



Carbon nanotubes/activated carbon hybrid with ultrahigh surface area for electrochemical capacitors



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ABSTRACT

A hybrid carbon materials with three dimensional network carbon nanotubes in activated carbon was prepared by an *in situ* activation process. This hybrid carbon material has ultrahigh specific surface area (2879 m²/g), pore volume (1.36 cm³/g) and developed small mesopore network, which is very favorable for fast electrolyte ion transport in the porous channel. As evidenced by N₂ adsorption, cyclic voltammetry and electrochemical impedance measurements, the hybrid carbon material shows superior capacitive behaviors (exhibiting a high capacitance of 140 F/g, better capacitance retention ratio of 80% even at very high sweep rate of 200 mV/s) and provides much higher power density while still maintaining good energy density. This hybrid carbon material offers a great potential in electrochemical capacitors, particularly for applications where high power output and good high-frequency capacitive performances are required.

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1. Introduction

In response to the increasing demands for clean energy technologies, electrochemical capacitors (ECs) are considered as the most promising energy storage and power output technology for portable electronics, electric vehicles, and renewable energy systems operated on intermittent sources such as solar and wind. Porous carbons, transition metal oxides, and conducting polymers are fundamental candidates as electrode materials of ECs. However, metal oxides and conducting polymers are disturbed by several key drawbacks. For example, the metal oxides are either too expensive (RuO₂) or poorly conductive (NiO, MnO₂, etc.), and the conducting polymers show short cycling life [1–11]. Porous carbon materials have been commercially applied in ECs as the availability with stable physicochemical properties, good conductivity, and low cost [1–11]. Even though, for the emerging applications, the fundamental improvements of carbon electrode materials are needed. Currently, the performance specifications of EC, e.g. power density and corresponding energy density, intensively depend on the characteristics of porous carbon. The porous textures and the conductivity of the carbon materials directly impact on the equivalent series resistance (ESR) and the

internal distribution of electrolyte resistance (IER) in the porous carbon [12–14]. These properties ultimately determine the power densities and energy densities of ECs. Therefore, two important parameters, the ESR of the electrode itself and ion transport resistance (which corresponds to the IER) of the electrolyte in pore channels, need to be controlled as low as possible [15–17]. Although activated carbon (AC) shows the advantage of higher energy density, their power densities are restrained by the microporous structure and low conductivity. As a result, a variety of mesoporous carbons have been developed. Especially, the hierarchical porous structure of porous carbon, where micropore is nesting inside mesopore, greatly improves the power performances of ECs. Carbon nanotubes (CNTs) have characteristics of high stability, low resistance, and narrow pore size distribution. It is promised that CNTs can resolve the low conductivity and adjust the pore size of the AC, if CNTs and AC were combined. Few papers have evaluated the effects of CNTs added in the AC on the ESR, IER and pore structure of AC [18]. In our previous research, we found that the characteristic of capacitance response versus frequency was improved and the electrode resistance was decrease by the addition of CNTs to activated carbon [19]. Meanwhile, the capacitance and the efficiency of energy storage for ECs were improved, when activated carbon was mixed with a mass fraction of 3–15% of multi-wall carbon nanotubes (MWNTs).

Based on the above outline of the porous textures and the conductivity of the carbon materials in ECs, this paper reports the

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one-step preparation of CNTs/AC hybrid by *in situ* activation process. The effects of CNTs on pore feature and electrochemical properties of CNTs/AC hybrid were intensively investigated. This approach minimizes both electrical resistance of CNTs/AC hybrid and ionic resistance of electrolyte in the resulting carbon electrodes. CNTs/AC hybrid shows the evidently improved characteristic of specific power and specific energy.

2. Experimental

2.1. Preparation and Characterization of CNTs/AC hybrids

CNTs were synthesized by catalytic decomposition of hydrocarbons using a floating catalyst method with a horizontal reaction furnace [20]. After that, the raw CNTs were purified by two-step oxidation process of a nitric acid refluxing and an air oxidation. Then the CNTs were immersed in hydrochloric acid and washed with distilled water until neutrality.

Phenol-formaldehyde resin (PF-resin) was used as the precursor of AC. After the resin was dissolved in KOH (a ratio of the resin and KOH = 1:4 by weight) ethanol solution in a plastic flask, the CNTs dispersed in ethanol were added to the above solution, and the solvents were removed at 393 K for 12 h in an oven to get the as-made sample. Hereafter, it was activated under the nitrogen atmosphere at 1073 K for 1 h. Finally, the mixture was impregnated in 0.1 M hydrochloric acid, washed with distilled water to eliminate residual acid, and dried at 393 K for 12 h to get the three dimension CNTs network embedded in CNTs/AC hybrid, where the yield of CNTs was around 5 wt.% of the CNTs/AC hybrid (In terms of the electrochemical performances and cost [19], around 5% CNTs was introduced to the hybrid carbon materials). In addition, AC without the CNTs was also prepared as the blank sample under the same experimental condition (designated as AC800).

Nitrogen cryo-sorption measurements were conducted on a Micromeritics ASAP2010M instrument; before measurements, the samples were evacuated at 473 K until the manifold pressure was lower than 2 Pa. The morphology and structures were characterized by SEM (LEO, SUPRA 35, 15 kV) and TEM (JEOL JEM 2010, 200 kV). The samples were dispersed in absolute ethanol and dropped onto the Cu rod for SEM or the grid for TEM observations.

2.2. Electrochemical measurements

A coin-type capacitor cell was used to examine the electrochemical performance of the AC800 and CNTs/AC hybrid electrodes, which consisted of a carbon film (8 mm in diameter and about 200 μm in thickness) and nickel foil as the current collector. This cell consisted of two facing carbon electrodes, sandwiching a cellulose filter paper as the separator. All electrochemical measurements were carried out using 6 M KOH as the electrolyte solution at room temperature. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measures were collected on Solartron 1287/1260 electrochemical systems from 5~200 mV/s. The potential range for CV was 0.0~1.0 V. The bias potential applied to the electrode during EIS was 0 V, the frequency ranges were 5 mHz to 100 kHz, and the ac signal amplitude was 10 mV. The constant-current charge–discharge measures were performed with a BT2000 Arbin cyler at different current densities from 0.01 to 10 A/g between 0 and 1.0 V.

3. Results and Discussion

3.1. The pore Structure Characterization of the CNTs/AC hybrid

SEM morphologies of the AC800 and CNTs/AC hybrid are presented in Fig. 1(a) and (b). The surfaces of the AC reserve the

caves etched by KOH (Fig. 1(a)). These cavities result from the removal of impregnated KOH and KOH-derived compounds, leaving the space previously occupied by the compounds. The AC particles in the CNTs/AC hybrid can be linked by the CNTs after the CNTs added in Fig. 1(b). Especially, the two ends of a few CNTs are located in different AC particles, respectively. The linking manner of CNTs and AC particle facilitates the electrons transportation between the AC particles. The TEM images distinctly show that AC particles are wound by CNTs (Fig. 1(c)), and the CNTs have been embedded in the AC particles (Fig. 1(d)). These results indicate that the three dimensional network of CNTs/AC hybrid is formed and the conductivity of the CNTs/AC hybrid is to be improved. Fig. 1(e) shows the SEM image of purified CNTs, revealing two types of the diameter distribution of CNTs. The one is between 15 and 20 nm. The other is between 100 and 200 nm. The ratio of length/diameter of CNTs is high to favor the formation of conductivity network. The CNTs are clean (no amorphous deposit) and separated, and are aggregated as small bundles. Thermogravimetric analysis (1 °C/min in air flow, Fig. 1(f)) shows only one well-resolved peak corresponding to sharp weight loss at 644 °C, corresponding to 99.4% of the initial weight, suggesting that CNTs are purified well and the catalyst is almost removed. The nitrogen adsorption isotherm of CNTs in Fig. 1(g) shows the specific characteristic of porous structure at different pressure. The isotherms are of a type I characteristic, as indicated by the fact that the amount adsorbed increases rapidly at ultra-low pressures ($P/P_0 = 10^{-6}$ to 0.01). The isotherm in the medium pressure zone ($P/P_0 = 0.01$ –0.45) shows a surface adsorption process in which the amount of nitrogen adsorption slowly increases. This is indicative of the existence of a nonporous surface, attributed by external surface of the CNTs. The capillary condensation can be observed occurring in the medium relative pressure range ($P/P_0 = 0.45$ –0.85), and results from capillarity in the mesopores. The hysteresis loop ($P/P_0 = 0.85$ –0.99) of the isotherms corresponds to the larger pores of 20.0–40.0 nm. The BET specific surface area of CNTs is around 120 m²/g. Consequently, the capacitance of CNTs is very small. Namely, it can be neglected that capacitance of CNTs contribute to ECs. A schematic illustration of a three dimensional network texture of CNTs/AC hybrid is shown in Fig. 1(h). The CNTs/AC hybrid is composed of CNTs embedding inside AC and winding AC. The improvement of capacitance property results from the increase of conductivity of the CNTs/AC hybrid.

Nitrogen adsorption–desorption isotherm with a relatively broad knee of the CNTs/AC hybrid, shown in Fig. 2(a), exhibits combined characteristics of type I/II [21,22], with a Brunauer–Emmett–Teller (BET) surface area of 2879 m²/g, a total pore volume of 1.36 cm³/g, a mesopore volume of 0.68 cm³/g, a mesopore to total pore volume ratio of 0.51, as well as an average pore diameter of 2.2 nm. These pore structure parameters of CNTs/AC hybrid are much higher than those of AC800 (1759 m²/g, 0.93 cm³/g and 0.45 cm³/g), although the isotherm type of AC800 is the same as CNTs/AC hybrid, indicative of CNTs play an important role on the 3 dimension network structure of CNTs/AC hybrid. The BET surface area and pore volume are illustrated in Table 1.

Specific surface area calculated from the t-plot method. Peak value of the pore diameter distribution curves obtained from the DFT method. The mesopore volume is determined by extracting micropore volume, which is obtained from t-plot analysis, from total pore volume.

The pore-size distributions derived from the density function theory (DFT), as shown in Fig. 2(b) and 2(c), are indicative of a quite uniform pore size distribution centered in micropore ranges of about 0.64 nm, 0.80 nm, 1.2 nm, 1.48–1.59 nm and in mesopore range of about 2.8 nm for CNTs/AC hybrid and AC800, respectively. The porous volume of CNTs/AC hybrid is distinctly higher than AC800, especially much higher at 1.2 nm and 2.8 nm. For CNTs/AC

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