Supercapacitors Using Single-Walled Carbon Nanotube Electrodes**

By Kay Hyeok An, Won Seok Kim, Young Soo Park, Young Chul Choi, Seung Mi Lee, Dong Chul Chung, Dong Jae Bae, Seong Chu Lim, and Young Hee Lee*

Recently, there have been considerable attempts to use carbon nanotubes (CNTs) for electrodes of electrochemical energy storage systems, such as Li-ion secondary batteries,[1–3] hydrogen storage for fuel cells and secondary batteries,[4,5] and supercapacitors.[6–8] The CNTs are attractive materials for electrodes of electrochemical energy storage devices due to their superb characteristics: chemical stability, low mass density, low resistivity, and large surface area. Recent developments in massive synthesis of carbon nanotubes[9–11] have accelerated a new application of these materials in the area of electrical energy storage systems.

Supercapacitors[12–15] (also called electrochemical capacitors, electric double layer capacitors, or ultracapacitors) have many advantages compared to the secondary battery; for instance long cycle life (> 100,000 cycles), simple principle and mode of construction, short charging time, safety, and high power density. Among them, the power density of supercapacitors is the most remarkable property as it is about ten times[16] larger than that of secondary batteries. The energy density of supercapacitors, however, is smaller than that of secondary batteries, which is a drawback for practical devices. Supercapacitors have been used as small-scale energy storage devices in stationary electronics, such as memory back-up systems, cold-starting assistants, and catalytic converter pre-heaters.[17] In order to apply the supercapacitors to various systems, novel devices such as load-levellers, hybrid capacitor-battery devices and solar batteries with semi-permanent charge-discharge modes of construction, short charging time, safety, and high power density. Among them, the power density of supercapacitors is the most remarkable property as it is about ten times[16] larger than that of secondary batteries. The energy density of supercapacitors, however, is smaller than that of secondary batteries, which is a drawback for practical devices. Supercapacitors have been used as small-scale energy storage devices in stationary electronics, such as memory back-up systems, cold-starting assistants, and catalytic converter pre-heaters.[17] In order to apply the supercapacitors to various systems, novel devices such as load-levellers, hybrid capacitor-battery devices and solar batteries with semi-permanent charge-discharge life-cycles. Now the prospect of supercapacitors with high power densities extends their application to various other novel devices such as load-leavers, hybrid capacitor-battery systems, cold-starting assistants, and catalytic converter pre-heaters.[17] In order to apply the supercapacitors to various practical devices, even to electric vehicles, the development of supercapacitors with both high power density and high energy density is necessary. The maximum power density of a supercapacitor is given by \( P_{\text{max}} = \frac{V_i^2}{4R} \) \( (V_i = \text{initial voltage}, R = \text{equivalent series resistance (ESR)}) \).[16] Therefore, the key factors determining the power of supercapacitors are the resistivity of the electrode itself, the resistivity of the electrolyte within the porous layer of the electrode, and the contact resistance between the electrode and the current collector. The maximum storage energy is given by \( CV^2/2 \), where \( C \) is the capacitance, and therefore maximizing the capacitance of the electrode is the key factor to increasing the energy density.

Recently, Niu et al.[6] have reported that supercapacitor electrodes prepared from catalytically grown multiwalled CNTs for which the surface area is 430 m²/g, show the maximum specific capacitance of 113 F/g and a power density of 8 kW/kg at an energy density of 0.56 Wh/kg in a solution of 38 wt.-% \( \text{H}_2\text{SO}_4 \) used as the electrolyte. Ma et al.[8] have used the CNT electrodes, where the electrodes are prepared similarly to the previous works but in this case they introduced a binder to form solid electrodes. They obtained the specific capacitances of 15–25 F/g in a solution of 38 wt.-% \( \text{H}_2\text{SO}_4 \). The CNT condition and electrode-preparation condition are critically important in determining the power and energy densities. In the present report, the single-walled CNTs are introduced to study the relation of the preparation conditions to the ESR, specific capacitance, energy density, and power density. We obtained a maximum specific capacitance of 180 F/g and a measured power density of 20 kW/kg at an energy density of 7 Wh/kg in a solution of 7.5 N KOH. The specific surface area and the specific capacitance increase with increasing annealing temperatures of the sample. It was found that most of the Brunauer–Emmett–Teller (BET) surface area of the electrode contributes to the theoretically estimated specific capacitance, in contrast with a previous report.[16] Minimization of the contact resistance is independent of the specific capacitance but directly related to the maximization of the power density.

The CNTs produced by arc discharge could be classified into three groups: collar, cathode, and chamber wall, depending on the part of the chamber from which they were collected. The CNTs from the chamber wall were the most abundant among the total yield of the produced CNTs. We used only the CNTs from the chamber for active electrode material. Figure 1a shows a field-emission scanning electron microscope (FE-SEM) (Hitachi S4700) image of as-grown CNTs from the chamber wall. As-grown CNTs are black sheet-like soots, sometimes called rubbery soots. The CNTs are randomly entangled and cross-linked, and some carbon particles are also observed. The CNTs consist of bundles with diameters of 10–20 nm. The sample purity was roughly estimated to be about 30%. Figure 1b shows the BET(N₂) specific surface area and average pore diameter of as-grown CNTs as a function of heat-treatment temperature (carried out for 30 min). With increasing temperature, the specific surface area increases, whereas the average pore diameter decreases and saturates at high temperature. The specific surface area at 1000 °C is 357 m²/g. This value is smaller than that of multiwalled CNTs (430 m²/g)[6] and is much smaller than that of activated carbons (2000–3000 m²/g).[18] However, what is more important is the distribution of the pore diameter, as can be seen from Figure 1c. The raw sample shows a peak at 150 Å and has less distribution in the smaller pore diameter.
Fig. 1. a) The FE–SEM image of the as-grown CNTs. b) The BET (N₂) specific surface areas and the average pore diameters of the CNT electrode as a function of heat-treatment temperature. c) The pore size distribution of the CNT electrode.

near 20 Å. With increasing heat-treatment temperature, the number of smaller pore diameters increases and reaches the maximum at 1000 °C, whereas the number of pore diameters ranging from 50–250 Å decreases. According to the IUPAC classification, there are three classes of pore sizes: i) micro pores of <20 Å; ii) mesopores of 20–50 Å; and iii) macropores of >50 Å. Ions in the electrolyte exist in a hydrated form in an aqueous solution. Since the size of hydrated ions are in the range of 6–7.6 Å, the minimum effective pore size should be greater than 15 Å. In general, it is known that pore sizes in the range of 30–50 Å are required to maximize the capacitance in the electric double-layer capacitor.[18–20] The hydrated ions in the macropores (>50 Å) are usually loosely bound to the surface layer and do not particularly contribute to the capacitance. The changes of the BET surface area and the pore size distribution are directly correlated to the specific capacitance, which will be discussed in the next paragraph.

Figure 2a shows the specific capacitances of the heat-treated electrodes at various temperatures as a function of the charging time. Capacitances increase abruptly and reach about 80 % of the maximum capacitance during the initial 10 min, regardless of the heat-treatment temperatures. The specific capacitance at a discharging current density of 50 mAh/g drops by about 30 % of the capacitance at 1 mA/cm². However, at high annealing temperature (1000 °C), the capacitance drops only by about 10 % even for large discharging current density.

Capacitances gradually increase further and saturate to the maximum values at long charging times. Persistent increase of the capacitance over a long time is generally observed from the porous electrodes and is attributed to the existence of various forms of pores and pore diameters in the electrode. The saturated capacitance increases with increasing heat-treatment temperatures and saturates to 180 F/g at 1000 °C. This value is larger than the previously reported value of 113 F/g from multiwalled CNTs.[6] We note that the capacitance is directly proportional to the specific surface area with increasing temperatures. The average pore diameter approaches 30 Å at 1000 °C and moreover the populations of such small diameters are highly weighted at 1000 °C, as shown in Figure 1b and c. In the electric double layer capacitor with planar electrodes, the charge densities of about 20–50 μA/cm² are commonly realizable.[13] In our case, the specific surface area is 357 m²/g at 1000 °C. We can calculate a rough estimate of the theoretical capacitance to be 71–178 F/g, in good agreement with the observed values in the upper bound. This suggests that the pore diameters are distributed heavily near 30–50 Å, which contribute mostly to the capacitance. This is in good contrast with the activated carbons, where the observed specific capacitance is about one-fourth of the theoretical capacitance in spite of high specific surface areas (2000–3000 m²/g).[12] High-temperature annealing in our CNT electrodes improves the quality of the sample not only by increasing the specific surface area but also by redistributing the CNT pore sizes to the smaller values near 30–50 Å.

Figure 2b shows the specific capacitance as a function of discharge current density at various heat-treatment temperatures, where the data were taken from the samples charged at 0.9 V for 10 min. At low temperatures below 700 °C, the specific capacitance at a discharging current density of 50 mAh/m² drops by about 30 % of the capacitance at 1 mAh/cm². However, at high annealing temperature (1000 °C), the capacitance drops only by about 10 % even for large discharging current density. The existence of the long flat region in the discharging current density is of practical importance for applications of supercapacitors to various realistic devices. Large capacitance drops at low annealing temperatures are caused by the internal resistance of the CNT electrode. Figure 2c shows the cyclic voltammetry (CV) behavior with a sweep rate of 100 mV/s at various temperatures. The inner integrated area (current × voltage) is the power density, which increases with increasing heat-treatment temperatures. The power density will be larger if the ESR, the slope of V/I (indicated by the dotted box in Fig. 2c), is smaller. The CV curve at 1000 °C is close to the ideally rectangular shape, indicating the smallest ESR in the CNT electrode. The magnitude of the ESR can be more clearly shown in the complex-plane impedance plots, as shown in Figure 2d. The electrolyte resistance, Rₑ, is constant and varies with the electrolyte. The sum of the resistance of the electrode itself and the contact resistance between the electrode and the current collector is represented by Rᶜ. The electrolyte resistance and the contact resistance are identical in all samples. Therefore, a decrease of the Rᶜ indi-
cates a decrease of the CNT-electrode resistance. The CNT-electrode resistance decreases very rapidly at high temperatures of 800 and 1000 °C. The $R_f$ is closely related to the power density, as evidenced by comparing two curves in Figures 2c and 2d. This will be further discussed in the next paragraph.

The ideally polarizable capacitance will give rise to a straight line along the imaginary axis ($Z^2$). In real capacitors with a series resistance, this line has a finite slope, representing the diffusive resistivity of the electrolyte within the pore of the electrode. With increasing heat-treatment temperature, the diffusive line comes closer to an ideally straight line, as shown in Figure 2d. The formation of abundant pore diameters of 30–50 Å with increasing temperature may also enhance the diffusivity of the hydrated ions in the pore, which in turn reduces the CNT-electrode resistance.

The contact resistance between the CNT electrode and the current collector is also an important factor in determining the performance of a supercapacitor. Figures 3a and 3b clearly show the relations between the ESRs, particularly the contact resistance and power density. In order to change the contact resistance, we introduced a polished Ni foil in addition to the plain Ni foil and a hybrid form of the CNT–Ni foam. All the samples were heat-treated at 1000 °C for 30 min, as described before. The plain Ni foil gives the largest ESR, as shown in Figure 3a, indicating poor contact formation between the CNT and the Ni foil. The contact resistance was reduced significantly by polishing the surface of the Ni foil, which is attributed to an increase of the contact surface area. It is interesting to see that the semicircle almost disappears in the complex-plane impedance plot for the hybrid electrode due to the extremely small contact resistance. The ESRs measured at 1 kHz are 246 mΩ for the plain Ni foil, 105 mΩ for the polished Ni foil, and 52 mΩ for the hybrid electrode. The contact area between the CNT and the Ni foam is maximized within the Ni foam in the hybrid electrode. The reduction of the ESR is directly related to a more efficient power density.

Figure 3b clearly presents how the small ESR directly affects the power density of a supercapacitor. At low power density ranging from 2–100 W/kg, the energy density in all cases of the contact preparation conditions do not alter. However, the energy density drops very rapidly with increasing power density particularly for the samples with large ESR. On the contrary, the energy density does not change...
appreciably with increasing power density for the hybrid electrode, which has the smallest ESR. We obtain very efficient energy storage devices using the CNT-Ni foam hybrid electrode with the power density of 20 kW/kg at the energy density of 6.55 Wh/kg.

In summary, we have investigated the key factors determining the performance of supercapacitors using single-walled CNT electrodes. We obtained a maximum specific capacitance of 180 F/g with a large power density of 20 kW/kg at an energy density of 6.5 Wh/kg. The heat treatment at high temperature was necessary to increase the capacitance and reduce the CNT-electrode resistance. The increased capacitance was well explained by the enhancement of the specific surface area and the abundant pore distributions at lower pore sizes of 30–50 Å estimated from the BET(N$_2$) measurements. The ESR should be minimized in order to obtain a high power supercapacitor. Our current approach demonstrates a possibility of the CNT application to the supercapacitor. There is still plenty of room to improve the performance of the supercapacitor using the CNT electrodes.

Experimental

Single-walled CNTs were synthesized by dc-arc discharge under a helium pressure of 100 torr, where a graphite rod (diameter: 6 mm) having a concentric hole (diameter: 4 mm) filled by a mixture of the graphite powder with 5 wt.% of Ni, Co, and FeS (1:1:1), was discharged in a bias of 22 V and a current of 55 A [21]. Single-walled CNTs were collected from the chamber wall. The procedure of the electrode preparation was as follows: the as-grown CNTs and pristine poly(vinylene chloride) (PVdC) as a binder (CNT/PVdC = 7:3) were mixed and dissolved in tetrahydrofuran (THF). The THF was then evaporated on the hot plate. A pellet of diameter of 15 mm was formed by pressing the sample with a cylindrical steel molder under 1000 psi. To avoid a possible crack formation in the pellet, the pellet was heat-treated at 500–1000°C for 30 min in an argon-gas atmosphere. The thickness of the electrode was about 150 μm. The measured apparent mass density of the electrode was 0.75 g/cm$^3$. A plain Ni foil of a thickness of 75 μm was used as a current collector. To minimize the contact resistance between the CNT electrode and the current collector, mechanically polished Ni foil was used. The hybrid electrode of the CNT–Ni foam was prepared by pressing the CNT sample on Ni foam with 120 pores per inch under 1000 psi.

A unit cell for the capacitor was fabricated with two CNT electrodes separated by a thin polymer (Celgard) in 7.5 N KOH aqueous solution as the electrolyte. The cell was charged at a constant voltage of 0.9 V for 30 s to 6 h, and then discharged at a constant current density of 1–50 mA/cm$^2$. The discharging capacitance of the test cell was then calculated by $I_{dc} \times t / \Delta V$, where $I_{dc}$ is the constant discharging current, and $\Delta t$ is the discharging time, which was measured from 0.54 V to 0.45 V (about 50–60% of the initial voltage), and the voltage change $\Delta V$ at a constant current discharge. We observed initially a voltage drop (IR drop) which originated from the internal resistance (equivalent series resistance; ESR) of the test cell. To avoid the effect of the internal resistance on the capacitance, the capacitance measurement was carried out in the voltage drop ranging from 0.54 V to 0.45 V in the $V$–$t$ curve, i.e., in the linear region. The energy density was measured as a function of constant-power discharge in the range of 2–20 kW/kg.

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The Generation of “Armored Latexes” and Hollow Inorganic Shells Made of Clay Sheets by Templating Cationic Miniemulsions and Latexes**

By Bodo zu Putlitz, Katharina Landfester, Hartmut Fischer, and Markus Antonietti*

The generation of hollow-shell structures or capsules with diameters in the colloidal size range (50–1000 nm) for the inclusion of liquid components is a topic of current interest. Some synthetic routes have been described, most of them starting with a spherical template such as a latex particle or an emulsion droplet, which is coated by some type of precipitation reaction. At the end, the template is removed and a hollow replica is obtained.[1]

Möhwald and co-workers used the layer-by-layer technique for depositing oppositely charged polyelectrolytes onto model latex spheres, which leads to a polyelectrolyte complex cap-

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[*] Prof. M. Antonietti, Dr. B. zu Putlitz, Dr. K. Landfester
Max Planck Institute of Colloids and Interfaces
Am Mühlenberg, D-14476 Golm/Potsdam (Germany)
Dr. H. Fischer
TNO/SPD Materials Research & Technology
De Weten 6, NL-5612 AV Eindhoven (The Netherlands)