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Behavior of electrical charge storage/release in polyaniline electrodes of symmetric supercapacitor

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ABSTRACT

This account investigated the behavior of the electrical charge storage/release in polyaniline (Pani) electrodes of a symmetric supercapacitor with 0.5 M H_2SO_4 electrolyte. Two Pani films with different morphologies were synthesized under various reaction pressures. The structural and morphological characterizations of Pani films were carried out by Fourier Transform infrared spectroscopy (FTIR) and Field emission scanning electron microscopy (FESEM). The electrochemical behavior of Pani films was characterized by several methods, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) cycling and electrochemical impedance spectroscopy (EIS). The performance of the electrodes assembled in a symmetric supercapacitor configuration was also characterized by GCD in different voltage windows. The contributions from the electric double-layer capacitance (EDLC) and the pseudo-capacitance (PSC) of Pani electrodes at different potential windows were evaluated and compared. The results suggested that the specific capacitance induced from EDLC and PSC for Pani films with porous nano-network morphology were obviously higher than those generated by the granular Pani films. This was attributed to the porous nano-network structure, which had a significant role in increasing the specific surface area. For symmetric Pani supercapacitors, the induced capacitance at the negative electrode was found dominated by PSC while accumulation/release of the electric charge at the positive electrode mainly followed an EDLC mechanism. The redox potential of Pani played a cut-off point between the potential range dominated by EDLC and PSC mechanisms. A working model was proposed to describe the electrical charge storage/release processes at different electrodes assembled in a symmetric capacitor configuration.

1. Introduction

Supercapacitors have many advantages over conventional batteries, including the high power density and good cycling stability [1–3]. The intrinsic characteristic, which integrates the performance of both conventional batteries and capacitors, makes it useful for many applications [4]. For these reasons, supercapacitors are used to couple with secondary batteries in most applications and provide high power densities together with elevated energy densities. The capability of supercapacitors to store energy follows the electric or electrochemical energy storage mechanisms, which are well described by the "electric double-layer capacitance" (EDLC) and the "pseudo-capacitance" (PSC) [5–8]. So far, it is confirmed that electrically conductive porous electrode materials, including porous carbon materials, exhibits excellent charge/discharge performance due to EDLC [9]. This is attributed to the high specific surface area and fast transfer of the electrical charge at the electrodes. Furthermore, EDLC may quickly be formed at the interface between porous electrode materials and electrolyte when a working voltage is applied to the electrodes [10]. The charge storage of electrochemically active materials, including transition metal oxides and conducting polymers (CPs) is mainly produced through a PSC mechanism [11–13].

Transition metal oxides and CPs usually undergo a fast and reversible Faradic reaction throughout the bulk volume of the electrode materials, which provide high specific capacitance when compared to that induced by carbon materials. In recent years, CPs as potential candidates for supercapacitor electrode materials have widely been investigated due to their unique properties, such as

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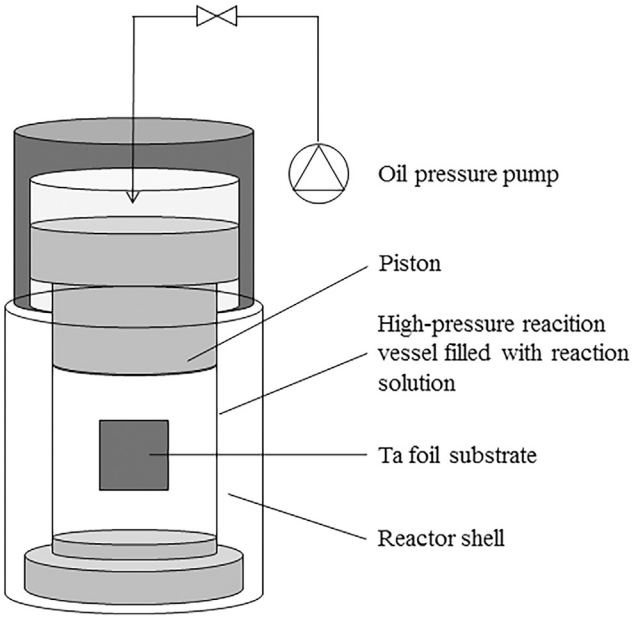

Fig. 1. Schematic representation of the experimental VHP synthesis setup used to prepare the Pani films.

facile thin film fabrication, ease of processability, light weight density, and good elasticity [14–17].

Pani is one of the most promising materials for supercapacitor applications. Because Pani in the conducting state (i.e. emeraldine salt state) has good electrical conductivity, the capacitance of Pani electrode is considered to follow an EDLC mechanism [18]. However, since Pani can be electrochemically oxidized and reduced, it also follows a PSC behavior [19]. In fact, Pani changes

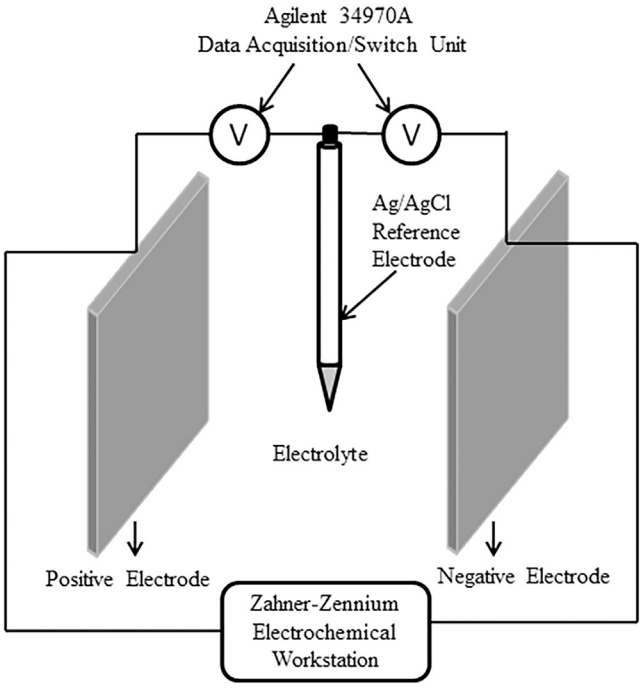

Fig. 2. A schematic view of the measuring system used in the GCD measurement for symmetric supercapacitors.

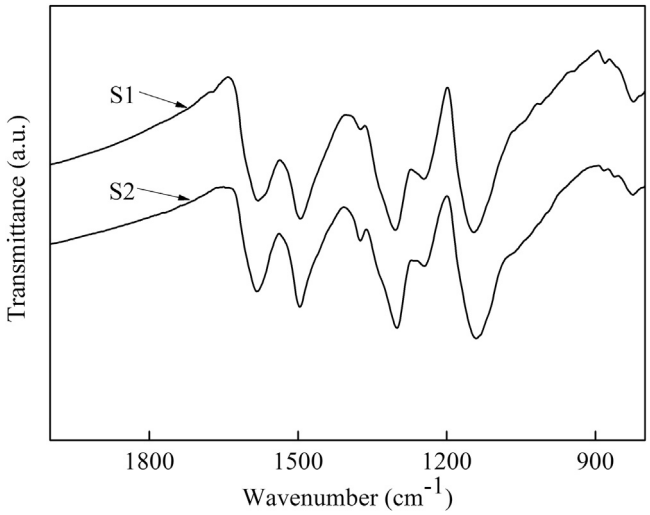

Fig. 3. FTIR spectra of S1 and S2.

chemically under suitably applied potential to induce Faradaic reaction process, which accompany with the transformation of the Pani redox state. This induces a capacitance based on PSC mechanism.

Overall, it is safe to state that the capacitance in Pani could be generated from EDLC and/or PSC. A literature review indicates that tremendous efforts have been devoted to investigating the nature of EDLC and PSC of Pani [20–26]. For example, the effect of redox state and counter ions on EDLC and PSC for Pani have systemically been investigated using electrochemical impedance spectroscopy (EIS) [21,22]. The experimental results indicate that both EDLC and PSC may occur together in Pani during dynamic measurements. Furthermore, analysis of the data of EIS reveals that the co-existence of EDLC and PSC could be observed in Pani electrode, where the overall specific capacitance obviously depends on the specific surface area [23–25].

In this account, the performance of the electrical charge storage/release in Pani electrodes of a symmetric supercapacitor was studied by focusing on the basic electrochemical behavior. Then, two similar electrodes of Pani in H_2SO_4 solution (0.5 M) as an electrolyte were constructed and assembled into a symmetric capacitor. The contribution from EDLC or PSC of both positive and negative electrodes was then investigated using galvanostatic charge-discharge (GCD) measurements on a three-electrode cell. The potential of both positive and negative electrodes varied in different directions during the charge/discharge processes, which induced different capacitance mechanisms at different electrodes.

2. Experimental

Two Pani films with different morphologies were synthesized at different reaction pressures, and the specific capacitance resulting either from EDLC, PSC or both were investigated. These samples were prepared through a conventional chemical *in-situ* polymerization route [27], using the synthesis apparatus illustrated in Fig. 1. The preparation process consists of first to dissolve aniline (115 μL) and ammonium peroxydisulphate (APS, 0.356 g) in hydrochloric acid (50 mL, 0.1 M) to form a homogeneous solution, of which 5.0 mL was then added into a high-pressure reaction vessel. Subsequently, a thoroughly cleaned square tantalum (Ta) foil substrate ($10 \times 10\,mm^2$) was vertically immersed in the solution at a temperature maintained between 0 °C to 5 °C during the whole synthetic process. During this process, the applied