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Effect of porosity variation on the electrochemical behavior of vertically aligned multi-walled carbon nanotubes

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Abstract

Electrochemical charge storage characteristics of vertically aligned multi-walled carbon nanotubes (MWCNTs) as a function of varying diameter and spacing are reported. It was observed that the specific capacitance of the MWCNTs increased as both diameter and inter-tube spacing decreased. The MWCNT films with 229 nm inter-MWCNT spacing exhibited specific capacitance of 228 F/g versus 70 F/g for 506 nm spacing, when tested in a non-aqueous electrolyte. Further, a trend in specific capacitance versus pore size is proposed. Coupled with previously reported trends observed in the sub-10 nm pore size regime, this is expected to offer better understanding of electrochemical behavior of porous carbon materials over a wide range of pore sizes.

1. INTRODUCTION

Carbon Nanotubes (CNTs) are interesting as electrode material in electrochemical double layer capacitors (ELDCs) [1] because of their nanostructured morphology, regular porosity, and electrical properties. They are also important in electroanalysis [2–4] for these same properties. Specific capacitance of electrodes depends on surface functionalities, surface area, and pore size distribution [5, 6]. The relationship between specific capacitance and pore size has been studied extensively for materials with pore size distribution under 100 nm [6–9]. For example, Ref [10] reports the effect of mean pore size on specific capacitance in the sub-10 nm regime. It has been proposed that constriction of the compact ion layer within a sub-1 nm pore increased the capacitance significantly due to distortion of the ion solvation shell [11]. Furthermore, specific capacitance increases with increasing surface area to a point [12]. To the authors' knowledge, investigation of this relationship has not been extended to materials with pore size greater than 100 nm and a high aspect ratio, such as vertically aligned CNTs. This work reports on the change in specific capacitance as pore size varies from 229 to 506 nm for vertically aligned multi-walled CNTs (MWCNTs) and discusses the broader transition from surface area- to pore size-dominated effects.

2. EXPERIMENTAL

2.1 CNT film growth

MWCNTs were grown using a 915 MHz Microwave Plasma Enhanced Chemical Vapor Deposition System. Fe-coated silicon substrates were heated to 850 C in 150 sccm of NH₃ in

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the PECVD system, followed by striking and stabilizing a plasma at 21 torr and 2.1 kW of magnetron input power. Substrates were then pretreated for pretreatment times of 5, 180, 1200, and 2400 s in the plasma to obtain samples with a range of porosity and surface area by varying the tube diameter and spacing. Following pretreatment, growth of the MWCNTs was accomplished by changing the gas flow to 150 sccm CH₄ and 50 sccm NH₃ for 120 s. The growth conditions were the same for all samples. The CNTs grown using this process are typically vertically aligned and multi-walled [13].

2.2 Electrochemical Setup

The electrochemical setup, sample preparation, and measurement protocol have been discussed in detail in a previous publication [14]. Briefly, a three terminal electrochemical cell with working, counter, and reference electrodes (K0235 by Princeton Applied Research) was used. The working electrode was the MWCNT film, the counter electrode was a platinum mesh (3 cm × 2.5 cm), and the reference was an Ag wire in 1 M tetrabutylammonium perchlorate (TBAP) and 0.01 M silver nitrate (AgNO₃) in acetonitrile (reference electrode - MF-2052 and its solution supplied by Bioanalytical). The reference electrode resided in a separate subsection of the cell connected to the region near the double layer interface of the working electrode by a Luggin-Haber capillary tube. The distance between the interface and the tube was at least twice the diameter of the tube. The electrolyte used was 1 M lithium perchlorate (LiClO₄) in acetonitrile. The potentiostat was a SP-300 (BioLogic). All chemicals were used as received.

2.3 Sample Preparation

The sample was mounted on a piece of sheet metal using copper tape. An electrical contact was made painting conductive silver epoxy on the MWCNT side. The nominal active area of the electrode was defined by a PTFE gasket.

2.4 Electrochemical Testing Procedure

Cyclic voltammetry (CV) was performed on all the samples at a scan rate of 15 mV/s between 0 and 1.1 V vs Ag/Ag⁺ ion to obtain specific capacitance and detect the presence of Faradaic activity, if any. A three-terminal galvanostatic charge-discharge technique was also used to obtain charge-discharge curves at a current density of 5.7 A/g and a voltage window of -0.1 to 1.2V. The galvanostatic technique was explained in detail previously [14].

2.5 Morphological Measurements

The vertical alignment and multi-walled nature of the CNTs were verified by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The diameter and spacing of the MWCNTs were measured from high-resolution SEM images using ImageJ software [15]. These images were thresholded to detect edges and then measurements were obtained at different points on each sample with a total of 22 measurements each for diameter and inter-MWCNT spacing. A similar approach to measure porosity has been reported previously [10].

3. RESULTS AND DISCUSSION

Figure 1 shows CV scans of all four samples. The charge storage capacity, represented by the area under the CV curve, increases substantially with reduction in inter-MWCNT spacing (*i.e.* pore size). No other significant electrochemical activity is apparent in the CV scans, indicating that most of the charge storage capacity comes from non-Faradaic double layer charging.

Figure 1 inset shows a typical constant current charge discharge curve for the sample with inter-MWCNT spacing of 506 nm at 5.7 A/g. Symmetric and linear anodic and cathodic halves can be seen, consistent with capacitive behavior. Note that following convention (for example, see [16, 17]), the term IR drop has been utilized in this inset to signify equivalent series resistance, although interfacial potential changes would also play a role on these time scales. Such capacitive charge-discharge behavior was observed for all samples. The specific capacitance was calculated for the four MWCNT samples from CV measurements. Figure 2 shows specific capacitance measured from the CV curves as a function of MWCNT diameter and spacing. For vertically aligned MWCNTs, the inter-CNT spacing is the effective porosity. Specific capacitance increased significantly as MWCNT diameter and spacing decreased.

The same trend and comparable values for specific capacitance were observed for the galvanostatic method and CV scans. The maximum capacitance (228 F/g) was obtained for the sample with the smallest diameter/spacing combination. A contributing factor to the relatively high specific capacitance is the regular pore distribution of aligned CNTs [18]. Specific surface area was calculated assuming the nanotubes to be an array of simple cylinders using a method similar to that of [19]. The specific interfacial capacitance obtained in this manner was in the range of 1.6 mF/cm² to 3.3 mF/cm² with an average value of 2 mF/cm². Figure 2 insets show that area specific capacitance remains constant with change in diameter and spacing. This shows that the increase in gravimetric capacitance with reduction in diameter and spacing is largely due to increase in surface area.

Both the spacing and diameter of the CNTs have an influence on the electrochemical properties but the data suggests that diameter may have a greater impact on capacitance. For example, the 344 nm and 442 nm samples have diameters that are very similar and hence the capacitance values are also similar, despite the different spacings. Inter-CNT spacing and diameter were varied simultaneously in the present work and their effects on measured capacitance cannot readily be separated. A numerical analysis of CNT curvature effects on the diffuse double layer has been performed [20] and can be used to deconvolve the effects of diameter and spacing on capacitance. However, that approach is only applicable to nanotubes with radii less than 20 nm and in low supporting electrolyte concentration. Thus, it could not be utilized in the present study because only the sample with the smallest radius meets this criterion and the supporting electrolyte concentration is high.

Three explanations were considered for the observed trend and overall improvement in electrochemical performance among these four samples:

1. more defect states (higher surface charge density may result from higher density of electrochemically active defects [21, 22]),
2. better ionic access (more CNT film permeation by ions), and
3. higher specific surface area (smaller pores will result in higher effective surface area).

Raman spectroscopy was performed on the samples and there was no significant variation in peak height for the I_D/I_G ratio. This suggested that the increase in specific capacitance was not due to a change in defect state density. It was previously observed that the MWCNTs used in this study were relatively more aligned near the base than the tip [23]. However, this morphological characteristic was common to all the samples, hence improved ionic access due to pore distribution did not appear to be the dominant factor in the observed trends. These observations supported the explanation that improved capacitance was primarily attributed to an increase in specific surface area by optimizing porosity. Thus, there is potential to further improve the pore structure of vertically aligned CNTs based on tube

geometry (diameter, spacing, alignment, *etc.*). The aspect ratio is higher than is observed in other carbon materials of similar porosity. This large aspect ratio of the pores may be contributing to the high specific capacitance.

Most CNT electrodes are made from non-aligned CNTs where pore size is neither easily controlled nor periodic. To the authors' knowledge, this work is the first to present a trend in specific capacitance for the pore size range of 229 to 506 nm for vertically aligned CNTs. The trend in specific capacitance is a function of the spacing and diameter. Smaller spacing and diameter leads to higher specific surface area and consequently higher specific capacitance. Combining these observations with previous reports reveals a qualitative trend between specific capacitance and pore size spanning the porosity regimes for porous carbon materials, shown in Figure 3.

The trend can be divided into three regions. In Region 1, specific capacitance is dominated by the electrochemically active surface area, increasing linearly with decreasing pore size. Region 2 begins when the pore size decreases to about 2× the size of the solvated ions. Space constriction effects hinder ion diffusion and cause the slope of the capacitance-pore size relationship to change, resulting in either a local maximum or saturation of specific capacitance as a function of pore size between regions 1 and 2 [8, 12, 24, 25]. In Region 3 (<1 nm pore sizes), there is an increase in specific capacitance due to distortion of the solvation shell of the ions [11]. This anomalous increase in specific capacitance in the sub-1 nm regime has been explained by using first-principles density functional theory (DFT) calculations [26]. This qualitative trend line links the three regions to provide a continuous description of the effect of pore size on the electrochemical behavior of double layer electrodes and how various phenomena become dominant in different pore size regimes. This understanding will aid engineering materials with hierarchical porosity for electrochemical capacitor applications.

Future work will investigate CNT geometries that extend Region 1 to smaller pore sizes that approach the local maximum and transition between Regions 1 and 2. Additionally, other electrochemical techniques will be used to obtain a deeper understanding of the role of porosity on vertically aligned CNTs.

CONCLUSION

Pore size of vertically aligned multi-walled CNTs was varied and the corresponding electrochemical behavior was studied. It was found that specific capacitance increased from 70 to 228 F/g as pore size decreased from 506 to 229 nm. This significant increase was attributed primarily to an increase in specific surface area via a reduction in pore size. Furthermore, a qualitative trend is proposed illustrating the variation in specific capacitance of porous carbon materials as a function of pore size.

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Highlights

Vertically aligned carbon nanotubes of varying porosity were grown

Carbon nanotube morphology was analyzed using computer assisted image analysis

Specific capacitance increased with decreasing pore size and nanotube diameter

Figure 1. CV scans for MWCNT samples with varying morphology. The numbers on the curves indicate MWCNT pore size. Inset: Galvanostatic charge-discharge curve at a constant current density of 5.7 A/g for sample with inter-MWCNT spacing of 506 nm.

Fig. 2a

Fig. 2b

Figure 2.

Variation in specific capacitance with varying (a) diameter and (b) inter-CNT spacing. 1σ error bars indicate variation in weight measurement. Numbers in parentheses are the corresponding spacing and diameter values in part (a) and (b), respectively. Inset: Variation in area specific capacitance as a function of (a) diameter and (b) spacing

Figure 3.
Qualitative trend of specific capacitance versus pore size.