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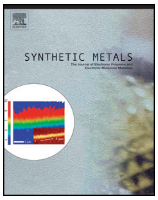

Development of a carbon foam supercapacitor electrode from resorcinol–formaldehyde using a double templating method

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ABSTRACT

Carbon foam (CFDT) has been fabricated by polycondensation of resorcinol and formaldehyde, using two kinds of polymethylmethacrylate as pore generators. In order to increase the specific surface area and improve the surface activity and wettability of the material in the electrolyte, physical activation (A-CFDT) with CO_2 and chemical modification (N-CFDT) with HNO_3 were carried out. CFDT showed poor supercapacitor properties, with a specific capacitance of 80.1 F/g at a 10 mV/s scan rate. N-CFDT exhibited the largest specific capacitance, with a value of 137.8 F/g at a 10 mV/s scan rate, when using 6 M KOH as the electrolyte. N-CFDT exhibited excellent cycle life stability as well.

1. Introduction

As the demand for electric vehicles, portable electronic devices, and more environmentally friendly technology increases, the development of new, low-cost, and eco-friendly energy storage systems exhibiting high power density has become increasingly important [1,2]. Supercapacitors, as ideal energy storage devices, have drawn considerable attention because of their high energy density, reversibility, and long cycle life [3].

Generally, supercapacitors are identified as either electrical double-layer capacitors (EDLCs) or redox pseudocapacitors, based on their charge–discharge mechanism. Metal oxide pseudocapacitors tend to have a higher specific capacitance because they undergo reduction–oxidation reactions. Unlike pseudocapacitors, carbon-based EDLCs achieve relatively low specific capacitance but have a longer life cycle [4,5].

The EDLC electrochemical double layer forms through the contact of an electrical conductor with an ionic one, leading to the generation of a charge separation on both sides of the interface [6]. EDLCs rely on the electrostatic absorption and desorption of charges at the double layer and the simultaneous inhibition of faradic reactions. These features allow EDLCs to exhibit high specific power, excellent cycle efficiency, fast charge and discharge capabilities, and stability to current changes [7].

Porous carbon materials have traditionally been used in supercapacitors due to their large surface area, structural regularity, thermal and chemical stability, ease of preparation, and low cost [8]. Therefore, the fabrication of these materials has been of tremendous interest, with templating being an especially popular method because of its ability to allow pore structure modulation and the generation of a uniform and interconnected pore network. Templating methods can usually be classified as either hard or soft [9,10].

Hard templating relies on zeolite, silica, alumina, and ludox backbones; overall, these methods tend to be very hazardous due to the need for hydrofluoric acid (HF) in removing the inorganic template [11]. HF is highly corrosive and can quickly and permanently damage eyes and lungs. Soft templating methods are therefore preferred; these rely on polymer backbones such as polystyrene (PS), polymethylmethacrylate (PMMA), and triblock copolymers like Pluronic F127 and P123. Triblock copolymers in particular play a vital role because they self-assemble to form ordered mesoporous structures in phenol–formaldehyde (PF) and resorcinol–formaldehyde (RF) resin. Soft templates can be removed through carbonization [12–15].

The specific capacitance of carbon foam is almost always improved by increasing surface area and modifying both pore size and surface features. This is usually accomplished through an activation stage that follows carbonization, which can be accomplished either through physical activation using an activating gas like CO_2 or H_2O or through chemical activation using an oxidizing agent like KOH or NaOH. While chemical activation needs lower temperatures and less time, it requires an additional washing step

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and is very corrosive and expensive. Physical activation is therefore the most commonly used method [16–18].

In this work, carbon foam was synthesized using a double templating method. RF resin was used as a carbon precursor, while variably sized PMMA molecules were used to modulate pore generation. In addition, the carbon foam was subjected to surface modification with HNO_3 in order to integrate oxygen-containing functional groups and improve its wettability in aqueous electrolyte [19,20].

2. Experimental

2.1. Materials

Resorcinol, formaldehyde (36% aqueous solution), sodium carbonate, methyl methacrylate (MMA), and potassium persulfate were purchased from Junsei Chemical (Japan). The PMMA brand SUNPMMA-S50 (4–8 μm) was supplied by Sunjin Chemical (South Korea). All chemicals were used without further purification.

2.2. Polymerization of MMA

Methyl methacrylate (10 g) was added to distilled water (90 g) and stirred for about 30 min at 300 rpm. The resulting solution was then heated to 90 °C and a mixture of 0.1 g of potassium persulfate and distilled water (10 g) was added, after which the solution was stirred for 24 h. The surfactant-free polymerization yielded PMMA particles with mean diameters of about 230 nm. SEM images and particle size distributions of the synthesized PMMA and purchased SUNPMMA-S50 are given in Fig. 1.

2.3. Preparation of RF resin

Resorcinol (4 g) and sodium carbonate (0.04 g) were dissolved in the synthesized PMMA colloid. SUNPMMA-S50 (5 g) was then added and the solution was mixed for 10 min at room temperature. Then, 5.97 g of the formaldehyde solution was added and the mixture was stirred for 24 h at room temperature. The molar ratios of resorcinol to sodium carbonate and of resorcinol to formaldehyde were 100 and 0.5, respectively. The RF resin was then dried at 60 °C for 3 days.

2.4. Carbonization and activation of carbon foam

The dried RF resin was carbonized in a furnace under an Ar atmosphere; the sample was heated from room temperature to 450 °C at a heating rate of 1.5 °C/min and maintained at 450 °C for 2 h upon reaching that temperature. The resin was then carbonized through heating to 950 °C at a heating rate of 2 °C/min and kept at 950 °C for 2 h. Non-activated carbon foam samples, denoted CFDT, were then cooled in the furnace using Ar gas flow and removed. Activated samples, denoted A-CFDT, were immediately activated following carbonization by being placed under CO_2 atmosphere at 950 °C for 1 h, after which they were cooled under Ar gas flow and removed.

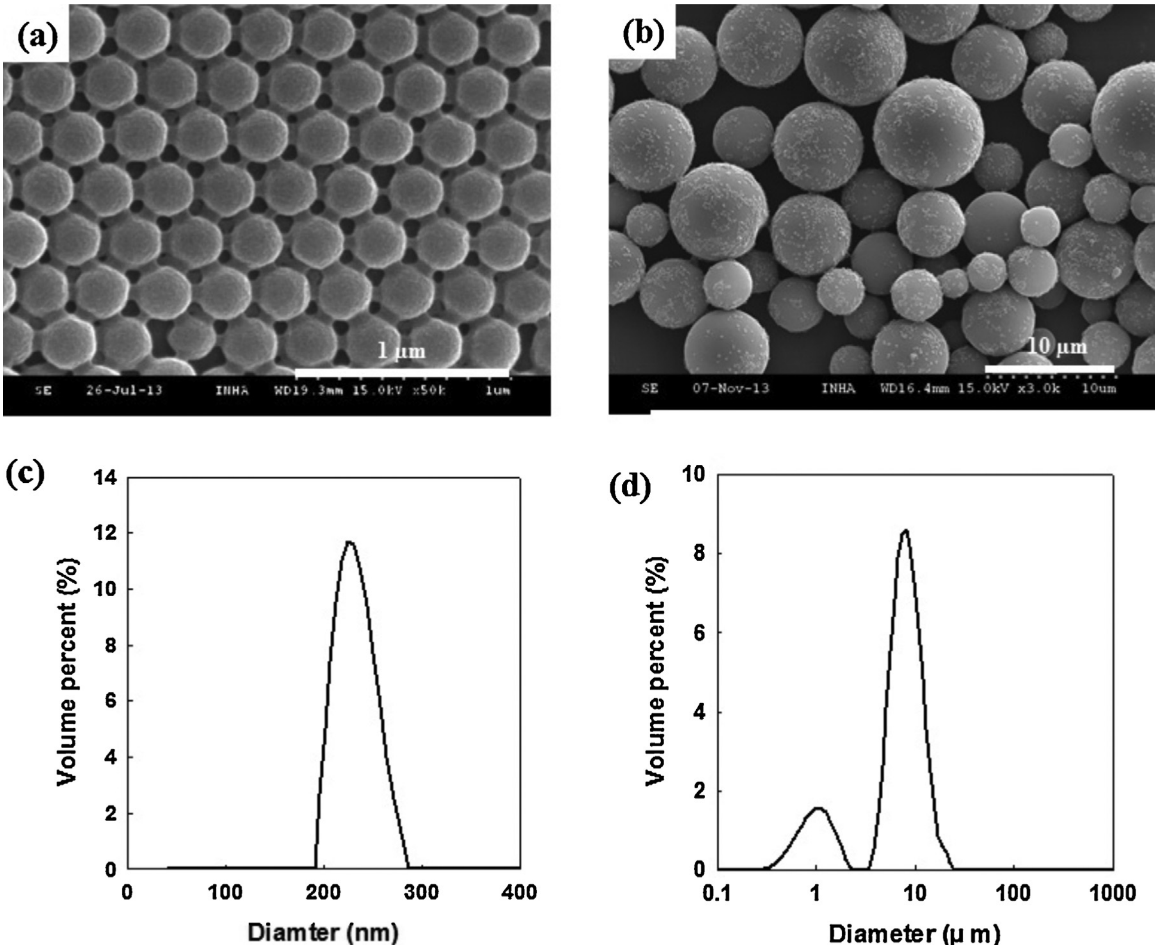

Fig. 1. SEM images of (a) PMMA (synthesized) and (b) SUNPMMA-S50 (purchased); particle size distributions of (c) PMMA (synthesized) and (d) SUNPMMA-S50 (purchased).