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The Development of Carbon Nanotubes/$RuO_2 \cdot xH_2O$ Electrodes for Electrochemical Capacitors

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Carbon nanotubes were refluxed with nitric acid to create acid sites on the surface. After such treatment, amorphous or nano-scale crystalline $RuO_2 \cdot xH_2O$ can be adhered to the surfaces of carbon nanotubes by a simple method. $RuO_2 \cdot xH_2O$ became more amorphous with decreasing the fraction of carbon nanotubes. The capacitance can be enhanced significantly by the adherence. When the weight fraction of $RuO_2 \cdot xH_2O$ in the composite electrodes reached 75%, a specific capacitance of 560 $F\,g^{-1}$ was achieved. On the other hand, carbon nanotubes/$RuO_2 \cdot xH_2O$ capacitors exhibit excellent power delivery behavior. So the processing of carbon nanotubes/$RuO_2 \cdot xH_2O$ composite electrodes is a new attempt to fabricate supercapacitors with both high energy and high power density.

Carbon materials such as activated carbon, activated carbon fiber cloth, and carbon aerogels are the most extensively examined materials for electrodes in electrochemical capacitors.[1—3] The large capacitance is caused by double layer capacitance on the carbon/electrolyte interface. Another kind of electrochemical capacitors using crystalline or amorphous RuO_2 has a capacitance several times higher than that of carbon materials, here the pseudocapacitance takes a majority part. A specific capacitance of 768 $F\,g^{-1}$ was obtained based on the amorphous $RuO_2 \cdot xH_2O$ electrode material.[4,5] Some authors have reported that the capacitance of carbon aerogel electrodes can be enhanced substantially by the deposition of ruthenium nanoparticles on carbon aerogels.[6] In reverse, the power density of the amorphous $RuO_2 \cdot xH_2O$ based capacitor could be improved significantly by mixing $RuO_2 \cdot xH_2O$ powders with about 20% weight fraction of carbon black to store more electrolyte.[7]

Recently, carbon nanotubes (CNTs) were found to exhibit excellent capacitance and power behavior.[8—10] Carbon nanotubes can be chemically treated with nitric acid so that metal clusters can be deposited onto surfaces.[11] In this paper, it was demonstrated that amorphous or nano-scale $RuO_2 \cdot xH_2O$ could be deposited to the surface of carbon nanotubes readily. The electrochemical capacitors based on CNTs/$RuO_2 \cdot xH_2O$ electrodes were studied specifically.

Experimental

Preparation of CNTs/$RuO_2 \cdot xH_2O$ Electrodes and Capacitors. Carbon nanotubes were produced catalytically by pyrolysis of C_2H_4/H_2 with Ni catalyst. The diameters of the nanotubes are between 20—30 nm. They were refluxed with 68% nitric acid at 140 °C for 1—2 h and then cleaned with distilled water. The final aqueous solution of carbon nanotubes should have a pH value of over 5.

The $RuO_2 \cdot xH_2O$ powder was prepared as follows. The required amount of $RuCl_3 \cdot xH_2O$ [37% weight percent (w/o) Ru] was dissolved in distilled water to give a concentration of 0.1 M (1 M = 1 mol dm^{-3}). The designed amounts of refluxed carbon nanotubes were dispersed in the solution. Then the solution of NaOH with concentration of 0.3 M was added slowly into the stirred $RuCl_3 \cdot xH_2O$/CNTs solution. The specific precipitation process was similar to that described by J. P. Zheng.[5] Then, the precipitated powders were filtered several times and finally annealed at 150 °C. After that, the black powders containing carbon nanotubes and $RuO_2 \cdot xH_2O$. (CNTs/$RuO_2 \cdot xH_2O$) were obtained.

The CNTs/$RuO_2 \cdot xH_2O$ powders were mixed mechanically with 10% phenol–formaldehyde (PF) powders. The pellets with a diameter of 2.2 cm and a thickness of 0.3—1 mm were fabricated by pressing the above powders in a cylindrical molder at 100 °C for 15 min.

To fabricate a test cell, the pellets were immersed in a 38 wt% solution of sulfuric acid. Then, two identical pellets were separated by a porous glass fiber separator and assembled in a plastic holder. The cells were charged to 1.0 V at a current of 100 mA and held at 1.0 V for 30 min, then discharged at a current of 10 mA. The d.c. capacitance was calculated from the constant current discharge process.

Results and Discussion

Refluxed Carbon Nanotubes. It is well known that refluxing carbon nanotubes with nitric acid creates acid sites on the surfaces. The infra red spectrum is shown in Fig. 1. The peak features on 3500 and 1600 cm^{-1} indicate the corresponding function groups of –OH and –COOH. So the existence of >C=O on the surfaces can be deduced. We have demonstrated that higher capacitance can be achieved through such attachment of functional groups.[9] The reason is that some pseudocapacitance can be added to the excess of electrostatic double layer capacitance. The pseudocapacitance was caused by the electrochemical faradic redox processes occurred at surface functionalities on carbon nanotubes

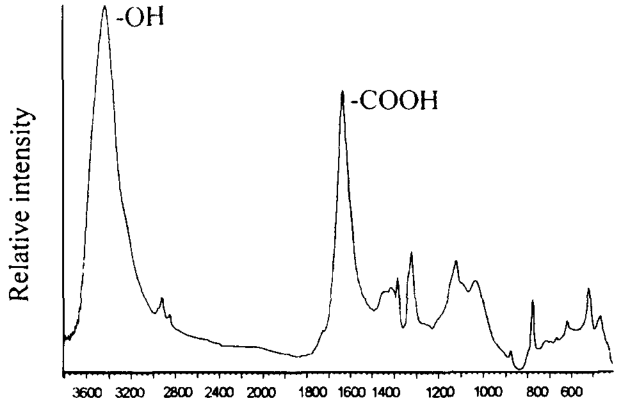

Fig. 1. Infra-red spectrum of refluxed carbon nanotubes.

surfaces.

Morphology and Crystallinity of RuO$_2$. The obtained CNTs/RuO$_2$·xH$_2$O powders were observed by TEM. The typical images are shown in Fig. 2. It reveals that amorphous or nano-scale crystalline RuO$_2$·xH$_2$O appears to be adherent to the carbon nanotube surface. The sites created by acid treatment can act as nucleation centers.[11] So the precipitated RuO$_2$·xH$_2$O powders are adhered to these places.

J. P. Zheng concluded that RuO$_2$·xH$_2$O was in amorphous phase at lower annealing temperature < 150 °C.[5] However, some crystalline structure information can be characterized by X-ray diffraction in our CNTs/RuO$_2$·xH$_2$O powders. The X-ray (Cu $K\alpha$) diffraction patterns of two different weight fractions of RuO$_2$·xH$_2$O (45%, 75%) are shown in Fig. 3. It can be seen clearly that the powders with the fraction of 75% RuO$_2$·xH$_2$O are more amorphous than that of 45%. The reason is that more carbon nanotube surfaces can provide more nucleation substrate to form crystalline RuO$_2$. So the composite powders became more amorphous with decreasing the fraction of carbon nanotubes.

The SEM image of as-produced CNTs/RuO$_2$·xH$_2$O pellet is shown in Fig. 4. Each pellet consists of randomly entangled and cross-linked carbon nanotubes. The pore size distribution of the electrodes is shown in Fig. 5. Most pore diameters are between 4—50 nm (radius of 2—25 nm), which is commonly known to be suitable for the immersion of sulfuric acid electrolyte. So the pore structure provides great possibility for the full utilization of RuO$_2$·xH$_2$O adherent to the surfaces of carbon nanotubes.

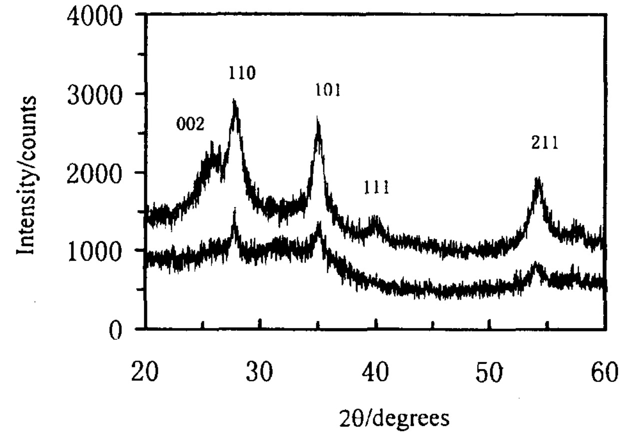

Fig. 3. X-Ray (Cu $K\alpha$) diffraction pattern of CNTs/RuO$_2$·xH$_2$O powers. (Up—45% RuO$_2$·xH$_2$O, Bottom—75% RuO$_2$·xH$_2$O, (002)—the diffraction peak of CNTs.).

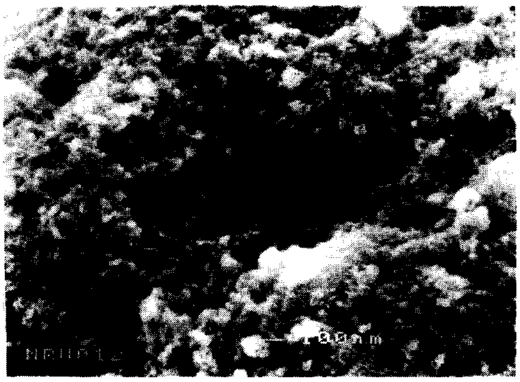

Fig. 4. SEM image of CNTs/RuO$_2$·xH$_2$O electrodes.

Capacitance Behavior. The measured single electrode specific capacitance (C) of mechanically mixing CNTs with 20% RuO$_2$·xH$_2$O is 98 F g^{-1}. However, a specific capacitance of 145 F g^{-1} was obtained by adhering the same

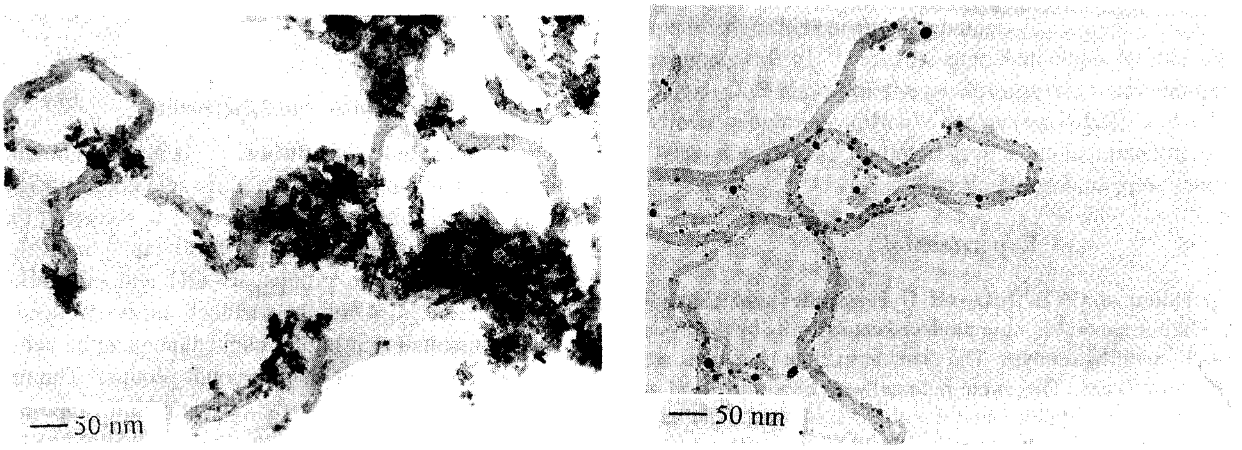

Fig. 2. TEM image of CNTs/RuO$_2$·xH$_2$O composite powders. (a) Amorphous RuO$_2$·xH$_2$O adhered to CNTs. (b) Nano-scale RuO$_2$·xH$_2$O adhered to CNTs.

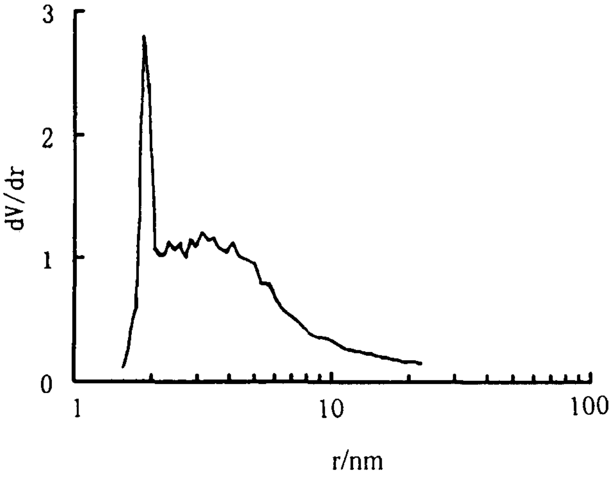

Fig. 5. Pore size distribution of CNTs/$RuO_2 \cdot xH_2O$ electrodes.

amount of $RuO_2 \cdot xH_2O$ to CNTs surfaces. It indicates that the cell prepared by the reflux and precipitation process exhibits a better capacitance performance. So the following experimental data are all based on reflux and precipitation processes.

A typical curve of charge and discharge cycles is shown in Fig. 6. The discharge curve is almost linear, indicating a constant discharge capacitance. The specific capacitance (C) values based on single electrode as a function of weight percent of $RuO_2 \cdot xH_2O$ in the composite electrodes are shown in Fig. 7. The overall capacitance will be contributed to by CNTs, amorphous and nano-scale crystalline $RuO_2 \cdot xH_2O$. If one assumes that the capacitance contributed by CNTs (C_d) and $RuO_2 \cdot xH_2O$ (C_Φ) is additive, the capacitance contribution by $RuO_2 \cdot xH_2O$ (C_Φ) to overall capacitance (C) can be calculated by the following equation:

$$C_\Phi = [C - F(\text{CNTs}) \times C_d]/\text{F}(\text{RuO}_2 \cdot x\text{H}_2\text{O}).$$

Here F(CNTs) refers to the fraction of carbon nanotubes in the composite electrodes and the same meaning is given to $F(\text{RuO}_2 \cdot x\text{H}_2\text{O})$. The value of C_d is taken as 90 F g^{-1}, the specific capacitance of refluxed carbon nanotubes.

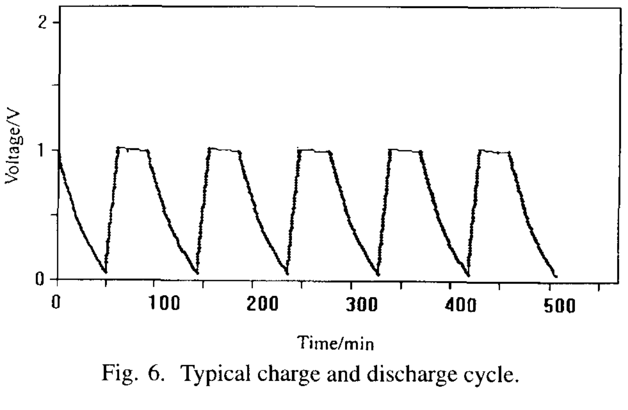

Fig. 6. Typical charge and discharge cycle.

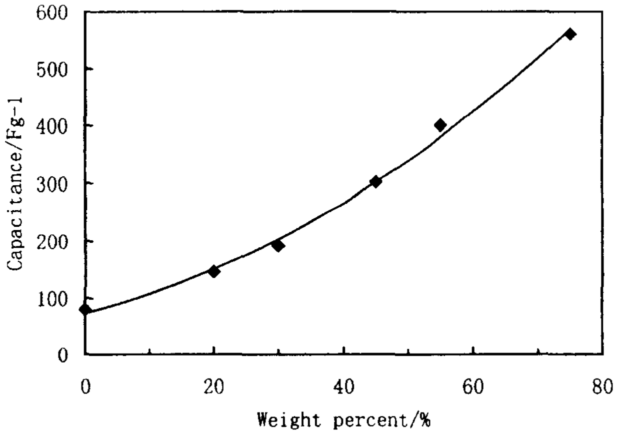

Fig. 7. Variation of specific capacitance to weight fraction of $RuO_2 \cdot xH_2O$.

Table 1. Specific Capacitance of Composite Electrodes and $RuO_2 \cdot xH_2O$

$RuO_2 \cdot xH_2O$: CNTs : PF	C	C_Φ
%	F g^{-1}	F g^{-1}
0 : 90 : 10	90	—
20 : 70 : 10	145	410
30 : 60 : 10	192	460
45 : 45 : 10	302	581
55 : 35 : 10	400	670
75 : 15 : 10	560	729

Based on the above assumptions, it can be calculated that amorphous and nano-scale crystalline $RuO_2 \cdot xH_2O$ adhered to carbon nanotube surfaces contribute 410—729 F g^{-1} to the overall specific capacitance (See Table 1). The values are much greater than that of 330 F g^{-1} based on RuO_2 nanoparticles deposited on the surface of carbon aerogels.[6] According to previous publications, crystalline RuO_2 has much lower specific capacitance than amorphous $RuO_2 \cdot xH_2O$. Because the morphology of $RuO_2 \cdot xH_2O$ became more amorphous with decreasing weight fraction of carbon nanotubes in our composite powders, the combined capacitance contribution (C_Φ) of the amorphous and nano-scale $RuO_2 \cdot xH_2O$ is not constant. When the weight fraction of $RuO_2 \cdot xH_2O$ reaches 75%, C_Φ is about 729 F g^{-1}, which is very close to the value of 768 F g^{-1} based on pure amorphous $RuO_2 \cdot xH_2O$ electrodes.

Power Behavior. Figure 8 shows the normalized capacitance based on the composite electrodes with different weight fractions of $RuO_2 \cdot xH_2O$ in relation to increased discharge current. It can be seen clearly that about 80—90% of the original energy density was retained with increasing discharge current in all capacitors. It seems that the higher the weight fraction of CNTs in the electrodes, the better the power performance.

Evidences has shown that the power density of the RuO_2 based capacitor could be improved significantly by increasing the electrode porosity to store more electrolyte to reduce ion depletion effect.[7] CNTs electrodes show a connected pore structure. So the CNTs substrate in the composite electrodes is very useful to improve the power behavior of the capacitors, just as high area carbon black does. In addition, the superior performance of the RuO_2-based capacitor is expected only from the thin films of RuO_2 as a result of the high ex-

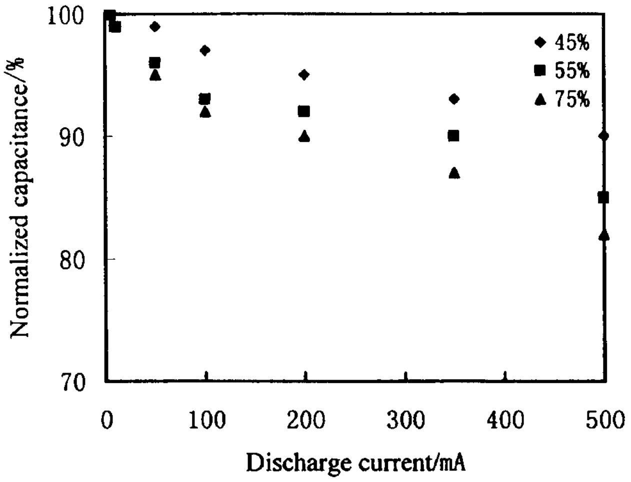

Fig. 8. Normalized capacitance of different electrodes in relation to discharge current.

change current density of the RuO_2 redox reaction.[12,13] In thick electrodes, this advantage is often neglected by the matrix resistivity. The resistivity of RuO_2 is in the order of 10^{-5} Ω·cm. Though amorphous $RuO_2 \cdot xH_2O$ has much higher specific capacitance than crystal RuO_2, the resistivity is in the order of 10^{-2}—10^{-3} Ω·cm.[5] Carbon nanotubes have measured resistivities of ca. 10^{-4} Ω·cm.[10] which is at least one order lower than that of amorphous $RuO_2 \cdot xH_2O$. So the low resistivity and high surface area CNTs substrate in the electrodes can retain the benefit of high exchange current density of the RuO_2 system. The adherence of nano-scale $RuO_2 \cdot xH_2O$ to CNTs surface is very promising to fabricate RuO_2-based high power capacitors.

Conclusions

Based on the results above, the adherence of amorphous or nano-scale $RuO_2 \cdot xH_2O$ to the surfaces of carbon nanotubes contributes significantly to the capacitance of carbon nanotubes/$RuO_2 \cdot xH_2O$ electrochemical capacitors. The specific capacitances of 145—560 F g^{-1} have been reached depending on the weight fraction of $RuO_2 \cdot xH_2O$ in the electrodes. Furthermore, the low resistivity and high surface area CNTs substrate in electrodes are helpful to retain the superior performance of the RuO_2 system. The processing of CNTs/$RuO_2 \cdot xH_2O$ composite can be employed to fabricate electrochemical capacitor with both high energy density and high power density.

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