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Ion Diffusion and Electrochemical Capacitance in Aligned and Packed Single-Walled Carbon Nanotubes

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Abstract: Direct measurement of ion diffusion in aligned, densified single-walled carbon nanotube electrodes showed that the diffusion coefficient for transport of ions (KSCN in acetonitrile) parallel to the alignment direction of the nanotubes was close to the theoretical limit of perfectly straight pores, achieving a value 20 times larger than that of activated carbon electrodes (1×10^{-5} vs 5×10^{-7} cm^2/s). In contrast, the diffusion coefficient for ion transport perpendicular to the alignment direction was an order of magnitude smaller (8×10^{-7} cm^2/s). As an example of the ramifications of this anisotropic diffusion phenomenon, the difference in performance of the aligned carbon nanotubes as electrochemical-capacitor electrodes was evaluated. At low discharge rates, the performances of the two orientations were identical, but as the discharge rate was increased, a more rapid decline in capacitance was observed for the perpendicular orientation (66 vs 14% decline in capacitance when the discharge current was increased from 0.01 to 1 A/g). Furthermore, the maximum power rating of the perpendicular electrode was lower than that of the parallel electrode (1.85 vs 3 kW/kg during operation at 1 V).

Ion transport in electrodes is a critical factor in determining the power performance (speed) and energy efficiency (loss) of batteries and supercapacitors.[1] The emergence of nanomaterials has provided the ability to fabricate electrodes with well-defined pore structures, as opposed to the random pore structure of traditional electrodes such as activated carbon (AC), thus potentially enhancing ion transport and hence power performance.[2] Carbon nanotube (CNT)-based electrodes have already enabled batteries and electrochemical capacitors to achieve higher power ratings.[3]

Aligned, densely packed single-walled carbon nanotubes (SWNTs) represent a prime example of a nanomaterial with a well-defined pore structure. These electrodes achieve higher power performance than AC electrodes, and this superior performance has been attributed to enhanced ion transport.[4] For aligned CNT/polymer-membrane structures, it has been shown that diffusion parallel to the nanotube orientation can be exceedingly fast, achieving nearly the same speed as ion diffusion in a bulk electrolyte.[5] In addition, for graphitic carbon it has already been shown that diffusion parallel to the graphene plane is several orders of magnitude faster than along the grain boundaries.[6]

As exemplified by these results, the importance of alignment is well-recognized, but the importance of the relative orientation of alignment on ion transport has not been shown to date. Also, because of difficulties in fabricating electrodes where ions travel parallel to the alignment direction of CNTs, the majority of CNT electrodes have a planar alignment with ion transport through the plane (i.e., perpendicular to the nanotubes).

In this work, we studied ion diffusion parallel and perpendicular to aligned, densely packed SWNTs with an intertube pore diameter of 3 nm. The diffusion coefficient (1×10^{-5} cm^2/s) in the parallel direction was 20 times larger than that for AC and close to the theoretical limit for perfectly straight pores, implying this material is ideal for fast ion diffusion. In contrast, in the perpendicular direction, the diffusion coefficient was 12 times smaller (although still larger than that for AC), demonstrating the importance of alignment. The impact of this anisotropic diffusion phenomenon on CNT electrochemical-capacitor electrodes was studied, and significantly superior rate performance and a higher maximum power rating (3 vs 1.85 kW/kg) in the parallel direction relative to the perpendicular direction was observed.

To achieve identical specimens differing only in alignment direction, millimeter-high vertically aligned SWNTs (forests) having an average diameter of 2.6 nm that had been synthesized by water-assisted chemical vapor deposition were utilized.[7] Through uniform compression from the sides, the sparse forest (density = 0.003 g/cm^3) was converted into a dense (density = 0.5 g/cm^3), aligned specimen denoted as solid-cube (Figure 1b); the tube-to-tube distance changed from 16 to 4 nm, as measured by X-ray diffraction.[8] The approximate effective pore diameter between the packed SWNTs was 3 nm. The degree of alignment of the nanotubes [Herman's orientation factor (HOF)] was calculated to be 0.64 from the intensity profile of the fast Fourier transform of the scanning electron microscopy (SEM) micrograph (Figure 1a); HOF = 1 would correspond to perfectly straight alignment.[9] The solid-cubes were then utilized as membranes between an electrolyte compartment (0.5 M KSCN in acetonitrile) and a solvent compartment (acetonitrile).[10] The solid-cubes were cut using a laser marker to achieve appropriately sized specimens, as discussed in the Supporting Information. The ionic conductivity of the solvent compartment was monitored over time and converted to a concentration profile (Figure 1c) using a conductivity−concentration calibration curve (Figure S2 in the Supporting Information). Fick's first law of diffusion and the ionic concentration time profiles (Figure 1c) were used to calculate the diffusion coefficient. For comparison, measurements on a common commercial electrochemical-capacitor AC electrode were also performed.[4] It should be noted that this AC electrode had similar density (0.6 g/cm^3) to the SWNT solid-cube.

As shown in Figure 1c, the sample with parallel orientation exhibited the fastest diffusion process, resulting in a diffusion coefficient of 1×10^{-5} cm^2/s, which is 20 times larger than that for the AC electrode (5×10^{-7} cm^2/s). Importantly, this value is close to the bulk electrolyte diffusion coefficient (2.6×10^{-5} cm^2/s) scaled by the porosity of the specimen (50%).

Tortuosity (τ) quantitatively describes the degree of pore straightness and is given by $\tau = FP$, where P is the porosity and F is the formation factor, defined as the ratio of the bulk electrolyte

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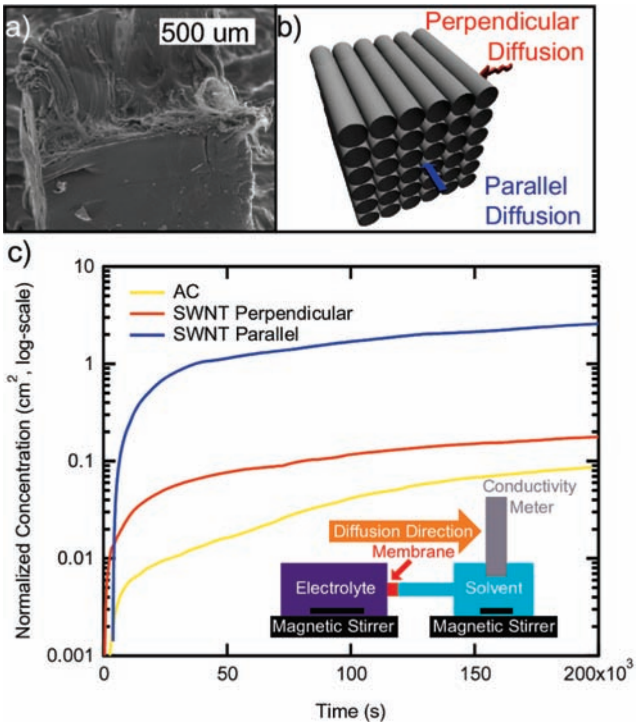

Figure 1. Solid-cube and diffusion measurements (a) SEM image of the solid-cube. (b) Schematic depiction of the solid-cube. (c) Diffusion measurement results: concentration−time profiles of the SWNT solid-cube in the parallel (blue) and perpendicular (red) configurations and of AC (yellow).

diffusion coefficient, D_0, and the diffusion coefficient of the same ions in the porous electrode, D (i.e., $F = D_0/D$).[10] For the SWNT solid-cubes in the parallel direction, τ was 1.3, and this value is close to the theoretical limit of 1 that corresponds to perfectly straight pores wherein ion transport is unhindered. This result implies that densely packed, aligned CNTs would be an ideal form of material for fast ion diffusion.

The tortuosity value of 1.3 is comparable to that of 1.1 reported previously for a CNT/polymer membrane specially designed in structure to have ions diffuse through the inside of opened, straight, and very short (5−10 μm) multiwalled CNTs.[5] In contrast, in this study the ions were transported through very long (0.1−1 mm) pores created between closely packed SWNTs, since the SWNTs utilized had closed caps as previously confirmed via high-resolution transmission electron microscopy (HRTEM) observations and nitrogen adsorption measurements.[11] It also should be noted that the SWNTs were not perfectly aligned, as evidenced by the fact that the HOF value of 0.64 is less than 1, and we thus envision further improvement from enhanced SWNT alignment.

For the perpendicular sample, a smaller diffusion coefficient of 8×10^{-7} cm^2/s (i.e., an order of magnitude smaller than that for the parallel direction but still larger than that for AC) was measured. In the perpendicular direction $\tau = 16$. The diffusion coefficient value for the AC electrode in this study was similar to literature values cited for AC in Table 1, confirming the reliability of the measurement method.[10]

To examine the impact of this anisotropic diffusion phenomenon, identical 1 mm^3 SWNT solid-cubes were utilized as electrochemical-capacitor working electrodes having all but one of their six faces open for ion access, as discussed in the Supporting Information. Two devices were constructed, one in which the alignment of the solid-cube would be parallel to the dominant direction of ion motion (Figure 2a) and one in which the alignment would be perpendicular to the direction of ion motion (Figure 2b). For electrochemical capacitors, an electrode thickness of 100 μm is typically used, but here, to emphasis the impact of diffusion on device performance, a much thicker electrode (1 mm) was utilized. To ensure that the performance of the devices would be dominated by the working electrode, a counter electrode having a much larger capacitance based on a large-area thin SWNT solid sheet (100 mm^2 × 0.1 mm) was utilized.[8] A common commercial electrochemical-capacitor electrolyte (1 M TEABF$_4$/propylene carbonate) was used to ensure that the results would be relevant. The devices were subjected to galvanostatic charge/discharge at different rates. While these SWNT electrodes have been previously shown to be operational up to 4 V, as in these devices a spacer/seal material had been utilized to ensure that no parasitic reactions would take place when a lower cell voltage (1 V) was used.[4] The capacitance of these SWNTs increases linearly as a function of voltage because of electrochemical doping. As such, the capacitance of the solid-cube device is lower than previously reported capacitance values for electrodes operated at higher voltages.[4]

At low discharge rates, there was almost no difference between the capacitances of the two devices (Figure 2c), and their Ohmic (*IR*) losses were almost identical (Figure 2d). However, as the discharge rate was increased from 0.01 to 1 A/g, the capacitance of the perpendicular solid-cube device decreased significantly (by 66%) whereas the parallel device had only a minor decline in capacitance (14%). It should be noted that these discharge rates were below the discharge rates (1−20 A/g) previously reported for the same SWNTs used in thin-electrode format (100 μm).[4] The *IR* loss profile of the perpendicular device exceeded that of the parallel device, resulting in a lower maximum power rating (1.85 vs 3 kW/kg). Overall, the parallel device exhibited better rate performance than the perpendicular device, as shown in the Ragone plot of energy versus power (Figure 2e). While the rate performance and maximum power rating of electrochemical capacitors relies on a combination of factors, such as the contact resistance between the

Table 1. Diffusion Coefficients (D), Formation Factors (F), and Tortuosities (τ) of Various Electrodes[a]

specimen	electrolyte	D (cm^2/s)	D_0 (cm^2/s)	F	τ
AC	KSCN/AN	5×10^{-7}	2.6×10^{-5}	52	NA
AC[b]	KSCN/AN	$2.9-7.2 \times 10^{-7}$	2.6×10^{-5}	36−89	7.9−15.6
CNT/polymer membrane ‖[c]	$Ru(NH_3)^{6+}/H_2O$	2.2×10^{-6}	7×10^{-6}	3.2	1.1
Graphite ‖[d]	$LiPF_6$/ EC:EMC	4.4×10^{-6}	3.7×10^{-6}	0.84	NA
Graphite ⊥[d]	$LiPF_6$/ EC:EMC	8.7×10^{-12}	3.7×10^{-6}	4.2×10^5	NA
SWNT[e]	$LiPF_6$/ EC:DMC	4.2×10^{-6} 4.8×10^{13}	NA	NA	NA
SWNT ‖	KSCN/AN	1×10^{-5}	2.6×10^{-5}	2.6	1.3
SWNT ⊥	KSCN/AN	8×10^{-7}	2.6×10^{-5}	32.5	16

[a] Abbreviations: AN, acetonitrile; EC, ethylene carbonate; EMC, ethyl methyl carbonate; DMC, dimethyl carbonate. [b] Data from ref 10. [c] Data from ref 5. [d] Data from refs 6 and 13. [e] Data from ref 12.

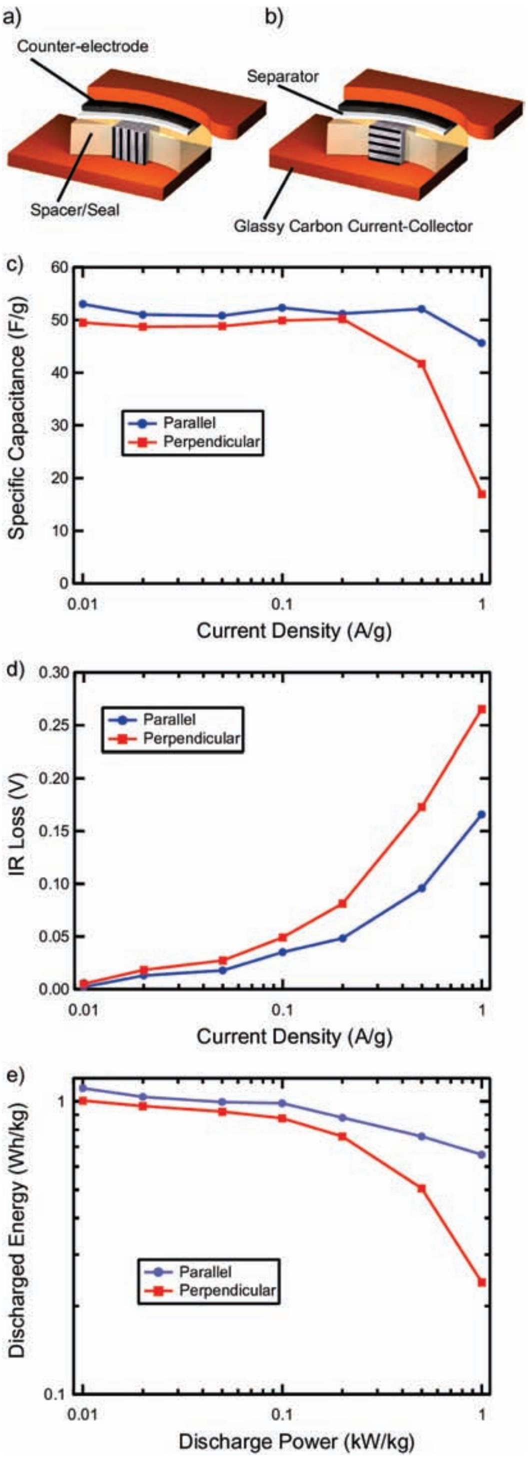

Figure 2. Impact of SWNT orientation on capacitance performance. (a) Cross-sectional view of the device with the solid-cube electrode in the parallel orientation. (b) Cross-sectional view of the device with the solid-cube electrode in the perpendicular orientation. (c) Capacitance vs discharge current. (d) *IR* loss vs discharge current. (e) Ragone plot of energy vs power.

electrodes and the current collectors, the results presented here suggest that the performance can be improved by utilizing aligned SWNT electrodes in the parallel direction.

At 1 A/g, the difference between capacitance values (170%) is greater than the difference in *IR* loss values (60%), suggesting greater anisotropy for ion transport than for electronic transport. Such a hypothesis is in agreement with the DC electronic conductivity values observed in the dry state: 24 S/cm (parallel) versus 16 S/cm (perpendicular).

Most prior studies have used electrodes in which the CNTs were stacked in a plane (e.g., buckypapers placed on current collectors) and thus perpendicular to ion transport. Even with this configuration, superior power performance relative to AC has been reported. Our results suggest that further improvement is possible. For example, on the basis of these results, it may be plausible to extrapolate that the power performance of the SWNT solid-sheet electrode operated at 4 V, which we previously reported to be 210 kW/kg, could be increased to beyond 300 kW/kg if oriented in parallel direction.[4]

In conclusion, we have shown that for densified, aligned SWNT electrodes, ion diffusion parallel to the alignment direction reaches almost the theoretical speed limit set by the porosity of the material. In contrast, diffusion perpendicular to the alignment direction is 12 times slower (8×10^{-7} vs 1×10^{-5} cm^2/s) yet still faster than that in AC (5×10^{-7} cm^2/s). The impact of this anisotropic diffusion property on capacitance performance was explored, and it was found that for identical aligned SWNT electrodes with ion transport limited to one direction, the performance was better when the transport direction was parallel to the SWNT alignment direction: the electrodes achieved a higher maximum power rating (3 kW/kg for the parallel direction vs 1.85 kW/kg for the perpendicular direction) and better rate performance (a 14% decline in capacitance for the parallel direction vs a 66% decline in capacitance for the perpendicular direction). These results suggest that as intuitively expected, in order to achieve higher power performance, aligned CNT electrodes should be oriented parallel to the dominant ion transport direction.

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Supporting Information Available: Details of capacitor assembly and diffusion measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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