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High power density electric double-layer capacitor based on a porous multi-walled carbon nanotube microsphere as a local electrolyte micro-reservoir

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ABSTRACT

A high rate capability is a primary requirement for an electric double-layer capacitor (EDLC) in practical applications, which is mainly governed by the ionic diffusion rate. Construction of the electrode structure with proper paths for the rapid transport of ions is an efficient method to facilitate the diffusion of ions in the electrode. In this study, we prepared multi-walled carbon nanotube microspheres (MWNTMS) with a stable porous structure *via* the spray drying method. The MWNTMS act as a local electrolyte micro-reservoir and provide stable ion transport paths in the EDLC electrode, which will facilitate the access of the electrode to the electrolyte and accelerate the diffusion rate of the ions. Using only MWNTMS as active materials, an areal capacitance of 105 mF/cm^2 at 30 A/g is observed at an areal density of 7.2 mg/cm^2. When the MWNTMS are combined with reduced graphene oxides (rGO) to form an rGO-MWNTMS hybrid electrode with an areal density of 3.0 mg/cm^2, a high areal capacitance of 136 mF/cm^2 at 100 A/g is observed. This rGO-MWNTMS-based EDLC presents a high areal power density of 1540 mW/cm^2. These favorable results indicate that MWNTMS are promising materials for applications in high power supercapacitors.

1. Introduction

The electric double-layer capacitor (EDLC) constitutes a typical category of energy storage devices in which the energy is stored/released when the ions are physically adsorbed/desorbed at the electric double-layer interface of the electrolyte and electrode materials. Because of this mechanism, EDLC possesses attractive characteristics such as rapid electric field response, high Coulombic efficiency and long cycle life. Because of these properties, EDLCs have significant potential applications in portable electronics, hybrid electric vehicles, and telecommunications, among others [1–6]. However, for practical applications, EDLCs also require a reasonable energy density, which is primarily governed by the specific surface areas of the active materials used in the devices [7–11]. However, most of the active materials with high specific surface areas have relatively narrow pores or are inclined to stack together, and thus impede the access of the surface of

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the active materials to the electrolyte as well as the ionic diffusion. The situation deteriorates when the areal density of the active materials becomes high, causing the electrode to be thicker and denser, resulting in a longer diffusion distance of the electrolyte ions in the electrode [12–14]. Therefore, the construction of rapid transport channels for electrolyte ions is the key component for realizing a high power delivery capability of the EDLC electrode for practical applications [15,16].

Because of the high ratio of surface area to volume, good chemical stability, excellent electrical conductivity, and ready commercial availability, carbon nanotubes (CNTs) and graphene have attracted extensive attention and have been explored as active materials for EDLC applications [17–19]. However, CNT and graphene prefer to form compact structures due to the strong van der Waals interaction, thus, the surfaces of CNT or graphene are not easily accessible to electrolytes, and the ionic diffusion rate is slow [20–23]. These factors will impede the performances of EDLC, especially leading to a low rate capability. Therefore, developing effective approach, such as constructing porous or aligned structures, to construct adequate ion transport paths is important to provide a high rate performance in CNT- or graphene-based EDLC electrodes, especially when the areal densities of the active materials increase. To date, few studies have been performed to prepare EDLCs with a high rate capability by constructing ideal electrolyte ion/electron transport pathways. Honda et al. have prepared a vertically aligned carbon nanotube EDLC electrode with 91% capacitance retention as the current changes from 0.1 to 10 A/g, with an areal density of 0.15 mg/cm^2 [24]. Zeng et al. have constructed an electrode using short carbon nanotube/reduced graphene oxides (rGO) with a 3D multilayer architecture, which shows 89% capacitance retention as the scan rate changes from 50 to 1000 mV/s with an areal density of ~3.75 mg/cm^2. This is because the short carbon nanotubes effectively inhibit the aggregation of rGO and maintain the diffusion paths of the ions [25]. Wang et al. have constructed an rGO/carbon black hybrid EDLC electrode, maintaining 61.3% capacitance as the scan rate increased from 0.005 to 5 V/s [26]. Xu et al. have realized a 3D holey graphene framework-based binder-free EDLC electrode, which shows an excellent rate performance of 262 F/g at 1 A/g and 180 F/g at 100 A/g under an areal density of 10 mg/cm^2 [27]. Therefore, the construction of an EDLC electrode with the proper porous structure will facilitate the ion diffusion, which will improve the specific capacitance of active materials, and thus enhancing the rate performance of the EDLC devices.

In this study, we prepared porous multi-walled carbon nanotube microspheres (MWNTMS) for the EDLC application by a spray drying method. MWNTMS constructed only with MWNTs are highly robust and can sustain the porous structure under a pressure of 10 MPa during electrode fabrication. These stable porous MWNTMS in the EDLC electrode can maintain the ion transport paths and provide easy access for the active materials to the electrolyte ions, even with a high areal density. In addition, these MWNTMS can be used as local electrolyte micro-reservoirs to shorten the ionic transport distance at a high current density by providing an abundance of ions for the nearby active materials. The MWNTMS EDLC electrode with a high areal density of up to 7.2 mg/cm^2 can provide a favorable areal capacitance of 118 mF/cm^2 at a 0.2 A/g current density and 105 mF/cm^2 at 30 A/g. When porous MWNTMS were used with rGO to construct the MWNTMS/rGO electrodes, the electrodes exhibited a good rate capability with areal capacitances of 293 mF/cm^2 and 136 mF/cm^2 with the applied current density from 0.2 A/g to 100 A/g for a 3.0 mg/cm^2 areal density in KOH aqueous electrolyte.

2. Experimental details

2.1. Materials

The multi-walled carbon nanotubes (MWNT, ⩾98%), short multi-walled carbon nanotubes (short-MWNT, >95%) and graphene oxide (GO, ≈98%) were purchased from Nanjing JC Nano Tech Co., Ltd. The sodium dodecyl benzene sulfonate (SDBS, analytical grade), hydrazine (analytical grade) and KOH (analytical grade) were purchased from Sinopharm chemical reagent Co., Ltd. The polytetrafluoroethylene (PTFE) emulsion (solid content 60%) was purchased from Daikin Industries (Japan). The cellulose filter membrane (0.22 μm) and polypropylene filter membrane (0.22 μm) were purchased from Millipore. The semi-permeating membrane (MD34, MWCO 3.5 kDa), purchased from Viscase (America) was used as the separator. The nickel foam (thickness 1.6 mm, porosity ⩾ 96%) was purchased from Dessco (Suzhou, China). The deionized water was obtained from the Mill-Q academic water purification system. All materials are used as received without further purification.

2.2. Preparation of MWNTMS

MWNT (8.0 g) was dissolved in a mixture of 80 ml ethanol and 800 ml deionized water and ultrasonicated for 2 h. The obtained well distributed MWNT suspension was then dried using the spray dryer. The working conditions of spray dryer were fixed to inlet air temperature of 200 °C, outlet air temperature of 100 °C and the velocity of flow was 500 ml/h. Subsequently, the MWNTMS powders were gathered from the collector of the spray dryer.

2.3. Preparation of the MWNTMS and MWNT films

SDBS (5.0 g) was dissolved in 500 ml deionized water at room temperature. Then, a PTFE emulsion containing 10 mg PTFE was added to the SDBS solution under 1000 rpm for 30 min to obtain a SDBS/PTFE hybrid mixture. MWNT (10 mg) and 80 mg MWNTMS were dispersed in 50 ml and 450 ml SDBS/PTFE solution under sonication, respectively. Then, the two dispersion solutions were mixed together to form the MWNT/MWNTMS mixture dispersion. The MWNTMS film was prepared by vacuum filtration of 100 ml MWNT/MWNTMS dispersion on a cellulose membrane with a pore size of 0.22 μm. After drying overnight at 80 °C, the cellulose membrane was dissolved by acetone. The obtained MWNTMS film was dried at 60 °C for 6 h under vacuum for subsequent use. The MWNT film with an equivalent mass was also prepared according to the above procedure.