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Effects of buffer agents on hydrogen adsorption and desorption at/within activated carbon for the negative electrode of aqueous asymmetric supercapacitors

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ABSTRACT

In this work, the effects of adding buffer agents into aqueous electrolytes on the hydrogen adsorption/desorption behaviour at/within activated carbon are systematically investigated for the negative electrode of asymmetric supercapacitors. Due to the poor electrochemical reversibility of hydrogen adsorption/desorption at/within activated carbon, the hydrogen responses at/within activated carbon are not suitable for pseudo-capacitive energy storage of high-performance asymmetric supercapacitor. The electrochemical adsorption of H atoms consumes protons and causes the local pH change at the activated carbon/electrolyte interface, leading to the negative shift in the H adsorption potential when weakly acidic, neutral, and weakly basic electrolytes without buffer agents are employed. The addition of buffer agents into electrolytes significantly improves the rate of proton supply and promotes the rate of hydrogen adsorption at/within AC. Interestingly, the onset potential of significant H adsorption obtained from the buffered electrolytes generally follows the Nernstian dependence, suggesting the Nerstian dependence of H^+/H_{ads} on AC at all pH values. In order to obtain the energy storage devices with high coulombic and energy efficiencies, the onset potential of significant H adsorption obtained from the electrolyte containing buffer agents is a reliable lower potential limit of the AC-coated negative electrode for aqueous asymmetric supercapacitors.

1. Introduction

The hydrogen adsorption/desorption behaviour at/within carbon materials in aqueous electrolytes has been widely investigated in the literature [1–3], where the mechanism of hydrogen adsorption at/within carbon materials was proposed as follow [3,4]:

$$C + H_2O + e^- \rightarrow CH_{ad} + OH^- \quad (1)$$

$$C + H_3O^+ + e^- \rightarrow CH_{ad} + H_2O \quad (2)$$

where CH_{ad} stands for the hydrogen atoms adsorbed at/within surface of carbon materials. Actually, various carbon materials, including carbon nanotubes, graphene sheets, and activated carbon (AC), have been demonstrated to be good candidates for electrochemical hydrogen storage due to long cycle life, low cost, and environmental friendliness [5–8].

With regard to aqueous supercapacitors, the hydrogen adsorption/desorption responses at/within carbon materials must occur from either water decomposition reaction (producing OH^- anions, shown in Eq. (1)) or consumption of H_3O^+ cations (Eq. (2)). As a result, the electrochemical adsorption of H atoms causes an increase of local pH value in the proximity to the AC/electrolyte interface. Therefore, when AC acted as the electroactive material for negative electrodes in supercapacitors, the hydrogen adsorption makes the potential limit of negative electrode very low in the charging process. This phenomenon is presumably to be severer in weakly acidic, neutral, and weakly basic aqueous electrolytes since the concentration change of local OH^- (or H_3O^+) significantly affects the pH value for this kind of aqueous electrolytes in comparison with concentrated alkaline and acidic solutions. Accordingly, it was reported utilising carbon materials as the electroactive material in negative electrode in either symmetric or asymmetric supercapacitors is advantageous since electrochemical hydrogen adsorption at/within carbon materials gives an unexceptional high overpotential of hydrogen evolving reaction (HER) (e.g., −1 V *vs.* NHE in Na_2SO_4 against −0.38 V of the

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theoretical water decomposition potential [9,10]). Thus, the enlarged potential window in neutral aqueous media can be obtained. Furthermore, pseudocapacitive current responses due to hydrogen adsorption/de-sorption at/within carbon materials were suggested to be capable to increase the specific capacitance in neutral aqueous electrolytes [3,9]. Therefore, the energy density of supercapacitors can be significantly improved owing to the both enhancements of specific capacitance and cell voltage of supercapacitors ($E = CV^2/2$).

Although the capacitive performance can be improved by utilisation of hydrogen adsorption/desorption at/within carbon negative electrodes, the peak potentials corresponding to hydrogen adsorption and desorption are hugely separated (e.g., hydrogen adsorption at −1.187 V *vs*. Ag/AgCl while desorption at 0.343 V in 1 M Na_2SO_4 [9]). Note that supercapacitors require the high-power delivery with acceptable coulombic and energy efficiencies in the rapid charge/discharge process. Since the electrochemical reversibility of the hydrogen adsorption/desorption at/within carbon negative electrodes is poor, it inevitably provokes the doubt of the practical application of the electrochemical hydrogen storage in supercapacitors.

According to the above considerations, we systematically studied the electrochemical hydrogen adsorption/desorption at/within a commercially available AC in aqueous electrolytes with various pH values in this work. Moreover, the electrochemical behaviour of the reaction of hydrogen adsorption/desorption is investigated in neutral aqueous medium with the addition of buffer agents to stabilise the local pH value. We also used the method of potentiostatic polarisation to present the effects of buffer agents on hydrogen adsorption/desorption at/within AC in the potential range for the negative electrode of aqueous asymmetric supercapacitors. A narrower potential window was found in the neutral electrolyte with buffer agents. In order to obtain the energy storage devices with high coulombic and energy efficiencies, the onset potential of significant H adsorption obtained from the electrolyte containing buffer agents is suggested to be the reliable lower potential limit of the AC-coated negative electrode for aqueous asymmetric supercapacitors. Besides, the use of potentiostatic polarisation indicates the occurrence of leakage current within the potential range of electrochemical hydrogen storage.

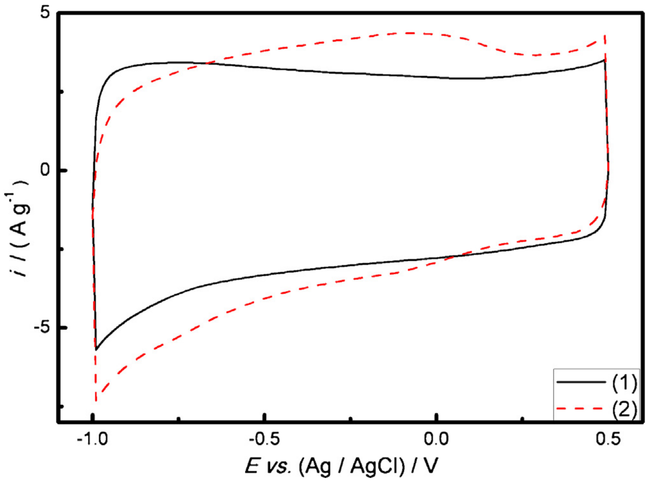

Fig. 1. Cyclic voltammograms of an AC-coated electrode measured at 25 mV s^{-1} in 1 M Na_2SO_4 (1) without and (2) with buffer agent (0.34 M NaH_2PO_4) at pH = 7.

2. Experimental

2.1. Preparation of activated carbon-coated graphite electrodes

The pre-treatments of the graphite substrates completely followed our previous procedure [11]. The exposed area of the working electrode was controlled to be 1 cm^2 for the electrochemical characterization. The activated carbon electrodes were prepared by mixing 89 wt% of activated carbon (ACS-679 from China Steel Chemical Corporation, Taiwan) and 11 wt% of polyvinylidene difluoride (PVDF) in 100 μL of N-methyl-pyrolidinone (NMP), followed by ultra-sonication for 30 min in order to completely disperse well into the solvent. The as-prepared solutions were drop casted on the graphite substrates and dried in the oven at 85 °C for overnight.

2.2. Electrochemical Characterization

The electrochemical properties were evaluated using an electrochemical analyzer system, CHI 6273E (CH instruments,

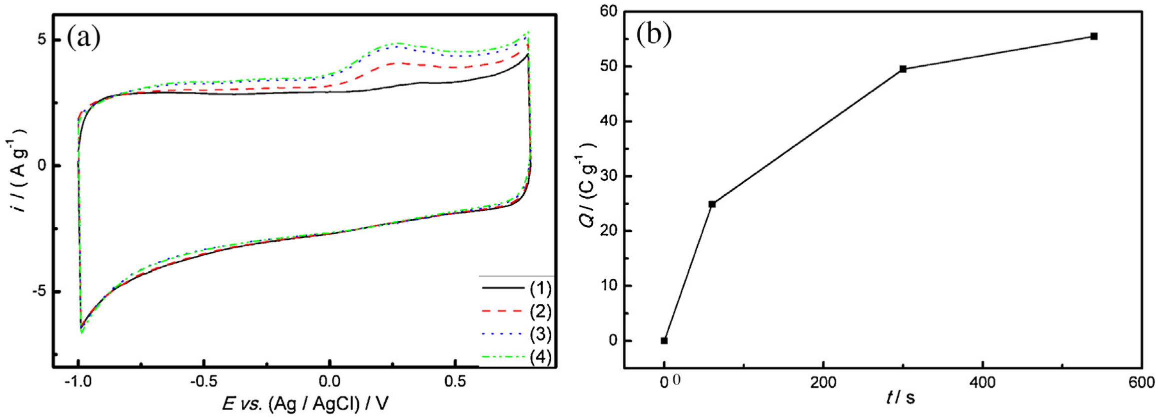

Fig. 2. (a) Cyclic voltammograms of an AC-coated electrode measured at 25 mV s^{-1} in 1 M Na_2SO_4, which has been fixed at −1.0 V for (1) 0, (2) 60, (3) 300, (4) 540 s, respectively; and (b) the corresponding charges of H desorption from the anodic humps shown in (a) against the polarization (floating test) time.