ARTICLE

Pseudo-capacitive Behavior of Cobalt Hydroxide/Carbon Nanotubes Composite Prepared by Cathodic Deposition

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A novel type of composite electrode based on multiwalled carbon nanotubes coated with sheet-like cobalt hydroxide particles was used in supercapacitors. Cobalt hydroxide cathodically deposited from $Co(NO_3)_2$ solution with carbon nanotubes as matrix exhibited large pseudo-capacitance of 322 F/g in 1 mol/L KOH. To characterize the cobalt hydroxide nanocomposite electrode, a charge-discharge cycling test, cyclic voltammetry, and an impedance test were done. This cobalt hydroxide composite exhibiting excellent pseudo-capacitive behavior (i.e. high reversibility, high specific capacitance, low impedance), was demonstrated to be a candidate for the application of electrochemical supercapacitors. A combined capacitor consisting of cobalt hydroxide composite as a cathode and activated carbon fiber as an anode was reported. The electrochemical performance of the combined capacitor was characterized by cyclic voltammetry and a dc charge/discharge test. The combined capacitor showed ideal capacitor behavior with an extended operating voltage of 1.4 V. According to the extended operating voltage, the energy density of the combined capacitor at a current density of 100 mA/cm^2 was found to be 11 Wh/kg. The combined capacitor exhibited high-energy density and stable power characteristics.

Key words: Cobalt hydroxide, Carbon nanotubes, Nanocomposite, Cathodic deposition, Supercapacitor

I. INTRODUCTION

Electrochemical capacitors (ECs) have greater power density than usual batteries and can be deeply discharged without any deleterious effect on lifetime [1]. Carbon, with various modifications, is the electrode material used most frequently for electrodes of ECs. Activated carbons (AC) are available with a specific surface area of up to 2500 m^2/g as powders, woven cloths, felts, or fibers [2]. Charge storage on AC electrodes is predominantly capacitive in the electrochemical double layer. Carbon based ECs come close to what one would call an electrochemical double layer capacitor (EDLC).

Amorphous ruthenium oxide is considered to be a promising material for a high energy density power source because the charge can be stored in the bulk of the amorphous materials [3]. However, the high material cost of $RuO_2{\cdot}xH_2O$ makes this material impractical for commercial applications. Therefore, in recent years, great efforts have been undertaken in order to find new and cheap materials. There are also other approaches, e.g. polymers [4], nitrides [5] and manganese oxides [6] and nickel oxides [7]. Although the usefulness of cobalt oxide has been recognized, the application of cobalt oxide as electrodes for ECs has not been studied extensively. Conway reported that Co_3O_4 and CoO_x are promising electrode materials for ECs due to their intercalative pseudo-capacitance properties [8]. Liu's study shows that cobalt oxide films exhibit pseudo-capacitance behavior over the potential range of −2 V to −1.56 V at a sweep rate of 20 mV/s [9]. Lin investigated the redox behavior and charging mechanism of an electrode prepared with the CoO_x xerogel calcined at 150 °C, and a maximum capacitance of 291 F/g was obtained [10]. However, cobalt oxide has too small an operating charge and discharge voltage —only 0.7 V [11]. Moreover, the sol-gel technique is relatively complicated and the electrochemical properties as well as electrical conductivity of the electroactive materials may be affected by the introduction of binders during the electrode preparation process [12]. Accordingly, an alternative preparation method, which can directly coat hydrous oxides with high reversibility and pulse power density in the potential window of water decomposition, is worth seeking.

Carbon nanotubes (CNTs) were discovered in 1991. Their high accessible surface area, low resistance and high stability suggest that CNTs are suitable materials for electrodes in ECs, which are being studied extensively in laboratory [13]. We report here the development of a nanocomposite of cobalt oxide and CNTs for ECs with high capacitance and low resistance. The purpose of this work is to present a suitable operating procedure for fabricating a cobalt hydroxide/CNTs deposit with ideally pseudocapacitive behavior for ECs.

Cobalt hydroxide electrodes for battery applications are generally fabricated by electrochemical impregnation of porous metal plaques by a one-step, cathodic reduction reaction. An α-form of cobalt hydroxide, isostructural with α-$Ni(OH)_2$, has also been successfully synthesized by electrodeposition reaction [14,15]. The motivation for the present study was to see if the

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cobalt hydroxide could be electrosynthesized in a similar fashion to pure and CNTs based composites for electrochemical supercapacitors. Combined capacitors using an EDLC-pseudocapacitor to increase energy density were introduced by Beliakov *et al.* [16]. The term "combined" means that this capacitor employs asymmetric electrodes with different operating voltage windows. These asymmetric electrodes are responsible for the ability to achieve an operating voltage over 1.2 V even in aqueous electrolyte. Wide operating voltage yields high energy density. If one of the electrodes of the cell is not polarizable, or is polarizable but not sufficiently when the potential of the other electrode is changing, a doubling of the electrical capacitance of the cell could result. In this paper, we propose a new combined capacitor consisting of cobalt hydroxide composite as cathode, activated carbon fiber as anode, and a 1 mol/L KOH as the electrolyte. This new type of EC has better maximum energy density and power density.

II. EXPERIMENTS

A. Preparation of CNTs and the CNTs electrode base for supercapacitor

CNTs were produced catalytically with Ni particles as the catalyst [17]. In a pipe stove, with reagent based on Ni and ethylene gas, raw multi-walled CNTs were produced at 700 °C. Polarizable CNTs electrode can be manufactured using carbonaceous material by any conventional method [18]. In the method used here, 95% CNTs, 5% Teflon binder and water were mixed in a blender or kneader. The paste-like mixture obtained was then rolled to form flexible films with a thickness of 0.2 mm. This film-like raw material for electrodes was cut into 1 cm×1 cm disks. The disk electrodes were then mounted on a porous Ni plaques. The CNTs electrode base for deposition of cobalt hydroxide was prepared in this way.

B. Preparation of cobalt hydroxide and cobalt hydroxide /CNTs by electrochemical cathodic deposition

The cobalt hydroxide was deposited electrochemically onto a 1 cm^2 nickel substrate and a CNTs/Ni base prepared as above. The cobalt hydroxide and composite electrode here were deposited at room temperature in a bath containing 1.8 mol/L $Co(NO_3)_2$ and 75 mmol/L $NaNO_3$ in a solvent of 50% (volume) ethanol using a cathodic current density of 3 mA/cm^2. The deposition time was 5 h. The cathodic reactions in the electrochemical deposition process are usually given as:

$$NO_3^- + 7H_2O + 8e^- \longrightarrow NH_4^+ + 10OH^- \quad (1)$$

$$Co^{2+} + 2OH^- \longrightarrow Co(OH)_2 \quad (2)$$

The weight of the $Co(OH)_2$ deposited and $Co(OH)_2$ /CNTs nanocomposite prepared can be estimated by subtracting the mass of nickel substrate current from the total mass of the electrode. The deposited electrode were washed with deionized water and heated in air at 100 °C for 2 h.

C. Preparation of activate woven carbon fiber cloth anode

Activated carbon fiber (ACF) was used as polarizable electrode material. The ACF material had the form of woven cloth with a specific weight of 2200 m^2/g, which was obtained form Sinopowerstar United Inc (Beijing, China). Onto the ACF cloth, aluminum powder particles (99.5% in purity 60-100 μm particle size) were sprayed along with an Ar plasma jet by using a plasma spraying apparatus to form an aluminum layer. The ACF cloth with aluminum coating layer was then punched into small disks for electrochemical measurement.

D. Electrochemical test of performance for composite electrodes and combined supercapacitor

Two test cells are introduced in this work. A beaker-type electrochemical cell equipped with a working electrode, a platinum counter electrode and a SCE reference electrode was used. The electrodes were simply dipped into the 1 mol/L KOH. The geometric surface area of the working electrode was 1 cm^2. The cyclic voltammograms (CVs) presented in this work were steady state ones after repeated potential sweeps. The electrochemically active surface area includes both the charge of the electrical double layer and that of the redox of the metal species; i.e. it reflects the pseudo-capacitance of the electrodes. These were connected to a CHI660B (CHENHUA, China) system that drove the voltage in either direction sequentially at predetermined constant sweep rates. The sweep rates range of 20 mV/s was used during testing. By integrating the area of the CV curve, the specific capacitance of a single electrode can be calculated.

Another cell is much more characteristic of an actual working device. The $Co(OH)_2$/CNTs composite cathode and ACF anode were pressed together and separated by a porous non-woven cloth separator. For such a combined capacitor, the weight ratio of electroactive materials (composite/ACF) was 1:3 for cells operating within a 1.4 V. The CV was obtained with the cell using $Co(OH)_2$/CNTs composite as the working electrode and ACF as the counter electrode. The direct current (DC) charge/discharge test was performed to evaluate the electrochemical performance of the combined capacitor with a current density from 10 mA/cm^2 to 100 mA/cm^2. All the above electrochemical measurements were carried out on a CHI660B.

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III. RESULTS AND DISCUSSION

A. XRD patterns of cobalt hydroxide

The powder X-ray diffractometer (XRD) patterns of α-$Co(OH)_2$ presented in Fig.1 had been studied extensively as shown in literature [19]. α-$Co(OH)_2$ shows a low angle reflexion at 7.73 Å followed by another at 3.35 Å. The pattern resembles very closely to that of α-$Ni(OH)_2$ and can be indexed on a hexagonal cell with a=3.09 Å and c=23.3 Å.

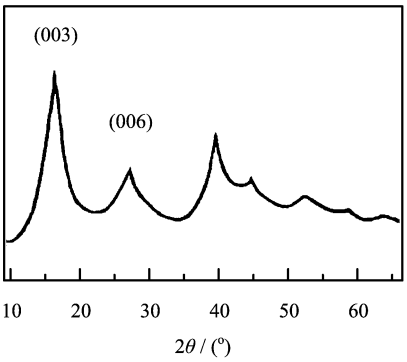

FIG. 1 The powder XRD patterns of α-$Co(OH)_2$.

B. SEM pictures of electrode materials

Figure 2(a) shows the scanning electron micrograph (SEM) image of multi-wall CNTs. The CNTs are randomly entangled and cross-linked. The nanotubes have a diameter of 15 nm to 50 nm and length of several microns to several tens of microns. From Fig.2(b), one can see that hydrous cobalt hydroxide prepared with electrochemical deposition shows unique sheet-like characteristics. The dimension of the hydroxide sheet prepared here is about 200-500 nm, while the thickness of the sheet is no more than 20 nm. Figure 2(c) is the SEM of the $Co(OH)_2$/CNTs composite prepared after 5 h of electrochemically cathodic deposition. Figure 2(c) reveals the nanotubes bundle to be surrounded with $Co(OH)_2$ particles indicating that *in situ* electrochemical deposition of the cobalt hydroxide was effectively achieved. The CNTs build up the network of the $Co(OH)_2$/CNTs nanocomposite electrode due to the long and entangled individual CNTs. This network of CNTs plays an important role as a pathway for electron transfer accumulated during the charging and discharging process in the electrode of the supercapacitor.

Figure 2(d) shows microscopic structures of the bundles of ACF. Figure 2(e) is a sectional view of an interface between the aluminum layer and the ACF cloth, showing a narrower view of the aluminum layer on the surface of the fiber. A number of grains of molten aluminum were found to accumulate on the ACF cloth to construct a continuous and bulky metal layer of about 100 μm thickness. Each aluminum particle penetrated deeply into the woven structure of the ACF cloth and made a strong contact with the ACF. It is evident from these experimental results and microscopic observations that, by use of the plasma spraying method, a continuous conductive coating of aluminum can be obtained even on such a jagged surface as a cloth composed of thousands of bundles of ACF.

C. A cyclic voltammetric measurement of electrode

A cyclic voltammetric measurement is helpful to understand the macroscopic electrochemical surface reactions at the electrode of the supercapacitor during the charging and discharging process. Cyclic voltammetries on the CNTs, ACF, $Co(OH)_2$ and $Co(OH)_2$/CNTs nanocomposite electrodes were performed to investigate the possible dominant mode of electrochemical energy storage on the three electrodes. Curve (a) in Fig.3 shows the CV curve of the CNTs-based electrode in the KOH electrolyte at a scan rate 20 mV/s. Curve (b) in Fig.3 shows the CV curve of the ACF-based electrode. The charging and discharging CVs are close to a rectangular shape, indicating typical electric double layer EDLC behavior. From integrating the CV curve, the CNTs and ACF electrode shows about 40 and 140 F/g specific capacitance as a single electrode capacitance respectively. Curve (c) and curve (d) in Fig.3 present the cyclic voltammetric behaviors of $Co(OH)_2$ and $Co(OH)_2$/CNTs nanocomposite electrodes at a sweep rate of 20 mV/s respectively. The $Co(OH)_2$ electrode clearly shows faradaic redox reactions, which are observed at 0.5 and −0.3 V with respect to the SCE reference electrode, representing the oxidation and reduction processes. From integrating the CVs (curve (c)), the $Co(OH)_2$ electrode exhibits about 280 F/g as a single electrode capacitance.

The nanocomposite electrode shows a shape basically similar to that of cobalt hydroxide electrode. However, the redox current of the nanocomposite electrode is about 1.5 times higher than that of the $Co(OH)_2$. Furthermore, the usable potential window of nanocomposite electrode is wider than that of the pure $Co(OH)_2$ electrode. The electrochemical capacitance scale of the composite is about 322 F/g, which is much larger than that of the individual materials. We can say from the CV that the $Co(OH)_2$/CNTs composite electrode shows the characteristics of a pseudocapacitive electrode and a double layer capacitive electrode simultaneously. This higher current scope for the nanocomposite electrode arises from the uniform deposition of $Co(OH)_2$ on the CNTs which effectively increased the number of active sites on the hydroxide particles. The effective surface area of the $Co(OH)_2$ surrounded by CNTs is enhanced distinctly in the nanocomposite in comparison with the $Co(OH)_2$ electrode, as mentioned above. Fur-

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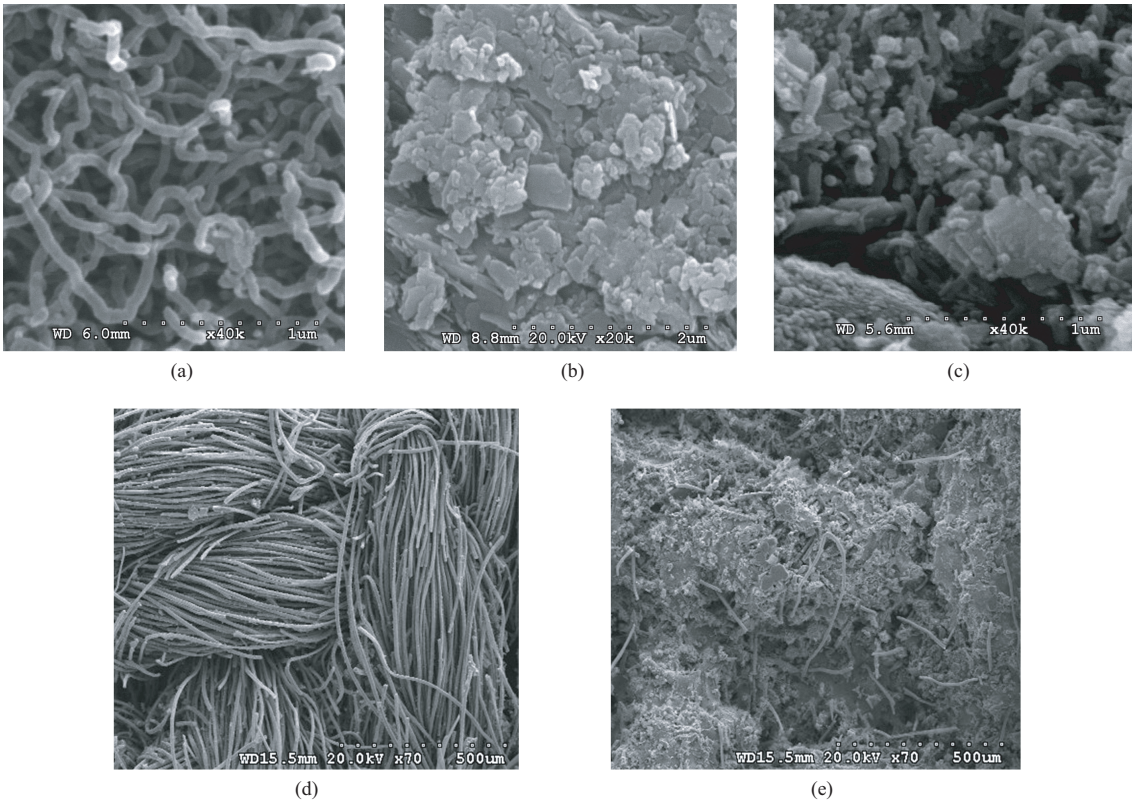

FIG. 2 SEM of (a) carbon nanotubes, (b) pure cobalt hydroxide, (c) cobalt hydroxide/CNTs composite, (d) activated carbon cloth fiber and (e) aluminum coated activated carbon cloth fiber.

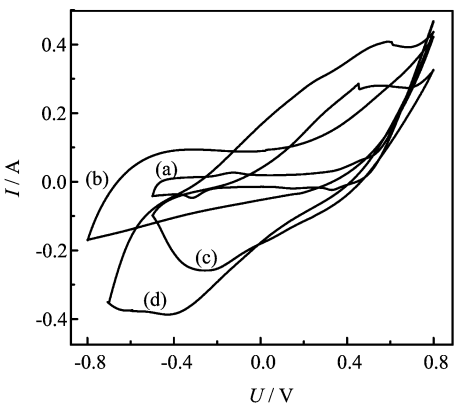

FIG. 3 Cyclic voltammogram of (a) the CNTs electrode, (b) the ACF electrode, (c) the $Co(OH)_2$ electrode and (d) the composite electrode.

ther, CNTs also serve as electrolyte reservoirs to reduce ionic diffusion resistance regardless of the charging/discharging current density. At the same time, the wide voltage scope shows that the high surface area of CNTs would contribute to the charge storage by the EDLC mechanism.

The pseudocapacitance of hydrous $Co(OH)_2$ prepared mainly came from the electrochemical energy stored by the faradaic redox transitions of interfacial oxycation species. In alkaline media, the redox transitions of hydrous cobalt hydroxide should include Co(III)/Co(II)(and/or Co(IV)/Co(III)) in the potential region prior to the oxygen evolution reaction. In addition, these redox transitions, which exchange protons (or OH^-) with the electrolyte should obey Eqs.(1) or (2) because the redox transitions of superficial oxycations followed a nonstoichiometric ratio [14,15].

$$CoO_\delta(OH)_{2-\delta} + \delta H^+ + \delta e^- = Co(OH)_2 \quad (3)$$

$$CoO_\delta(OH)_{2-\delta} + \delta H_2O + \delta e^- = Co(OH)_2 + \delta OH^- \quad (4)$$

where $CoO_\delta(OH)_{2-\delta}$ indicates the interfacial cobalt hydroxides at higher oxidation states. Note that hydrous $Co(OH)_2$ were estimated to have mixed or nonstoichiometric properties rather than well-defined oxidation states. The value δ is believed to range from 1 to 2, and is strongly dependent upon the average electron transfer number of the redox couples between the higher and lower oxidation states.

D. An impedance analysis of the electrode

Figure 4 presents the complex-plane plots for the CNTs, $Co(OH)_2$ and $Co(OH)_2$/CNTs nanocomposites.

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The CNTs shows much lower impedance than the cobalt hydroxide and nanocomposite electrode. The impedance spectra of the pure $Co(OH)_2$ and the composite exhibit a small time constant in the high frequency which is related to the electrical charge transfer in the electrode material. The internal resistance of the pure $Co(OH)_2$ is very large, which will result in the serious deterioration of the capacitance at high discharge current. Although the internal resistance of the $Co(OH)_2$/CNTs nanocomposite electrode is still large compared to that of the CNTs electrode, the internal resistance of the nanocomposite electrode is much smaller than that of the pure $Co(OH)_2$. It can be seen from the Fig.4 that the resistance of the nanocomposite electrode is still very low even when the electrode potential is increased to 0.6 V. With the introduction of the CNTs into the $Co(OH)_2$, the phase angle of tan $(R_{\rm imag}/R_{\rm real})$ at the low frequency region is close to 90°, indicating a significant reduction of the internal resistance in the $Co(OH)_2$/CNTs nanocomposite electrode. All these data suggest that the CNTs obviously affects the specific capacitance and internal resistance in the composite electrode.

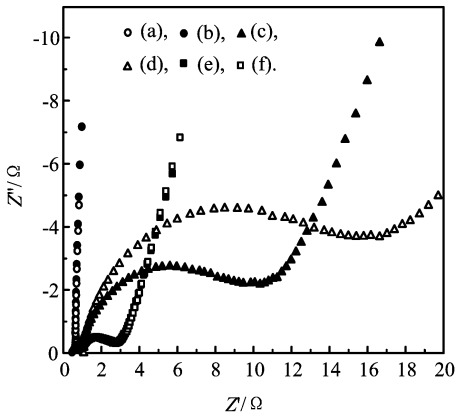

FIG. 4 The impedance plot for (a) the CNTs electrode at 0 V, (b) the CNTs electrode at 0.6 V, (c) the $Co(OH)_2$ electrode at 0 V, (d) the $Co(OH)_2$ electrode at 0.6 V, (e) the $Co(OH)_2$/CNTs composite electrode at 0 V, and (f) the $Co(OH)_2$/CNTs composite electrode at 0.6 V.

E. The electrochemical performance of the combined capacitor

In contradistinction to RuO_x pseudo-capacitors and ACF based EDLC possessing wide window of potentials in anode and cathode areas, the difference between potentials of the discharged electrode—$Co(OH)_2$ and charged electrode—CoOOH is not significant (<0.7 V). Thus, it is not expedient to create "pure" pseudo-capacious systems, such as [+CoOOH/KOH/$Co(OH)_2^-$]. We also found the maximum working voltage of the cell composed of two identical composite electrodes is no more than 0.8 V according to the voltage profile in Fig.5. Moreover, the power characteristic of the cell is poor. The specific capacitance of the cell decreased greatly, especially with a larger discharging current. Thus, it is not helpful to create "pure" pseudo-capacious systems.

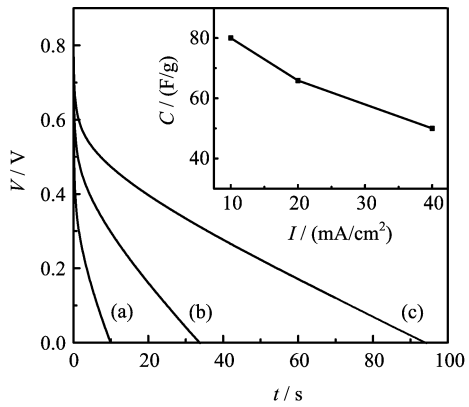

FIG. 5 The discharge curve for the [+CoOOH/KOH /$Co(OH)_2^-$] cell and specific capacitance of the cell as a function of charge/discharge current density. (a) 40 mA/cm^2, (b) 20 mA/cm^2, (c) 10 mA/cm^2.

Therefore, in order to widen the working voltage window, ACF-based material and $Co(OH)_2$/CNTs based material have been adapted to an anode and a cathode respectively. This electrochemical system can be written as the following: [+CoOOH/KOH/ACF$^-$]. The charge of $Co(OH)_2$ is based on transferring of charge throughout the interface of phase. During the process of charging of the negative carbon electrode, a double electric layer is being created. The electrodes included into the system are notable for their reversibility. The process of discharge for this new type super-capacitor is a process of portonization of crystal grid CoOOH and destruction of the layer of hydrated ions on a negative carbon electrode. We can also expect that replacement of the anode electrode from $Co(OH)_2$/CNTs to ACF contributed to improving the energy density of the ECs. Furthermore, the ACF-based anode which has the power characteristics of an EDLC would contribute to improving the power characteristics of a combined capacitor as in this study.

Figure 6 shows the CV curves of the combined capacitor consisting of composite electrode as the cathode and ACF as the anode in 1 mol/L KOH. The CV were obtained with the two-electrode cell described in experimental section (II.D). The combined capacitor shows ideal capacitor behavior with rectangular CV shape and mirror symmetry. It is noteworthy that an operating voltage window of 1.4 V can be achieved even in aqueous electrolyte. We believe that the extended operating voltage of the combined capacitor comes from a combination of positive stability of the $Co(OH)_2$ electrode and negative stability of the ACF electrode.

The DC charge/discharge test was carried out to in-

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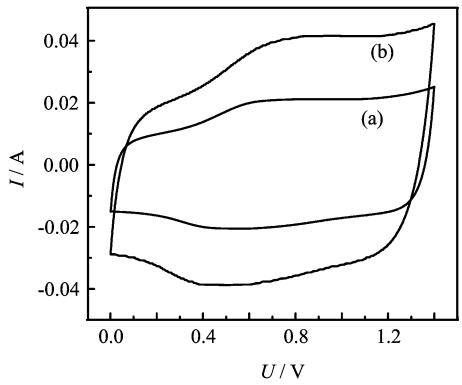

FIG. 6 CV of combined capacitor with scan rate of (a) 20 mV/s and (b) 40 mV/s.

vestigate the performance of the composite/ACF combined capacitor as an electrochemical capacitor. Figure 7 is a representative charge/discharge voltage profile of the combined capacitor at a current density of 10 mA/cm^2. The voltage increases and decreases almost linearly with time between 0 and 1.4 V.

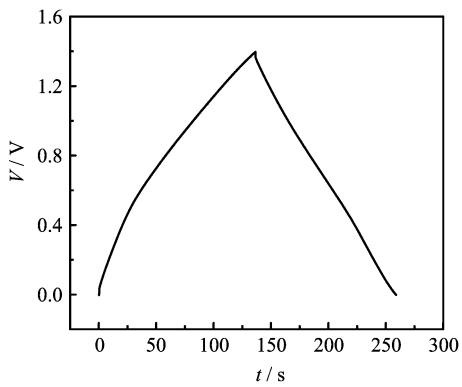

FIG. 7 DC charge/discharge voltage profile of combined capacitor at 10 mA/cm^2.

The specific capacitance of the combined capacitor can be evaluated from the charge/discharge test together with the following equation.

$$C = \frac{I\Delta t}{\Delta V} \tag{5}$$

where C is the capacitance in Farads (F); I is the discharge current in ampere (A); and Δt is the time period in seconds for the potential change ΔV, in volts. By comparing the linearity of the voltage change with respect to time during the discharge period, the capacitance C was calculated by the potential change from 0 V to 1.4 V. The specific capacitance of the combined capacitor was calculated as 47 F/g at 10 mA/cm^2 current density. In turn, one can also calculate the energy density of this system as using the following equation

$$E = \frac{1}{2}C_s V^2 \tag{6}$$

where C_s and V are specific capacitance (F/g) and operating voltage, respectively. The energy density of the combined capacitor was found to be 12.7 Wh/kg at 10 mA/cm^2. This value is superior to the energy density of an ACF-based double layer capacitor.

Figure 8 shows the specific capacitance of the cell as a function of charge/discharge current density for (a) ACF-based EDLC, (b) the combined supercapacitor and (c) ECs composed of two identical composite electrodes. Although the capacitance of the ACF is lower compared with the pseudocapacitance of the composite, the ACF-based EDLC showed better power characteristics between 10 and 100 mA/cm^2 current density (line (a)). From line (a) and line (b) in Fig.8, it is known that the specific capacitance of an ACF-based EDLC cell is enhanced by changing the anode from ACF to $Co(OH)_2$/CNTs. For the combined capacitor, the maximum specific capacitance of 47 F/g was obtained by dividing the unit cell capacitance by the total mass of two electrodes (active material: including CNTs, $Co(OH)_2$ and ACF). The value was almost 1.3 times that obtained from the ACF-based cell. On one hand, we can see that the power characteristics of the combined cell were decreased very slightly with increasing of discharging current density (line (b)). On the other hand, the combined capacitor exhibited much more stable power characteristic compared with the cell composed of two identical composite electrodes (line (c)). The specific capacitance and energy density of the combined capacitor was found to be 41 F/g and 11 Wh/kg at a current density of 100 mA/cm^2, respectively. It is obvious that the combined capacitor exhibits high-energy density and stable power characteristics simultaneously.

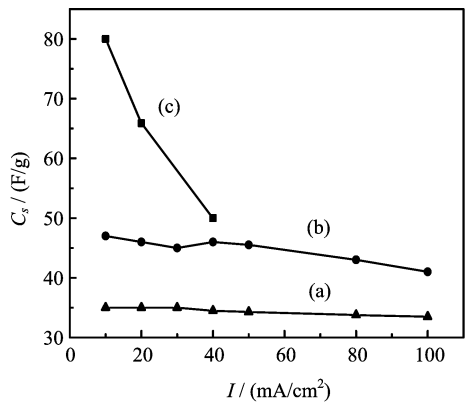

FIG. 8 Specific capacitances of the cells as a function of current density (a) [+ACF/KOH/ACF$^-$], (b) [+CoOOH /KOH/ACF$^-$] and (c) [+CoOOH/KOH/$Co(OH)_2{}^-$].

IV. CONCLUSION

A $Co(OH)_2$/CNTs nanocompostite electrode was introduced to improve the specific capacitance of the supercapacitor by combining the electric double layer and

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faradic redox reaction. Compared with pure cobalt hydroxide, the nanocomposite shows high specific capacitance and low impedance. The high specific capacitance of the composite is due to the fact that the CNTs were uniformly covered with cobalt hydroxide particles, and the CNTs increased the number of active sites on the cobalt hydroxide particles. The introduction of CNTs in cobalt hydroxide increased the capacitance by reducing the internal resistance of the electrode. We also have introduced a new electrochemical capacitor, the composite/ACF combined capacitor with an operating voltage of 1.4 V, high energy density, high power density and excellent stability. The energy at a current density of 100 mA/cm^2 was found to be 11 Wh/kg. It should also be noted that the combined capacitor delivers high power without profound loss in energy as compared to the composite/composite capacitor.

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