Applications of Carbon Nanotubes to Energy Storage Devices

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Energy storage in secondary batteries and supercapacitors using various materials is of utmost importance from a technological point of view. However, the performance of secondary batteries and supercapacitors is insufficient for practical use and is limited by the efficiency of the electrode material. Secondary batteries and supercapacitors using carbon nanotubes (CNTs) as a novel type of active electrode material are introduced as candidates for large-capacitance and high-power electrochemical energy storage devices. We have investigated the relationship of the preparation conditions for CNT electrodes with the equivalent series resistance, specific capacitance, energy density, and power density and other nanocomposites with conducting polymers.

1. Introduction

Recently, there have been numerous attempts to use carbon nanotubes (CNTs) as active materials of energy storage systems, such as electrochemical hydrogen storage systems, lithium (Li-)ion secondary batteries, and supercapacitors. The CNTs are attractive materials for use as energy storage systems due to chemical and mechanical stability, low mass density, low resistivity, and large surface area.

The Li-ion cell is an outstanding battery system because of its good performance in terms of high operating voltage, large energy density, long cycle life, no memory effect, and environmental compatibility. It is well known that the performance of Li-ion battery strongly depends on the active material for the cathode. Therefore, much more effort has been exerted for the development of active materials for the cathode with high performance.

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Since the discovery of CNTs as a novel form of carbon, progress in the synthesis of CNTs has accelerated significant worldwide investigation on new applications of CNTs as the cathode material of Li-ion batteries. CNTs have been suggested as a candidate anode material with large energy density for Li-ion batteries.

Supercapacitors (also called electrochemical capacitors, electric double-layer capacitors, or ultracapacitors) have many advantages compared to the secondary battery, namely, long cycle life (> 100,000 cycles), simple principle and mode of construction, short charge time, safety, and high power density.\(^{[11-14]}\) Among them, the power density is the most remarkable property of supercapacitors. The power density of supercapacitors is larger than that of the secondary battery by about ten times,\(^{[15]}\) although the energy density of supercapacitors is smaller than that of the secondary battery, which is a drawback for application in practical devices.

The application of CNTs as electrode materials for supercapacitors has promoted significant worldwide investigations of their microscopic and macroscopic porous structures and electrochemical behaviors.\(^{[6-10,16-21]}\) The CNT electrodes exhibit a unique pore structure and high usage efficiency of specific surface areas.\(^{[6,9,10,22-24]}\) The CNT electrodes for the electric-double-layer type of supercapacitor (EDLC) have excellent absorption characteristics due to the accessible mesopores formed by the entangled individual CNTs.\(^{[6,7,9,10,24]}\) Our laboratory has been pursuing applications of CNTs to energy storage systems. Here, we show the results of our research on the development of applications of CNTs to energy storage systems.

2. Li-Ion Battery Using Single-Walled Carbon Nanotubes

We have surveyed the relationship between the specific capacity of the Li-ion battery using single-walled carbon nanotube (SWNT) electrodes and the mechanism of lithium intercalation taking into account the structure of SWNTs. SWNTs are 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 with a mixture of graphite powder with 5 wt% each of Ni, Co, and FeS (1:1:1), is discharged at a bias of 22 V and a current of 55 A.\(^{[25]}\) Two types of SWNT electrodes are prepared in order to investigate the Li-intercalation site in SWNTs. One is fabricated with no treatment of the as-grown SWNT powder, and the other is prepared with the SWNT powder ball-milled for two h to disintegrate the as-grown SWNT bundles.

Figure 1 shows the specific capacity, the discharge efficiency, and the cyclability of the SWNT electrodes. The as-grown SWNT electrode has a very large charging capacity of 1327 mAh/g at the first cycle. However, the specific discharge capacity at the first cycle is 560 mAh/g, indicating a large irreversible specific capacity of 767 mAh/g. This suggests that the undesirable large irreversible specific capacity may be due to Li adsorption on carbonaceous particles that are present in pristine samples of CNT powders. These particles disintegrate easily during the charging and discharging process. Therefore, the irreversible specific capacity may be decreased with increasing cycle number. Gao et al. reported that the irreversible specific capacity can be attributed to the large surface area of the SWNT electrode, estimated to be \(\sim250\) m\(^2\)/g by \(\text{N}_2\) BET measurement.\(^{[26]}\) After the first cycle, it is found that the reversible specific capacity of the as-grown SWNT electrode is uniformly maintained, as shown in Fig. 1(a). We emphasize that the discharge efficiency and the
cyclability are also excellent, which is very important for application to practical devices. The discharge efficiency and the cyclability of the ball-milled SWNT electrode are also excellent. However, the ball-milled SWNT electrode shows a smaller capacity (a charging specific capacity of 1019 mAh/g and a discharging specific capacity at the first cycle of 385 mAh/g) than the as-grown SWNT electrode, implying that the number of Li-reversible intercalation sites is decreased by ball milling. The large drop of the reversible specific capacity of the SWNT electrode by ball milling may indicate that Li intercalates with the interstitial bundles of SWNTs. Therefore, after disintegration of the bundles of SWNTs by the ball milling, the reversible specific capacity of ball-milled SWNT electrode decreases, due to the reduction of the number of Li-reversible intercalation sites. The possibility that Li atoms exist inside CNTs can be excluded, since cutting CNTs into smaller sizes opens the tube ends and this should increase the storage capacity of Li atoms in the capillaries of the CNTs.

3. Supercapacitors Using SWNT Electrodes

In recent years, high-power supercapacitors based on the CNT electrodes using aqueous electrolytes have been reported. Niu et al.\(^{(6)}\) showed that supercapacitor electrodes prepared from catalytically grown multiwalled CNTs whose specific surface area was 430 m\(^2\)/g exhibited a maximum specific capacitance of 113 F/g and a power density of 8 kW/kg at the energy density of 0.56 Wh/kg in an aqueous solution of 38 wt% H\(_2\)SO\(_4\) used as the electrolyte. Ma et al.\(^{(8)}\) also used CNT electrodes prepared in a manner similar to that of the previous work; however, they introduced a binder to form solid electrodes and obtained specific capacitances of 15 to 25 F/g in an aqueous solution of 38 wt% H\(_2\)SO\(_4\). Frackowiak et al.\(^{(9)}\) investigated the electrochemical characteristics of supercapacitors built from MWNT electrodes with the specific surface area of 430 m\(^2\)/g in 1 M KOH aqueous solution as well as the correlation of microtexture with the elemental composition of the materials. They argued that the presence of mesopores due to the central canal and/or the entanglement of CNTs is the reason for the easy access of the ions to the electrode/electrolyte interface for charging the electric double layer. They detected pure electrostatic attraction of ions as well
as quick Faradaic reactions upon varying surface functionality, which was induced during acidic oxidation. The values of specific capacitance varied from 4 to 135 F/g, depending on the type of nanotubes and/or their post-treatments (acidic oxidation).

Zhang et al. studied supercapacitors using MWNT electrodes in organic electrolyte systems. The MWNT electrodes exhibited a specific surface area of ~100 m²/g and a measured specific capacitance of up to 18.2 F/g (16.6 F/cm²) with 1 M LiClO₄ in a mixture of ethylene carbonate and propylene carbonate (1:1 volume ratio) as the organic electrolyte solution. They found that the specific capacitance was lower than that reported by other groups using aqueous electrolytes, due to the low specific surface area of the MWNT electrode and the organic electrolyte solution used. However, the energy density of the supercapacitor can reach 20 Wh/kg at 10 mA discharge current density, depending on the organic electrolyte solution system. The relative volume of mesopores and macropores of the used electrode exceeds 92%, and micropores are nearly negligible. In the case of the organic electrolytes, because of their large molecular structures, only mesopores and macropores are accessible and are much larger than those of activated carbons for supercapacitors.

The CNT morphologies and the electrode-preparation conditions are critical for determining the power and energy densities of supercapacitors. In this review, the relationship of the electrode preparation conditions with the specific capacitance, equivalent series resistance (ESR), energy density, and power density is discussed using SWNT electrodes for high-power supercapacitors. Various sample preparation conditions are investigated, although many of them are still to be determined in order to obtain the best performance for actual applications.

The procedure for SWNT electrode preparation is as follows: as-grown SWNTs and 20 ~ 50 wt% pristine polyvinylidene chloride (PVDCl) as binder were mixed and dissolved in tetrahydrofuran (THF). The THF was then evaporated on a hot plate. A pellet with a diameter of 15 mm was formed by pressing the sample with a cylindrical steel mold at 1000 psi. To avoid crack formation in the pellet, the pellet was heat-treated at 500–1000°C for 30 min in argon-gas ambient. The thickness of the electrode was approximately 150 µm. The measured apparent mass density of the electrode was 0.75 g/cm³. A plane Ni foil of 75 µm thickness was used as the current collector. To minimize the contact resistance between the SWNT electrode and the current collector, mechanically polished Ni foil was also used. A hybrid electrode of the SWNT-Ni foam was prepared by pressing the SWNT sample on Ni foam having 120 pores per inch at 1000 psi.

A unit cell for the capacitor was fabricated with two SWNT 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 ~ 6 h, and then discharged at a constant current density of 1 ~ 50 mA/cm². The discharge capacitance of the test cell was then calculated by $I_{dc} \times \Delta t / \Delta V$, where $I_{dc}$ is the constant discharge current, $\Delta t$ is the discharge time, measured from 0.54 V to 0.45 V (about 60 ~ 50% of the initial voltage), and the voltage change $\Delta V$ at a constant current discharge. We initially observed a voltage drop (IR drop) that 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 range 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 W/
kg ~ 20 kW/kg.

In order to fabricate a unit cell for the electrochemical evaluation of the supercapacitor with the SWNT electrode, we chose polyvinylidene chloride (PVdC) as a binder. This binder was mixed with an active SWNT material to determine the influence of the mixing ratio of SWNT to PVdC on the specific capacitance and ESR. The results are shown in Fig. 2. The specific capacitance does not change much at high contents of SWNTs. The SWNT electrode without PVdC binder shows a decrease in the specific capacitance. The minimum ESR appears at 70 wt% SWNTs in the electrode with maximum specific capacitance. Therefore, further research is conducted only for the electrode made with 70 wt% SWNTs (30 wt% PVdC binder). The role of the binder is not only to strengthen the electrode during pellet formation, but also to realize appropriate pore size formation, as will be discussed in the next section. It is noted here that the choice of the binder is also an important factor. For instance, we tried using poly(vinyl alcohol) (PVA) as a binder. The optimal composition gave a specific capacitance of 70 F/g, which was lower than that of the current PVdC binder. Therefore, research to find better binders should be conducted.

Figure 3(a) shows the BET ($N_2$) specific surface area and the average pore diameter of

![Fig. 2](image)

Fig. 2. Specific capacitance and ESR as a function of wt% of SWNT in electrodes heat-treated at 750°C for 30 min.

![Fig. 3](image)

Fig. 3. (a) BET ($N_2$) specific surface area and average pore diameter of the SWNT electrode as a function of heat-treatment temperature, and (b) pore size distribution of SWNT electrodes.
as-grown SWNTs and electrodes with 30 wt% PVdC as a function of heat-treatment temperature 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, and this value is smaller than that of multiwalled CNTs (430 m²/g). However, what is more important is the distribution of the pore diameter, as can be seen from Fig. 3(b). The raw sample shows a peak at 150 Å and has a smaller distribution at smaller pore diameters near 20 Å. With increasing heat-treatment temperature, the number of pores with small diameters increases and reaches a maximum at 1000°C, whereas the number of pores with diameters ranging from 50 to 250 Å decreases. According to IUPAC classification, there are three classes of pore sizes: i) micropores (<20 Å), ii) mesopores (20 to 50 Å), and iii) macropores (>50 Å). Ions in the electrolyte exist in the hydrated form in an aqueous solution. Since the size of hydrated ions lies in the range of 6 to 7.6 Å, the minimum effective pore size should be larger than 15 Å. In general, it is known that pore sizes in the range of 30 to 50 Å are required to maximize the capacitance in the electric double-layer capacitor. 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 with the specific capacitance, as will be discussed in the next paragraph.

Figure 4(a) shows the specific capacitance of the heat-treated electrodes at various temperatures as a function of charge time. The specific capacitances increase abruptly and reach about 80% of the maximum capacitance during the initial 10 min, regardless of the heat-treatment temperature. The specific capacitances increase gradually to saturate at maximum values after a long charge time. The persistent increase of the capacitance over a long time is generally observed for the porous electrodes and is attributed to the existence of various forms of pores and pore diameters in the electrode. Figure 4(b) presents the saturated specific capacitances of the heat-treated electrodes at various temperatures in Fig. 4(a). The specific capacitance increases with increasing heat-treatment temperature, eventually reaching saturation at 180 F/g at 900°C. This value is larger than the previously reported value of 113 F/g for multiwalled CNTs, where sulfuric acid was used as the

Fig. 4. (a) Specific capacitance of electrodes heat-treated at various temperatures as a function of charging time at a charging voltage of 0.9 V, where the capacitance was measured at a discharge current of 1 mA/cm², and (b) saturated specific capacitance as a function of heat-treatment temperature.
electrolyte. Our value is expected to improve if sulfuric acid is used as electrolyte. We note that the capacitance is directly proportional to the specific surface area with increasing temperature. The average pore diameter approaches 30 Å at 1000°C; moreover, the populations of such small diameters are highly weighted at 1000°C, as shown in Figs. 3(a) and 3(b). In the electric double-layer capacitor with plane electrodes, the charge densities of about 20 to 50 mF/cm² are realizable. In our case, the specific surface area is 357 m²/g at 1000°C. We can roughly estimate 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 mainly distributed near 30 to 50 Å; this contributes markedly to the capacitance. This is in contrast with activated carbons, where the observed specific capacitance is about one-fourth of the theoretical capacitance in spite of the high specific surface area (2000–3000 m²/g). High-temperature annealing of our CNT electrode improves the quality of the sample not only by increasing the specific surface area but also by redistributing the CNT pore size to smaller values near 30 to 50 Å.

Figures 5(a) and 5(b) show the specific capacitances as a function of the discharge current density at various heat-treatment temperatures, where the data are taken from samples charged at 0.9 V for 10 min. In general, the specific capacitances decrease gradually with increasing discharge current density. Too-large currents may block the entrance of the micropores and thus reduce the specific capacitance. At temperatures below 750°C, the specific capacitance at a discharge current density of 50 mA/cm² drops by about 30% compared to the capacitance at 1 mA/cm², as shown in Fig. 5(b). However, at high annealing temperatures (900 – 1000°C), the capacitance drops only by about 10% even at large discharge current density. Figure 5(b) clearly shows the capacitance drops at 1 mA/cm² and 50 mA/cm². The existence of the long flat region in the high discharge current density region is of practical importance for applications of supercapacitors to various devices. The large drops of capacitances at low annealing temperatures are caused by the internal resistances of the SWNT electrodes, i.e., different pore sizes formed during the annealing process.

Figure 6 shows the cyclic voltammetric (CV) behavior with a sweep rate of 100 mV/s.

![Graphs](image_url)

**Fig. 5.** (a) Specific capacitance of electrodes heat-treated at various temperatures as a function of discharge current density at a charging voltage of 0.9 V for 10 min, and (b) differences in specific capacitance at discharge current densities of 1 mA/cm² and 50 mA/cm².
at various temperatures. The inner integrated area, the current times voltage, is the power density, which increases with increasing heat-treatment temperature. This power density will be larger if the ESR, the slope of $V/I$, indicated by the dotted box in Fig. 6, is smaller. The CV curve at 1000°C is close to an 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 Fig. 7. The electrolyte resistance, $R_e$, is constant and varies with the electrolyte used. The sum of the resistance of the electrode itself and the contact resistance between the electrode and the current collector is represented by $R_f$. The electrolyte resistance and the contact resistance are identical in all samples. Therefore, the decrease of $R_f$ indicates the decrease of the CNT-electrode resistance. The CNT-electrode resistance decreases very rapidly at high temperatures of 800 and 1000°C. $R_f$ is closely related to the power density, as evidenced by comparing the two curves in Figs. 6 and 7. This

![Cyclic voltammetric (CV) behavior (sweep rate, 100 mV/s) of SWNT electrodes at various heat-treatment temperatures.](image)

![Complex-plane impedance plots for SWNT electrodes at various heat-treatment temperatures at an ac voltage amplitude of 5 mV. Z': imaginary impedance, Z: real impedance.](image)
will be further discussed in the next paragraph. The ideally polarizable capacitance will give rise to a straight line along the imaginary axis ($Z''$). In real capacitors with series resistance, this line has a finite slope, representing the diffusive resistivity of the electrolyte within the electrode pores. With increasing heat-treatment temperature, the diffusive line approaches an ideal straight line, as shown in Fig. 7. The formation of pores with diameters of 30 to 50 Å with increasing temperature may also enhance the diffusivity of the hydrated ions into the pores, 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. In order to change the contact resistance, we introduced a polished Ni foil as a current collector in addition to the plane Ni foil and the hybrid form of the CNT-Ni foam. All samples were heat-treated at 1000°C for 30 min, as described earlier. Figure 8 presents the specific capacitance as a function of discharge current density at various current collectors (plane and polished Ni foil, and Ni foam), where the data are taken from the samples charged at 0.9 V for 10 min. Figure 9 shows the CV behaviors at a sweep rate of 100 mV/s for various current collectors. It can be seen that the capacitance behavior is similar for all cells with various current collectors, as shown in Figs. 8 and 9. However, the slopes of $\Delta V/\Delta I$ in the CV curves show some differences. The linearity from the initial to the final saturation stage of the Ni foam sample is the best.

Figures 10 and 11 clearly show the relationship 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 plane Ni foil and hybrid form of the SWNT-Ni foam. All samples were heat-treated at 1000°C for 30 min, as described earlier. The plane Ni foil gives the largest ESR, as shown in Fig. 10, indicating poor contact formation between the SWNT and the Ni foil. The contact resistance was reduced significantly by polishing the surface of the Ni foil, which is attributed to the increase of the contact surface area. It is interesting to note that the semicircle almost disappears in the complex-plane impedance plot for the hybrid electrode due to the extremely small contact resistance. The ESRs

![Graph](image_url)

**Fig. 8.** Specific capacitance as a function of discharge current density for various current collectors (plane and polished Ni foil, and Ni foam); the data were taken from samples charged at 0.9 V for 10 min.
Fig. 9. CV behaviors at a sweep rate of 100 mV/s for various current collectors.

Fig. 10. Complex-plane impedance plots of the SWNT electrodes fabricated by different methods.

Fig. 11. Ragone plots for electrodes fabricated by different methods.
measured at 1 kHz are 246 mΩ for the plane Ni-foil, 105 mΩ for the polished Ni foil, and 52 mΩ for the hybrid electrode. The contact area between the SWNT and Ni foam is maximized within the Ni foam in the hybrid electrode. The reduction of the ESR is directly related to the high power density.

Figure 11 clearly presents how the small ESR directly affects the power density of a supercapacitor. In this case, only the electrode mass is considered for the calculations of power density and energy density. At low power densities ranging from 2 W/kg to 100 W/kg, the energy density in all cases of the contact preparation conditions does not change. However, the energy density drops very rapidly with increasing power density, particularly for samples with large ESR. In contrast, the energy density does not change appreciably with increasing power density for the hybrid electrode that has the smallest ESR. We were able to obtain a very efficient energy storage device using the SWNT-Ni foam hybrid electrode with a power density of 20 kW/kg at an energy density of 6.5 to 7 Wh/kg.

In summary, 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 SWNT-electrode resistance. The increased capacitance is explained well by the enhancement of the specific surface area and the large pore distribution at small pore sizes of 30 to 50 Å estimated from the BET (N₂) measurements. The ESR should be minimized in order to obtain a high-power supercapacitor. Our current approach demonstrates the possibility of applying the CNT to a supercapacitor. There is still plenty of room for improvement of supercapacitor performance using the CNT electrodes.

4. Supercapacitors Using SWNT-Nanocomposite Electrodes

Even if the CNT electrodes exhibit a unique pore structure and high usage efficiency of specific surface areas, and some processes for disintegrating the bundle structure of the CNTs may enhance the utilization efficiency of their surface area, there is a limitation to widening the effective surface area of the CNTs. The specific capacitance of supercapacitors using CNT electrodes is still smaller than those of supercapacitors using activated carbon and activated carbon fiber, which are commonly used as electrode materials for supercapacitors. Therefore, it is necessary to improve the SWNTs in order to realize a large capacitance. The small specific energy density of a supercapacitor is a serious drawback for its use in practical devices, and consequently, the focus of interest is to improve the capability of supercapacitors to deliver high specific capacitance and energy density.

Currently, there is considerable interest in a new type of nanocomposite that uses CNTs and conducting polymer to improve the conductivity, electronic transport, and electromagnetic properties of organic conducting polymers. The nanocomposites are regarded as one of the fascinating candidates for applications in nanoelectronic element and electrooptical devices. In addition, the nanocomposite of CNTs and conducting polymers, which is the hybrid of an electric double-layer system and a Faradaic system, may serve as a candidate for the supercapacitor with high specific capacitance and energy density.

Recently, Jurewicz et al. demonstrated that the composite electrode based on MWNTs coated with polypyrrole (Ppy) could be used as a supercapacitor. They found that a homogeneous layer of Ppy could be deposited on nanotubular materials by the electrochemi-
cal polymerization of pyrrole. The composite electrodes enhanced the specific capacitance in all cases. They obtained a maximum value of 163 F/g for MWNTs prepared at 600°C, where a 5-nm-thick Ppy layer was deposited on MWNTs, compared to only 50 F/g for pristine nanotubes. They proposed that the nanocomposite electrode favors the formation of a three-dimensional electrical double layer, thereby allowing a more effective contribution to the Faradaic properties of Ppy.

Frackowiak et al. also reported a composite electrode based on MWNTs deposited with Ppy for a supercapacitor, although they prepared the nanocomposite electrode of MWNTs and Ppy by chemical polymerization of pyrrole using an oxidant in acidic solution. The specific capacitance obtained from the MWNT electrode modified by Ppy reached 172 F/g, about twice that of pristine MWNTs (ca. 80 F/g) or pure Ppy (ca. 90 F/g). They also observed pseudocapacitance, and discussed its origin by introducing surface functionalities, metallic particles or conducting polymers.

In this review, we will present the nanocomposite of SWNTs and conducting polymer for the supercapacitor with high capacitance. SWNT-polypyrrole (Ppy) nanocomposite electrodes are fabricated to improve the specific capacitance of the supercapacitor. The combination of two types, the electric double layer and the redox system, has been developed for enhancing the performance of supercapacitors.

The formation of the nanocomposite of SWNT and Ppy was carried out by in situ chemical polymerization of the pyrrole monomer with SWNTs. Ferric chloride (FeCl₃, 10 mmol) and sodium p-toluenesulfonate (CH₃C₆H₄SO₃Na, 20 mmol) as oxidants for the polymerization of pyrrole were added to SWNTs (0.4 g) suspended in 100 mL of DI water. After ferric chloride and sodium p-toluenesulfonate were completely dissolved, pyrrole monomer (50 mmol) was slowly added dropwise to the above SWNT suspension with constant magnetic stirring for four h at room temperature. After the polymerization was completed, the SWNT-Ppy powder that formed was filtered and rinsed with DI water and methanol until the filtrate became colorless. The prepared SWNT-Ppy powder was then dried in vacuum at 60°C for 24 h.

The electrode for the supercapacitor was prepared as follows. The SWNT-Ppy powder was mixed with 5 wt% suspended PTFE (polytetrafluoroethylene) as a binder in isopropyl alcohol. The mixture was kneaded and rolled by a bar coater to form a sheet of about 250 µm thickness. The prepared sheet was cut into 3 cm × 3 cm squares for use as a supercapacitor electrode. The working electrode for the supercapacitor was prepared by pressing the cut sheet on Ni foam with 120 pores per inch at 1000 psi. The prepared working electrode was then dried in vacuum at 60°C for 24 h. A unit cell for the capacitor was fabricated with two SWNT-Ppy nanocomposite electrodes separated by a thin polymer (Celgard 3501) in 7.5 N KOH aqueous solution as the electrolyte.

The unit cell was charged at a constant voltage of 0.9 V for 10 min, and then discharged at a constant current density of 10 – 100 mA/g. To characterize SWNT-Ppy nanocomposite electrodes, charge-discharge cycling tests for measuring specific capacitance, cyclic voltammogram, and AC impedance were executed. The AC impedance of a unit cell in the frequency range from 100 kHz to 10 mHz was measured by an electrochemical impedance analyzer (Jahnke Electrik IM6, Germany). Cyclic voltammetric measurement was performed with a potentiogalvanostat (EG&G 273A, USA), which was measured in a
conventional three-electrode beaker cell using 7.5 N KOH aqueous solution as electrolyte. A platinum plate (3 cm × 3 cm) served as the counter electrode and Ag/AgCl was used as the reference electrode.

Figure 12 shows field-emission scanning electron microscope (FE-SEM, Hitachi S4700) images of as-grown SWNTs, pure Ppy, and SWNT-Ppy powder formed by in situ chemical polymerization. The as-grown SWNTs are entangled and cross-linked, and some carbon nanoparticles are also observed, as shown in Fig. 12(a). The purity of the as-grown SWNTs was roughly estimated to be about 30 wt%.(39) From Fig. 12(b), one can see that the pure Ppy synthesized without SWNT shows a typical granular morphology. The granule size of the pure Ppy is about 0.2 ~ 0.3 μm. Figure 12(c) reveals that the individual nanotube bundles are uniformly coated with Ppy, indicating that in situ chemical polymerization of pyrrole is achieved. Compared to the as-grown SWNTs, the SWNTs coated by the Ppy are very thick (about 20 ~ 30 nm). The carbon nanoparticles are also coated uniformly by Ppy. Although the purity of SWNTs is about 30 wt%, the SWNTs are the main components for building up the network of the SWNT-Ppy nanocomposite electrode due to their long and entangled morphology. This network created by the SWNTs plays an important role as a pathway for the transfer of electrons that accumulated during charging and discharging processes in the electrode of the supercapacitor.

The specific surface areas of as-grown SWNT, pure Ppy, and SWNT-Ppy nanocomposite electrodes are measured by a surface area analyzer (Micromeritics ASAP 2010, USA) though the measurement of the N₂ adsorption isotherm at 77 K. The measured specific surface areas of as-grown SWNT, pure Ppy, and SWNT-Ppy nanocomposite electrodes are about 215, 23, and 65 m²/g, respectively. The specific surface area of the particle-free SWNTs is about 100 m²/g, about half that of the as-grown sample. The estimated specific surface area of the contained carbonaceous particles is about 260 m²/g. However, the specific capacitance of the particle-free SWNTs is reduced only by about 30%. This indicates that although the purity of the SWNTs in the as-grown sample is about 30%, the SWNT network contributes mostly to the specific capacitance.

Pure Ppy shows a much smaller specific surface area than the as-grown SWNTs and the nanocomposite electrodes. We emphasize that the effective surface area of the Ppy is enhanced by about three times in the SWNT-Ppy nanocomposite. In this case, SWNTs act as a nanosized backbone for the polymerization of pyrrole in order to increase the surface area of the coated Ppy. The nanoparticles contained in the as-grown sample also serve as a nanosized backbone for the polymerization of Ppy.

Fig. 12. FE-SEM images of (a) as-grown SWNT, (b) pure Ppy, and (c) SWNT-Ppy powder.
Cyclic voltammetric measurement is helpful for understanding macroscopic electrochemical surface reactions on the electrode of the supercapacitor during the charging and discharging process. Cyclic voltammetry measurement of the as-grown SWNT, pure Ppy, and SWNT-Ppy nanocomposite electrodes is performed to investigate the possible dominant mode of electrochemical energy storage in the three electrodes. Figures 13(a) ~ 13(c) present the cyclic voltammetric behaviors of as-grown SWNT, pure Ppy, and SWNT-Ppy nanocomposite electrodes at a sweep rate of 5 mV/s. In the case of the as-grown SWNT electrode (Fig. 13(a)), the shape of the charging and discharging cyclic voltammogram is close to a rectangle and there is no current peak caused by the redox reaction, indicating a typical electric double layer behavior, while the pure Ppy electrode clearly shows Faradaic redox reactions that are observed at 0.47 V and 0.4 V with respect to the Ag/AgCl reference electrode, representing oxidation and reduction processes, respectively. The cyclic voltammetry measurement of the SWNT-Ppy nanocomposite electrode shows a shape that is basically similar to that of the pure Ppy electrode that exhibits Faradaic redox behavior. However, the redox current of the SWNT-Ppy nanocomposite electrode is much higher than that of the pure Ppy electrode (note that the current scale in Fig. 13(c) is much larger than that of the individual materials in Figs. 13(a) and 13(b)). This higher redox current of the SWNT-Ppy nanocomposite electrode is due to the uniformly coated Ppy on the SWNTs, which effectively increases the active sites on the Ppy chains. The effective surface area of the coated Ppy on SWNTs is enhanced by about three times in the SWNT-Ppy nanocomposite.

Fig. 13. Cyclic voltammetric behaviors of (a) as-grown SWNT, (b) pure Ppy, and (c) SWNT-Ppy nanocomposite electrodes at a sweep rate of 5 mV/s.
compared to that of the pure Ppy electrode, as mentioned above.

The electrochemical processes taking place at the conducting polymers are electrochemical redox reactions associated with sequential Lewis acid or Lewis base producing steps so that neutral polymer molecules are converted to multiply charged structures though electrochemical Lewis-type reactions involving electron withdrawal or electron donation.\(^{40}\) In the charging process, a positive charge is introduced on the Ppy chains by p-doping, resulting from the Lewis ionization process involving oxidation with electron transfer. The discharge process involves reduction with the release of hydroxyl ions. It is known that this Lewis ionization process requires a quasi-linear, one-dimensional cylindrical Helmholtz-like double layer developed with the involvement of counter ions of the electrolyte.\(^{40}\) Therefore, the pseudocapacitance produced by Faradaic redox processes in conducting polymer-based electrochemical capacitors is dominant, although about 2 ~ 5% of the double-layer capacitance is included in the total specific capacitance.\(^{40,41}\)

Figure 14 shows the specific capacitance of as-grown SWNTs, pure Ppy, and SWNT-Ppy nanocomposite electrodes as a function of discharge current density, where the data are taken from the samples charged at 0.9 V for 10 min. In comparison with the pure Ppy and as-grown SWNT electrodes, the SWNT-Ppy nanocomposite electrode shows very high specific capacitance that decreases gradually with increasing discharge current density. With respect to the CNT, the specific capacitance of the CNT-Ppy composite is larger than that of as-grown SWNT due to the pseudocapacitance provided by Ppy, whereas with respect to the Ppy electrode, the specific capacitance of the CNT-Ppy composite is larger than that of pure Ppy due to an increase in surface area provided by the CNT substrate.

The specific capacitance of the as-grown SWNT electrode increases slightly and saturates at a maximum value with increasing discharge current density, while those of pure Ppy and SWNT-Ppy nanocomposite electrodes show a gradual decrease with increasing discharge current density. The slight increase of the specific capacitance for the as-grown SWNT electrode at high discharge current densities may be attributed to the existence of various forms of pores and pore diameters in the electrode. It seems that some pores with

![Graph](image-url)

Fig. 14. Specific capacitances of the as-grown SWNT, pure Ppy, and SWNT-Ppy nanocomposite electrodes as a function of discharge current density at a charging voltage of 0.9 V for 10 min.
small diameters can be invaded by ions in the electrolyte at a high charge current density. For the pure Ppy electrode, the specific capacitance at a discharge current density of 100 mA/g drops by about 95% compared to that at 10 mA/g, while the capacitance of the SWNT-Ppy nanocomposite electrode drops by only about 25% even at a high discharge current density. The deterioration of the specific capacitance of the pure Ppy electrode is caused by the large internal resistance of the electrode compared to that of the SWNT electrode. The large internal resistance (or equivalent series resistance, ESR) 829 causes a large IR drop at high discharge current density, resulting in the decrease of the specific capacitance and the power density. The magnitude of the ESR can be clearly observed in the complex-plane impedance plots in Fig. 15. In general, conducting polymer electrode materials do not have long-term stability and long cycle life during cycling in alkaline media, which may be a fatal problem in actual applications. Swelling and shrinking of electroactive conducting polymers is well known and may lead to degradation during cycling. 80,81

Figures 15(a) – 15(b) present the complex-plane impedance plots for as-grown SWNT, pure Ppy, and SWNT-Ppy nanocomposites. The impedance behavior of the as-grown SWNT electrode is close to that of an ideal EDLC. Accordingly, the as-grown SWNT electrode shows much lower impedance than the pure Ppy and SWNT-Ppy nanocomposite electrodes. The internal resistances measured at 1 kHz are 76 mΩ for the as-grown SWNT electrode, 175 mΩ for the pure Ppy electrode, and 124 mΩ for the SWNT-Ppy nanocomposite electrode. The internal resistance of the pure Ppy electrode is very large, resulting in marked deterioration of the specific capacitance at a particularly large discharge current density of 100 mA/g. Although the internal resistance of the SWNT-Ppy nanocomposite electrode is much smaller than that of the pure Ppy electrode, it is still large compared to that of the as-grown SWNT electrode.

In order to reduce the internal resistance of the SWNT-Ppy nanocomposite electrode, 5 ~ 20 wt% of a conducting agent (acetylene black) is added to the SWNT-Ppy nanocomposite electrode, when the electrode is prepared. The complex-plane impedances of the SWNT-Ppy nanocomposite electrodes containing 5 ~ 20 wt% of the conducting agent are shown in Fig. 16. With increasing amount of conducting agent, the phase angle of tan (R_{imag} / R_{real})

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**Fig. 15.** Complex-plane impedance plots at an ac amplitude of 5 mV for (a) as-grown SWNT and SWNT-Ppy nanocomposite electrodes, and (b) pure Ppy. Z': imaginary impedance, Z: real impedance.
in the low-frequency region is close to 90 degrees, indicating a significant reduction of the internal resistance of the SWNT-Ppy nanocomposite electrode. The internal resistance of the SWNT-Ppy nanocomposite electrode with conducting agent above 15 wt% becomes smaller than that of the as-grown SWNT electrode. These suggest that the conducting agent affects the specific capacitance of the nanocomposite electrode supercapacitor.

The effects of conducting agent on the specific capacitance of the SWNT-Ppy nanocomposite electrode are shown in Fig. 17. The maximum specific capacitance appears at 15 wt% of the conducting agent, where the data are taken from the samples charged at 0.9 V for 10 min. The effect of the conducting agent is clearly seen particularly at high discharge current densities. The specific capacitance significantly increases with increasing amount of the conducting agent up to 15 wt% and decreases at 20 wt%. We obtained a maximum specific capacitance of 265 F/g for the SWNT-Ppy nanocomposite electrode containing 15

Fig. 16. Complex-plane impedance plots at an ac amplitude of 5 mV for SWNT-Ppy nanocomposite electrodes containing 5 – 20 wt% of the conducting agent.

Fig. 17. Specific capacitance of SWNT-Ppy nanocomposite electrodes containing 5 – 20 wt% of the conducting agent as a function of discharge current density.
wt% of the conducting agent. This value is larger than the value of 180 F/g for the heat-treated pure SWNT electrode. The conducting agent contributes to the specific capacitance by reducing the IR drop. However, an excess of the conducting agent diminishes the effective portion of the active electrode material, resulting in the reduction of the specific capacitance. The difference in specific capacitance between the discharge current densities of 10 mA/g and 100 mA/g is larger at a small amount of conducting agent due to the larger internal resistance.

In summary, we have introduced the SWNT-Ppy nanocomposite electrode to improve the specific capacitance of the supercapacitor by combining the electric double layer and the redox reaction. In comparison to pure Ppy and the SWNT electrode, the SWNT-Ppy nanocomposite electrode shows very large specific capacitance. We show that this large specific capacitance of the SWNT-Ppy nanocomposite electrode is due to the uniformly coated Ppy on the SWNTs, which increases the active sites on Ppy chains. We obtained a maximum specific capacitance of 265 F/g from the SWNT-Ppy nanocomposite electrode containing 15 wt% of the conducting agent. The addition of conducting agent to the SWNT-Ppy nanocomposite electrode increases the specific capacitance by reducing the internal resistance of the supercapacitor.

5. Future of Energy Storage Devices Using Carbon Nanotubes

One of the important challenges in this world is to realize optimal energy conversion, storage, and distribution. These are clearly related to the development of several key technologies such as transport, communications, and electronics. The environmental problems and economic aspects related to the development and use of electrochemical energy storage devices are of significance.

In particular, the new application and development of supercapacitors and Li-ion batteries are directly related to technologies for manufacturing electric vehicles (EVs) and hybrid electric vehicles (HEVs). The supercapacitor in EVs or HEVs will serve as a short-time energy-storage device with high power density. It will also reduce the size of the primary power source (batteries (EVs), internal combustion engine (HEVs), fuel cell) and keep them running at an optimized operation point. High-power supercapacitors for EVs or HEVs will require a high working voltage of 100 to 300 V with low resistance and large energy density by series and parallel connections of elemental capacitors, in which very uniform performance of each supercapacitor unit is essential.

Another prospect is the micro-supercapacitor and micro-battery for use in micro- (or nano-) electromechanical systems (MEMS or NEMS). In recent years, MEMS (or NEMS) technologies have attracted much attention worldwide for their potential applications that include medical, communication equipment, sensors, and actuators. Many technical problems have to be solved for the successful development of these types of micro-devices. One of the most important challenges is to develop an optimal micro-power source for operating these devices. The MEMS (or NEMS) has, in many cases, extremely low current and power requirements. This may be realized by using micro-supercapacitors and micro-batteries as power sources for these devices.
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References