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Controlling hydrazine reduction to deposit iron oxides on oxidized activated carbon for supercapacitor application

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ABSTRACT

Activated carbon/iron oxide composites were synthesized by the chemical reduction of activated carbon/FeO(OH) using hydrazine hydrate as reducing agents to optimize the hydrazine concentration. Changes in the crystal structures of iron oxide are observed as the concentration of hydrazine is varied. These changes affect the redox reactions and kinetics of iron oxide during charge–discharge process, which can significantly affect the supercapacitive performance. The characterization of morphology and microstructure of the as-prepared composites demonstrates that FeO(OH) is successfully formed on the activated carbon surface and reduced to Fe_3O_4 by hydrazine reduction. The capacitive properties of the as-prepared composites are evaluated using cyclic voltammetry, galvanostatic charge/discharge testing, and electrochemical impedance spectroscopy in a three-electrode experimental setup using a 1 M Na_2SO_3 aqueous solution as the electrolyte. The capacitive property of the activated carbon/Fe_3O_4 electrode which is reduced by 5 ml of hydrazine shows excellent electrochemical performance (168.5 F g^{-1} at a current density of 2 A g^{-1}). It is anticipated that these optimized process to prepare activated carbon/ironoxide composite is a promising fabrication method for supercapacitor electrodes.

1. Introduction

The increasing popularity of various portable electronic devices and motor vehicles has increased the demand of energy storage devices. In this regard, energy storage and conversion from alternative energy sources has been attracting extensive interest in both fundamental research and technological development. In many application areas, some of effective and practical technologies for electrochemical energy conversion and storage are batteries, feul cells, and supercapacitors. Among these, supercapacitors, also called electrochemical capacitors or ultra-capacitors represent an emerging class of energy storage devices that have attracted increasing attention because of a number of important features including high power density, fast charge/discharge rate, and excellent cycle stability [1].

Usually, according to the underlying charge storage mechanism, supercapacitors can be divided into two groups: (i) EDLCs (electrochemical double-layer capacitors), the capacitance of EDLCs solely comes from the charge separation arising at interface between the electrode and electrolyte and (ii) pseudo-capacitors, in which the pseudo-capacitance arises from faradic reactions occurring at the electrode interface [2]. Typical electrode materials for EDLCs include various carbonaceous materials, such as activated carbon, graphene, carbon nanotube which is convenient for storing energy in a double layer formed on the surface [3]. On the other hand, transition metal oxides such as ruthenium oxide, manganese oxide, and iron oxide are most widely used in electrode materials for pseudo-capacitor because of their fast reversible faradic reaction [4].

Among EDLCs materials, activated carbon is the most widely used electrode materials for EDLCs because of their extremely large surface area, low cost, nontoxicity, easy processability, and cycling stability [5]. However, a disadvantage of EDLC materials including activated carbon is that their energy densities are much lower than those of batteries [6]. Conversely, metal oxides provide much higher energy density than EDLC materials. As pseudo-capacitive material, Ruthenium oxide has been found to have high capacitance due to redox transition that even penetrates into the bulk of material; however, the cost of ruthenium is one of the concerns for commercial acceptance [7]. Therefore, the present trend in the ongoing research on supercapacitors is to develop economical electrode materials with a high capacity of charge storage and

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energy density. In this regard, iron oxide is candidate for promising material for use in electrochemical capacitors due to its cost effectiveness, abundance, and environment-friendly nature. However, because of stability window and cyclic stability, metal oxide including iron oxide is still limited to potential application [8].

Many recent studies have concerned the synthesis of carbon materials/iron oxide composites for hybrid capacitor electrodes, resulting synergistic effect of combination electric double-layer capacitive and pseudo-capacitive properties. Wang et al. reported that graphene/Fe_2O_3 composites exhibit a specific capacitance of 151.8 F g^{-1} at a current density of 1 A g^{-1} [9]. Liu et al. also reported ultrathin nanoporous Fe_3O_4/carbon nanosheets with surface area of 229 m^2 g^{-1} and a specific capacitance of 163.4 F g^{-1} at a current density of 1 A g^{-1} [10].

As stated above researches, Iron oxide can be classified as Fe_2O_3 and Fe_3O_4 depending on their crystalline structure. Interestingly, different crystalline structures of iron oxide can affect different redox reactions and kinetics during charge/discharge process, which can significantly affect the electrochemical performance. Therefore, Wang et al. reported that the specific capacitance of Fe_3O_4(133 F g^{-1}) is much higher than those of Fe_2O_3 (40 F g^{-1}) at 1 A g^{-1} of current density because the more vigorous faradic redox reaction is occurred on the Fe_3O_4 surface [11]. In this point, Fe_3O_4 is more promising material than Fe_2O_3 for supercapacitor application. However, there is limitation to apply pure Fe_3O_4 for supercapacitor electrode materials because Fe_2O_3 coexists with Fe_3O_4 during the synthesis process of Fe_3O_4.

In this study, we propose a facile synthesis of superfine activated carbon/Fe_3O_4 nanocomposites using the inorganic salt $FeCl_3$ and hydrazine as Fe precursor and reducing agent, respectively. As reducing agent, the hydrazine can be the most important role in the synthesis of Fe_3O_4 particles by controlling degree of Fe precursor reduction. Therefore, hydrazine concentration should be optimized to form Fe_3O_4 without coexistence of Fe_2O_3 on the activated carbon. Materials synthesized with various hydrazine concentrations were characterized, and their electrochemical performances were investigated using CV (cyclic voltammetry), galvanostatic charge/discharge, and EIS (electrochemical impedance spectroscopy) measurements. Specific capacitance and cycling retention were also analyzed.

2. Experimental

2.1. Oxidation of activated carbon

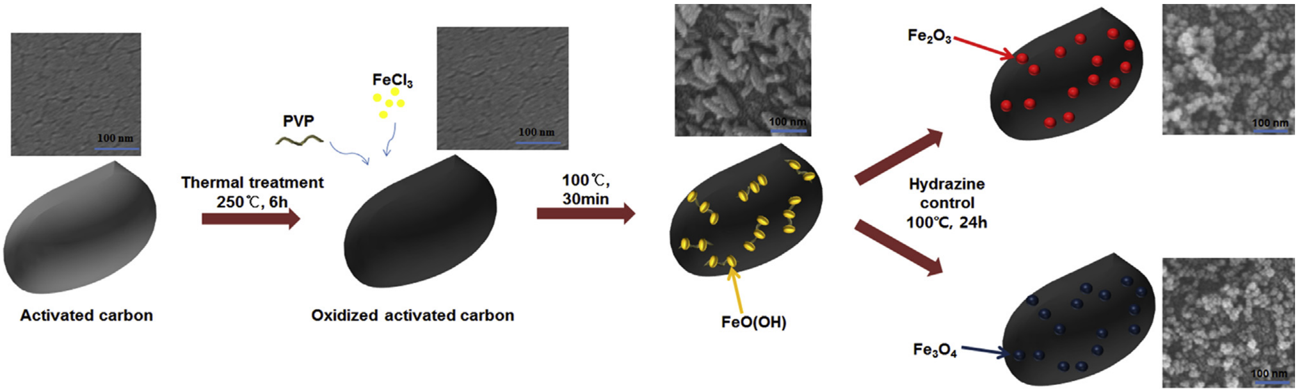
Before synthesizing activated carbon/iron oxide composites, oxidation of activated carbon carried out to obtain oxygen group on the activated carbon surface which plays role in anchoring site to facilitate adsorption of iron oxide precursor on the activated carbon surface [12]. Oxygen groups were obtained by thermal treatment at 250 °C in an oxygen atmosphere for 6 h. Because of the negligible extent of carbon gasification at this temperature, weight gain due to oxygen chemisorption, rather than weight loss, was observed. Oxidized activated carbon will be denoted AC hereafter.

2.2. Fabrication of the AC/FeO composites

As in typical methods for the synthesis of these composites, the process started with the addition of 0.2 g of AC and 2.5 g of PVP (K30, Daejung) to 200 ml of deionized water. This mixture was dispersed by ultrasonication for 20 min at room temperature. Then, with vigorous stirring, 2.1 g of $FeCl_3 \cdot 6H_2O$ was added to the suspension. Subsequently, the mixture was heated to 100 °C and retained for 30 min in order to provide a homogeneous dispersion of FeO(OH) covering the AC. Afterwards, 0, 1, 3, 5, and 7 ml of hydrazine monohydrate (80%, Daejung) was added to the mixture, which was then kept at 100 °C for 24 h. After that, the AC/FeO composites were collected by filtration and washed several times with deionized water and methyl alcohol. Finally, the composites were dried in a vacuum oven at 80 °C for 24 h. The obtained products were denoted as AC/FeO(0), AC/FeO(1), AC/FeO(3), AC/FeO(5), and AC/FeO(7) where the number in parentheses indicates the amount (in ml) of added hydrazine hydrate.

2.3. Characterization

The morphology of the as-prepared samples was investigated by using a field emission scanning electron microscope (FE-SEM, SIGMA, Carl Zeiss). The XRD (X-ray diffraction) patterns were collected with a new D8-Advance (Bruker-AXS) instrument, at a scan rate of 1° s^{-1} with a 2θ range of 15–70° and Cu $K_{\alpha 1}$ radiation (0.154056 nm). XPS (X-ray photoelectron spectroscopy) analysis was carried out on a VG Microtech ESCA 2000 system using a Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer. In the subsequent curve fitting, the Gaussian peak widths were kept constant for each spectrum. Composition of the samples was investigated by thermogravimetric analysis (TGA, TA Instruments, TGA-2050) at a heating rate of 10 °C min^{-1} in air flow. The BET (Brunauer–Emmett–Teller) surface areas were determined using an Autosorb-iQ 2ST/MP (Quantachrome) system using nitrogen adsorptive at 77 K. Prior to the measurements, the samples were degassed under vacuum at 200 °C for 12 h.



Scheme 1. Schematic illustration of synthesis of iron oxide on oxidized activated carbon.