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Effect of manganese dioxide on supercapacitive behaviors of petroleum pitch-based carbons

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ABSTRACT

Petroleum pitch is activated with KOH, and different concentrations of MnO_2 nanoparticles are impregnated on petroleum pitch-based activated carbons with a simple chemical reaction. Fiber-like MnO_2 is successfully grown on the surface of the activated carbons. The specific capacitance of A-PP-0.02 is 92 F/g in 0.5 M Na_2SO_4. This increase is due to the appropriate combination of the pore structure and MnO_2 that allows electrolyte ions to easily reach the electrode. The results indicate that MnO_2 is a promising metal oxide for increasing the specific capacitance of petroleum pitch-based activated carbons and can overcome the low energy density.

Introduction

Supercapacitors, which are also called electrochemical capacitors (ECs), are promising energy storage systems and categorized as either electrical double-layer capacitors (EDLCs) or faradic pseudocapacitors. The former stores energy in the electrical double-layer at the interface between the surface; they have excellent electrochemical stability because of just charge rearrangement, but low specific capacitance. On the other hand, the latter stores energy via fast and reversible redox reactions and exhibits high specific capacitance. Supercapacitors have several advantages such as good safety, long cycle life, high power, and high power density because of their fast charge/discharge processes. For these reasons, supercapacitors are increasingly being used in portable electronic devices and hybrid electric vehicles [1–3].

Activated carbons (ACs) have been used in supercapacitor electrode materials, due to their high specific surface area and good electrical conductivity; moreover, the narrow pore diameters of ACs resulted in high pore accessibility [4–10]. AC-based supercapacitors have high power density, but usually suffer from a lower energy density. Recently, metal oxides such as RuO_2 [11,12], NiO [13–15], IrO_2 [16], Co_3O_4 [17,18], and MnO_2 [19–23] have been studied to overcome this problem because they have a high surface area and pseudocapacitances [24]. In particular, MnO_2 is considered to be a promising pseudocapacitive material because of its low cost, non-toxicity, abundance, and excellent electrochemical performance. Moreover, MnO_2 nanoparticles perform better electrochemical performance than large MnO_2 particles [25–29].

Recently, petroleum pitch was used as an electrode material. Petroleum pitch is a mixture of polyaromatic molecules and heterocyclic compounds with high carbon content. Petroleum pitch is inexpensive because it is obtained from the pyrolysis of petroleum residues. Moreover, physically or chemically activated petroleum pitch has a high N_2 BET surface area [30–33]. In this study, we prepare MnO_2/petroleum pitch-based ACs composites with different amounts of MnO_2 to investigate the electrochemical behavior of the resulting composites.

Experimental

Preparation of MnO_2/petroleum pitch composites

First, petroleum pitch was stirred with HCl to remove any impurities. Then, the petroleum pitch was filtered, washed with distilled water, and dried at 80 °C for 12 h. To obtain petroleum pitch-based ACs (A-PP), the petroleum pitch was first mixed with KOH (1:4, w/w) and the resulting mixture was heated at 850 °C for 1 h at a heating rate of 2 °C/min in N_2 flow [34]. After activation of the petroleum pitch, the sample was washed with distilled water, filtered, and dried at 80 °C for 24 h.

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Next, 0.8 g of A-PP was mixed with 100 mL of 0.01, 0.02, 0.05, and 0.10 M $KMnO_4$ solutions and stirred for 1 h. After $KMnO_4$ was introduced on the surface of the A-PP, 100 mL of 0.15 M $Mn(Ac)_2{\cdot}4H_2O$ solution was added dropwise at 100 °C, and the resulting solution was stirred for 8 h. The mixture was then filtered, washed with distilled water and ethanol, and dried at 80 °C for 24 h in a vacuum oven. The samples were defined as A-PP-0.01, A-PP-0.02, A-PP-0.05, and A-PP-0.10 according to the $KMnO_4$ concentrations.

Structural characterization

The morphologies of the composites were observed using scanning electron microscopy (SEM, SU 8010, Hitachi Co., Ltd.)

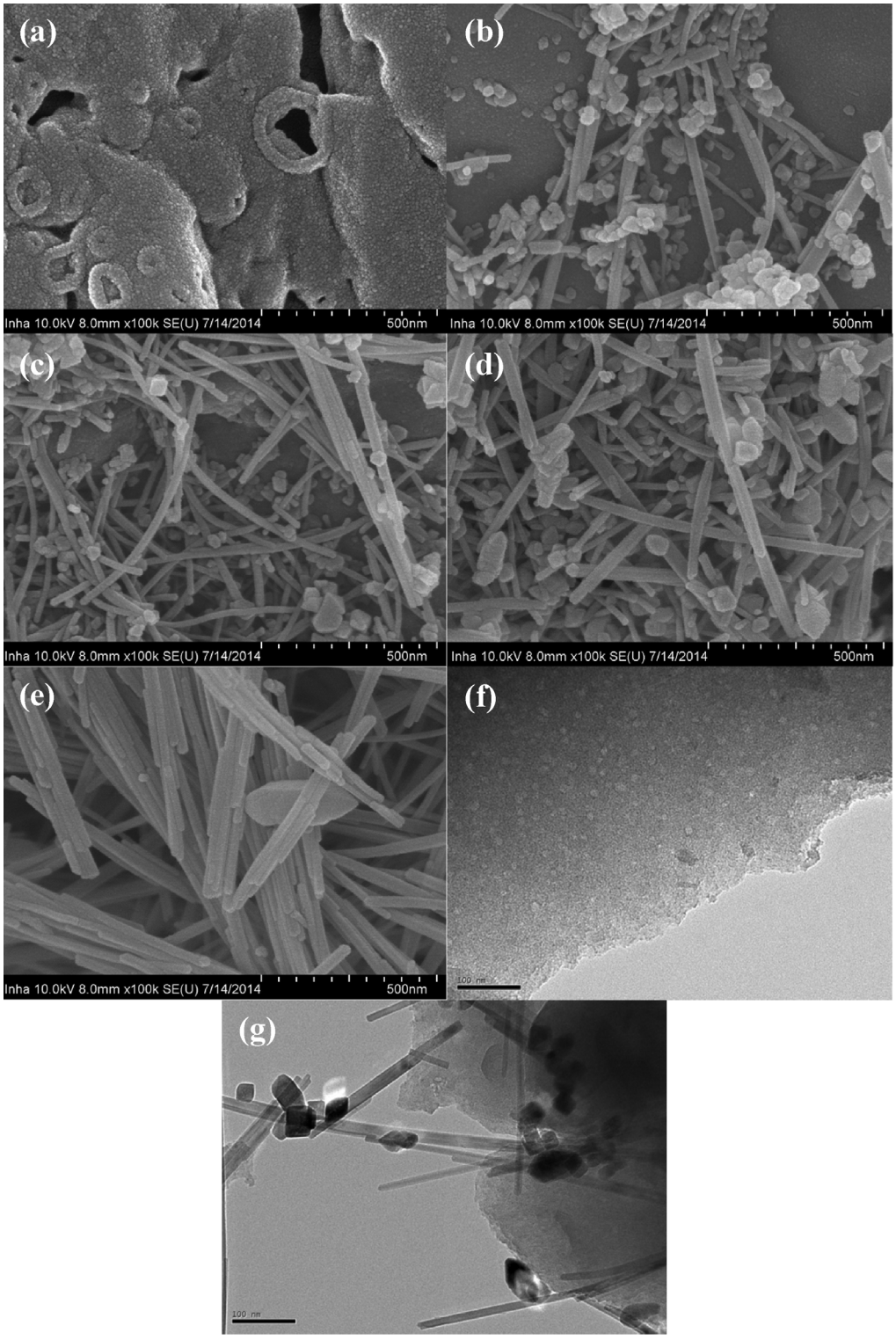

Fig. 1. SEM images of (a) A-PP, (b) A-PP-0.01, (c) A-PP-0.02, (d) A-PP-0.05, and (e) A-PP-0.10, and TEM images of (f) A-PP and (g) A-PP-0.02.