalicylic acid (SSA) and dodecylbenzenesulfonic acid (DBSA). To some extent, the morphology of PANI films depends on the type of anion, just as reported in several papers [5–8]. Huang and Wan [9] investigated that doped PANI was synthesized in the presence of different sulfonic acids, and they reported that the morphology, solubility in m-cresol as well as electrical properties of the doped PANI differed with the variation of the molecular structure of the selected sulfonic acids. Neoh et al. [10] reported that the depth of penetration of the anion into the PANI film was greatly dependent on the anion size, which demonstrated that the ClO_4^- and TSA anions were able to be protonated to a substantial depth of the base film, whereas the SSA and DBSA anions were confined to the surface regions only. The behaviour of emeraldine salt (ES) film obtained from an emeraldine base (EB) with aqueous organic sulfonic acids was studied by Ayad and Zaki [12], who using a quartz crystal microbalance (QCM) revealed that the kinetics of the doping reaction displayed a slow diffusion process.

However, the effects of counterions on the pseudocapacitance behaviours of PANI materials were rarely reported, though the investigations into the enhancement of the specific capacitance of PANI electrodes were published extensively such as in these papers [13–15]. Therefore, this article will attempt to shed some light on this aspect. A layer of PANI film (1–10 μm) on a glassy carbon substrate was electrodeposited and then was studied in different electrolytes which were typical acids: inorganic (H_2SO_4) and organic (p-TSA). The results for the PANI film exhibited different pseudocapacitance performances for these two electrolytes. The corresponding explanations for this apparent difference are offered in detail within this paper.

2. Experiment

2.1. Chemicals and PANI film synthesis

Aniline (>99.5%, Bodi Chemical Co. Ltd. Tianjin) was purified by distillation twice. Sulfuric acid and p-toluenesulfonic acid were used as received. The dilute H_2SO_4 (>96%, Damao Chemical Co. Ltd. Tianjin) and aqueous solution of p-TSA (>96%, Damao Chemical Co. Ltd. Tianjin) were prepared from doubly distilled water.

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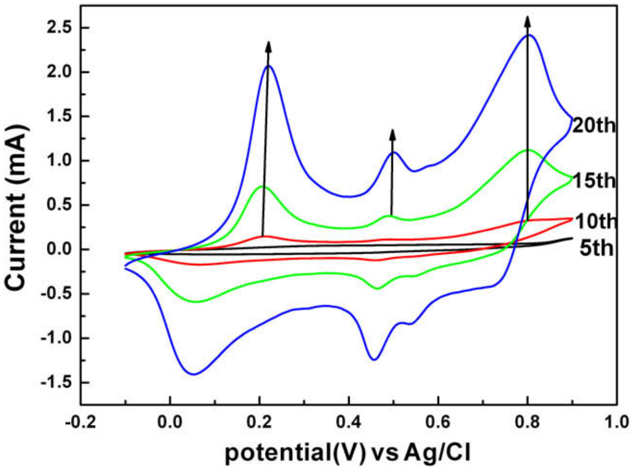

Fig. 1. Cyclic voltammograms for the PANI deposited on GC electrode in 0.5 M H_2SO_4 + 0.1 M aniline solutions at the scan rate of 20 mV s^{-1} with 20 cycles.

The PANI film was electrodeposited by cyclic voltammetry (CV) with a standard three-electrode cell containing 0.1 M aniline and 0.5 M H_2SO_4 and using a platinum column as the counter-electrode, while a commercially available column glassy carbon (Aiji Carbon Co. Ltd. Shanghai) (Φ = 4 mm) served as the working electrode, with Ag/AgCl (Shanghai Electrical Instrument Works) being the reference electrode. The column glassy carbon was polished with 0.5 M diamond paste, ultrasonically washed with acetone and distilled water in turn, and then activated through the electrochemical method in 0.5 M H_2SO_4 prior to each run. The PANI film electrodes were rinsed by with 0.5 M H_2SO_4 and doubly distilled water in turn after polymerization.

2.2. Measurements

All experiments were carried out within a conventional three-electrode electrolytic cell with a PANI/GC electrode as the working electrode and platinum foil ($A = 0.5\ cm^2$) as the counter-electrode. CV tests were conducted in the potential range −0.1 to 0.8 V at various scan rates. The Impedance Spectrum Analyzer, IM6e (ZAHNER, Germany), with Thales software was employed to measure and analyze the AC impedance spectra of the PANI/GC electrode obtained at 0.5 V (vs. Ag/Cl). The potential amplitude of the AC was kept as 5 mV and a wide frequency range from 10 mHz to 100 kHz was used. Single Potential Step Chronoamperometry (SPSC) experiments were conducted in 0.5 M H_2SO_4 followed by experiments in 0.5 M p-TSA, at −0.1 V initial potential with 0.8 V step-potential, and their current–time curves were recorded. The solutions were deaerated by purging with purified nitrogen gas for 30 min before the start of each experiment. CV and SPSC tests were realized on the LK9805Z electrochemical workstation system (Lanlike Company, Tianjin). The microstructure of the samples was

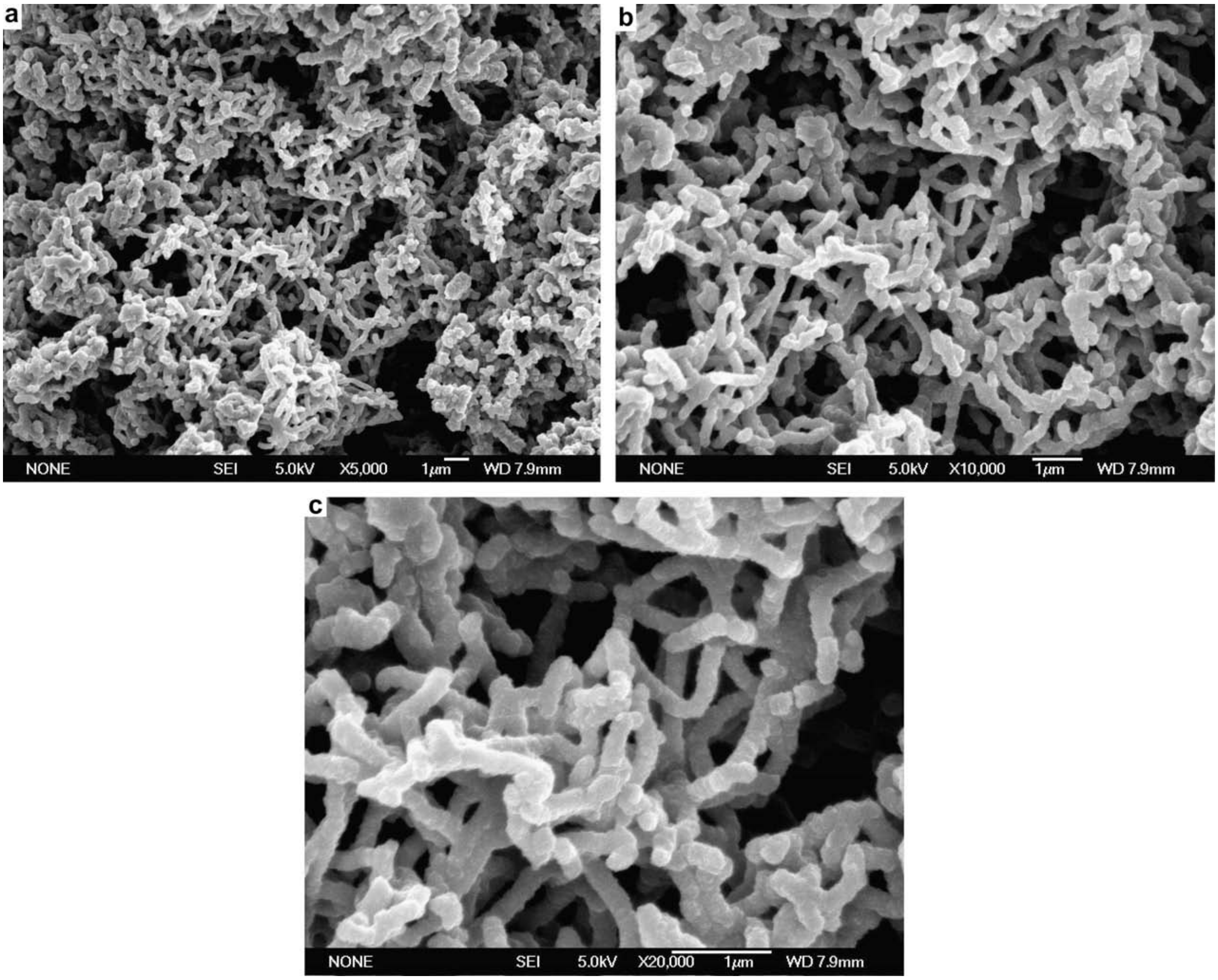

Fig. 2. SEM morphologies of PANI film at different magnification.