

# 电化学阴极沉积制备氧化镍/碳纳米管 复合电极的准电容特性

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**摘要:** 采用催化裂解的方法制备了碳纳米管,其比容量为 12 F/g. 采用碳纳米管作为电极基体,采用阴极电化学还原  $\text{Ni}(\text{NO}_3)_2$  的方法在碳纳米管基体表面均匀的沉积了纳米氧化镍颗粒并由此制备了氧化镍碳纳米管复合电极材料. 采用循环伏安、恒流充放电、交流阻抗及扫描电镜等方法考察了复合电极材料的容量特性、阻抗特性、自放电特性以及电极表现特征. 实验表明复合电极具有良好的电化学特性,碳纳米管基体在明显降低氧化镍材料的阻抗的同时还提高了电极材料的电化学容量并拓宽了电极材料的有效工作电位窗,复合电极在 6 mol/L KOH 电解液中比容量达到 25 F/g 且表现了良好的电化学可逆性. 与碳纳米管基电容器相比,采用氧化镍复合电极材料组装的电容器具有较低的自放电率.

**关键词:** 氧化镍; 碳纳米管; 超电容器; 纳米复合电极; 阴极沉积

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## Pseudocapacitive Behavior of Nickel Oxide/Carbon Nanotubes Composite Prepared by Cathodic Deposition

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**Abstract** A novel type of composite electrode based on multiwalled carbon nanotubes coated with nano nickel oxide particles has been used in supercapacitors. Nickel oxide cathodically deposited from  $\text{Ni}(\text{NO}_3)_2$  solution with carbon nanotubes as the matrix exhibited large pseudocapacitance of 25F/g in 6 mol/L KOH. The morphology of composites was examined by scanning electron microscope (SEM). To characterize the CNTs/nickel oxide composite electrode, a charge-discharge cycling test for measuring specific capacitance, cyclic voltammetry, and ac impedance test is executed. The nickel oxide composite exhibiting excellent pseudocapacitive behavior (i. e. high reversibility, high specific capacitance, and low self-discharge rate) has been demonstrated to be a potential candidate for the application of electrochemical supercapacitors.

**Key words** Nickel oxide, Carbon nanotubes, Supercapacitor, Nanocomposite electrode, Cathodic deposition

### 1 Introduction

Electrochemical capacitors (hereafter ECs) have

greater power density than usual batteries and can be deeply discharged without any deleterious effect on life time<sup>[1]</sup>. Compared to dielectric capacitors, ECs have

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greater energy density<sup>[2]</sup>. Carbon in various modifications is the electrode material used most frequently for electrodes of electrochemical capacitors. Reasons for using carbon are manifold such as (i) low cost, (ii) high surface area, (iii) availability, and last but not least (iv) established electrode production technologies. Carbons are available with a specific surface area of up to  $2.5 \times 10^3 \text{ m}^2/\text{g}$  as powders, woven cloths, felts, or fibers. The charge storage on carbon electrodes is predominantly capacitive in the electrochemical double layer. Carbon based electrochemical capacitors come close to what one would call an electrochemical double layer capacitor. There are however contributions from surface functional groups which are in general present on activated carbons and which can be charged and discharged giving rise to pseudo-capacitance.

The 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 material<sup>[3]</sup>. However, the high material cost of  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  and low porosity which causes depletion of the electrolyte adsorbed on the electrode as well as the rapid decrease of power density observed at high charge/discharge rates makes this material inadequate for commercial applications<sup>[4]</sup>. Therefore, in recent years, great efforts were undertaken in order to find new and cheaper materials. Nickel oxides prepared by the sol-gel<sup>[5]</sup>, electrochemical<sup>[6]</sup> or other techniques<sup>[7]</sup> have been proposed to be suitable materials for the application of EC supercapacitors. sol-gel derived  $\text{Ni}_x\text{O}/\text{Ni}$  thin film electrodes or nickel oxide prepared in electrochemical route calcined at  $300 \text{ }^\circ\text{C}$  provide a specific capacitance of 40 to 65 F/g as a whole cell capacitance<sup>[5]</sup>. These materials show high pseudocapacitance. However, the difference between potentials of discharged electrode and charged electrode is not significant (about 400 mV for nickel oxide) in contrast to carbon based double layer capacitors possessing wide window of potentials (more than 1V)<sup>[5-7]</sup>. Moreover, the conductivity of the oxide is not so good as some carbon material such as carbon black. So the performance of pure pseudocapacious

systems based on nickel oxide is poor.

Carbon nanotubes (CNTs) were discovered in 1991<sup>[8]</sup>. Their high accessible surface area, low resistance and high stability<sup>[9-11]</sup> suggest that carbon nanotubes are suitable materials for electrodes in electrochemical double layer supercapacitors, which are being studied extensively in laboratory<sup>[12-14]</sup>. In these papers, the supercapacitors using carbon nanotubes electrode with a maximum specific capacitance of 12 F/g in a solution of 6 mol/L KOH have been reported. It is found that the specific capacitance of supercapacitors using CNTs electrode is still smaller than that of supercapacitors using activated carbons and activated carbon fibers. Therefore, it is necessary to improve the capacitance of CNTs for practical applications. We report here the nanocomposite of CNTs and nickel oxide for supercapacitors with high capacitance. The electrochemical reversibility of hydrous nickel oxide is improved by the introduction of carbon nanotubes matrix in the nickel oxide. The purpose of this work is to present suitable operating procedures for fabricating an amorphous hydrous nickel oxide/CNTs deposit with ideally pseudocapacitive behavior (i.e. high reversibility, high specific capacitance, and low self discharge rate property) for ECs.

## 2 Experimental

### 2.1 The preparation of carbon nanotubes and the CNTs electrode base for the supercapacitor

Carbon nanotubes were produced catalytically with Ni particles as the catalyst<sup>[15]</sup>. In a pipe stove, with reagent based on Ni and ethylene gas, raw multi-walled carbon nanotubes were produced at  $700 \text{ }^\circ\text{C}$ . These nanotubes contained many impurities, such as  $\text{SiO}_2$ , Al, Ni, etc., which must be eliminated. First, all the as-prepared carbon nanotubes were put into 20% hydrofluoric acid for 5 h and were then filtered. Second, they were put into 22% nitric acid for 10 h and then washed in distilled water several times, until the pH of the carbon nanotube solution approached 7. Finally, having been dried, carbon nanotubes of 98% purity were obtained.

The polarizable CNTs electrode can be manufactured using the carbonaceous material according to the invention by any conventional method known in the art<sup>[16]</sup>. Thus, 95% carbon nanotubes, 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 disks in 1 cm × 1 cm dimension. The disk electrodes were then mounted on a Ni foam-current collector. The CNTs electrode base for deposition of nickel oxide was prepared in this way.

## 2.2 The preparation of nano nickel oxide and CNTs/nickel oxide by electrochemical cathodic deposition

The nano nickel oxide was deposited electrochemically onto a 1 cm<sup>2</sup> bare nickel substrate and a CNTs/Ni base prepared above. The nano nickel oxide and composite electrode here were deposited at room temperature in a bath containing 1.8 mol/L Ni (NO<sub>3</sub>)<sub>2</sub> and 0.075 mol/L NaNO<sub>3</sub> in a solvent of 50% volume percent ethanol using a cathodic current density of 20 mA/cm<sup>2</sup>. The deposition needs 2 h. The weight of the nickel oxide deposited and CNTs/nickel nanocomposite prepared can be estimated by subtracting the mass of nickel substrate or nickel current from the total mass of the electrode. The deposited electrode was washed in deionized water and heated in air at 100 °C for 2 h.

## 2.3 Electrochemical test of performance for composite electrodes and composite based supercapacitor

Two test cells were introduced in this paper. A beaker-type electrochemical cell equipped with a working electrode, a platinum counter electrode and an SCE reference electrode were used. The electrodes were simply dipped into the 6 mol/L KOH. The geometric surface area of the working electrode was 1 cm<sup>2</sup>. The cyclic voltammograms presented in this paper were steady state ones after repeated potential sweeps. The electrochemically active surface area included both the charge of the electrical double layer and that of the redox of the metal species i. e. it reflected the pseudo-

capacitance of the electrodes. These were connected to the CHI 608A system which drove the voltage in either direction sequentially at predetermined constant sweep rates. The sweep rates range of 20 mV/s was used during testing.

Another cell was much more characteristic of an actual working device. The CNTs/nickel oxide anode and cathode were pressed together and separated by a porous non woven cloth separator. The cells were tested either by discharging through a fixed resistance in the conventional manner ( here one can see an exponential decay in voltage caused mainly by resistance of the cell ). The charge/discharge measurements at constant current were carried out in an Arbin cycler. A range of constant current from 20 mA to 160 mA was used. The capacitance of the cell was obtained from equation(1)

$$C = \frac{I\Delta t}{\Delta V} \quad (1)$$

where  $C$  is the capacitance in Farads (F) ;  $I$  is the discharge current in ampere (A) ;  $\Delta t$  is the time period in seconds for the potential change  $\Delta V$ , 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 to 1.4 V.

## 3 Results and Discussion

Fig. 1 shows the scanning electron microscope image of multi-wall carbon nanotubes prepared. The carbon nanotubes are randomly entangled and cross-linked. The nanotubes have a diameter of 15 to 50 nm and length of several microns to several tens of microns. From Fig. 2, one can see that the pure nickel oxide prepared with electrochemical deposition shows a typical nano scale and porous characteristic. The size of the pure nickel oxide particles prepared here is about 20 – 30 nm. Fig. 3 is the SEM of the CNTs/nickel oxide composite prepared after 2 h electrochemically cathodic deposition. The Fig. 4 reveals the individual nanotube bundles to be coated with nano nickel oxide particles indicating that *in situ* electrochemical deposition of the nickel oxide is

effectively achieved. Compared to the as grown carbon nanotubes, the CNTs coated by nickel oxide are very thick. The carbon nanotubes build up the network of the CNTs/nickel oxide nanocomposite electrode due to the long and entangled individual CNTs. This network of CNTs plays an important role as a pathway of electron transfer accumulated during charging and discharging process in the electrode of supercapacitor

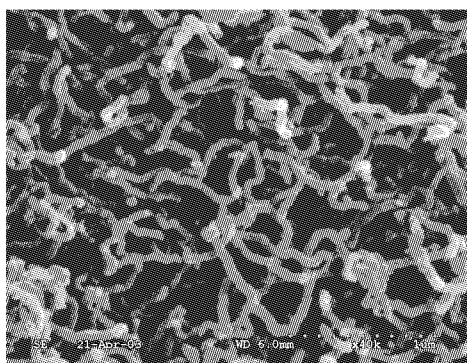


Fig.1 SEM image of carbon nanotubes prepared with Ni particles catalyst

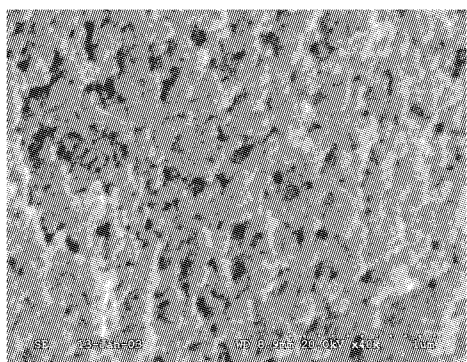


Fig.2 SEM image of nickel oxide particles prepared in cathodic deposition

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 voltammograms on the carbon nanotubes and CNTs-hydroxide nanocomposite electrodes are performed to investigate the possible dominant mode of electrochemical energy storage on the three electrodes. Fig. 4 shows the CV curve of the CNTs-based electrode in the KOH electrolyte at scan rate of 20 mV/s. The charging and discharging cyclic voltammogram CV is

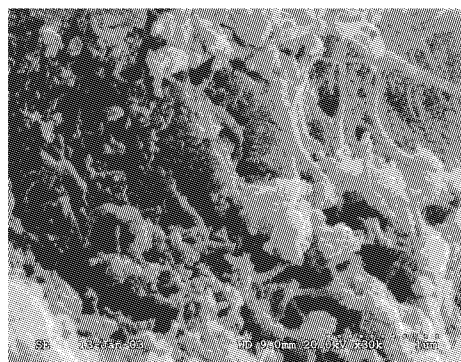


Fig.3 SEM image of CNTs/nickel oxide nano-composite prepared in electrochemical deposition

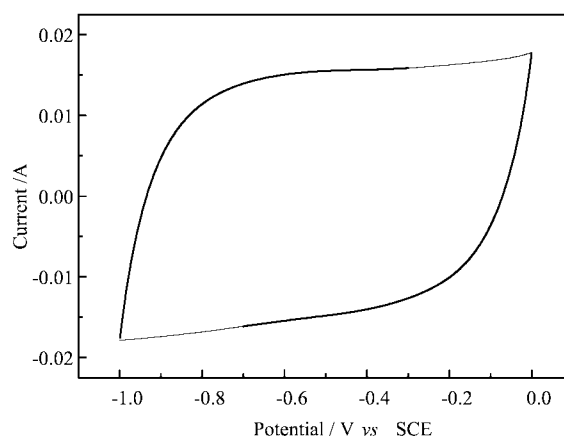


Fig.4 Cyclic voltammetric behaviour of carbon nanotubes electrode in 6 mol/L KOH

close to a rectangular shape, indicating a typical electric double layer EDLC behavior because no peaks of oxidation and reduction are observed. From integrating the CV curve, the CNTs electrode shows about 12 F/g specific capacitance as a whole cell capacitance.

Figure 6 and Figure 7 present the cyclic voltammetric behaviors of pure nickel oxide, and nanocomposite electrodes at a sweep rate of 20 mV/s respectively. The pure Nickel oxide electrode clearly shows faradaic redox reactions, which are observed at 0.5 and 0.1 V with respect to the SCE reference electrode representing oxidation and reduction processes. The nanocomposite electrode shows a shape exhibiting the both characteristic of CNTs and pure nickel oxide electrode basically. The cycling voltammogram of the composite has the distinct faradaic redox behavior at high potential. However, the redox

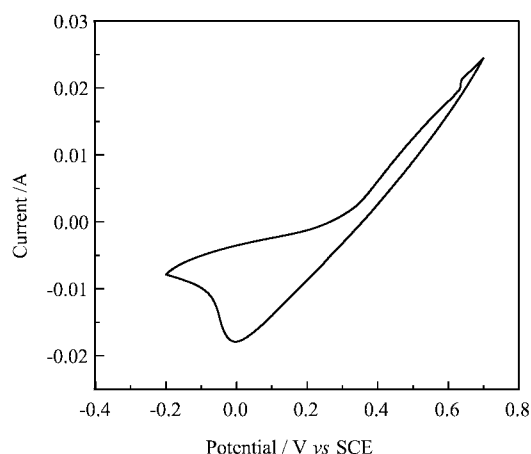


Fig. 5 Cyclic voltammetric behaviour of pure nickel oxide electrode in 6 mol/L KOH

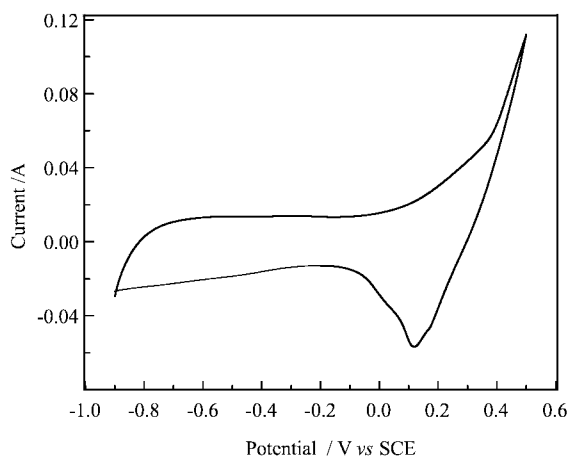


Fig. 6 Cyclic voltammetric behaviour of nano composite electrode in 6 mol/L KOH

current of the CNTs/nickel oxide nanocomposite electrode is about two times higher than that of the pure nickel oxide. Furthermore, the usable potential window of nanocomposite electrode is much wider than that of the pure nickel oxide electrode. The capacitive behaviors are observed at a wide range of voltage. Consequently, the electrochemical capacitance scale of composite is much larger than that of the individual materials. We can say from the CV curves that the CNTs/ Nickel oxide composite electrode shows the characteristics of a pseudocapacitive electrode and a double layer capacitive electrode simultaneously. This higher current scope for the Nickel oxide nanocomposite electrode arises from the uniformly deposition of nickel oxide on the carbon nanotubes

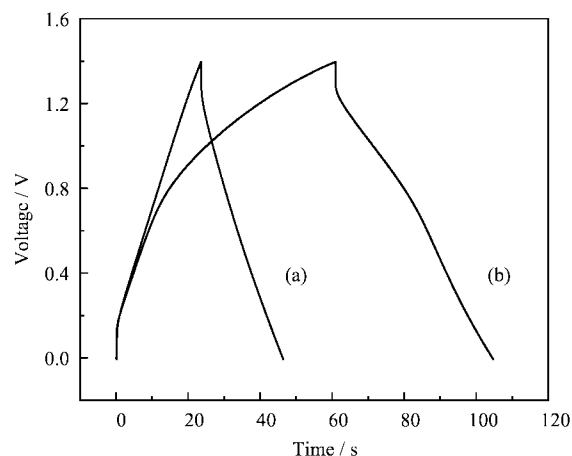


Fig. 7 Dc charge/discharge voltage profile at 20 mA/cm<sup>2</sup> of CNTs based capacitor and nanocomposite based capacitor in 6 mol/L KOH aqueous electrolyte  
a. CNTs based capacitor, b. Nanocomposite based capacitor.

which increase effectively the active sites on the roxide particles. The effective surface area of the nickel oxide surrounded by carbon nanotubes is enhanced distinctly in the nanocomposite in comparison to the pure nickel oxide electrode, as mentioned previously. Further, Carbon nanotubes also serve as an electrolyte reservoir to reduce ionic diffusion resistance regardless of 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.

Typical chronopotentiograms of the CNTs/ nickel oxide composite electrode measured in 6 mol/L KOH at a constant current of 20 mA/cm<sup>2</sup> between 0 and 1.4 V are shown in Fig. 7. Note the high capacitance of the cell when the measured potential is above the 0.8 V, indicating the presence of a pseudocapacitance of the nickel oxide in this potential range. This phenomenon again is attributed to the faradaic nature of the reaction. On the other hand, when the potential window is located in the range of 0 ~ 0.8 V, the mean capacitance of the nickel oxide/CNTs composite electrode is larger than that of carbon nanotubes. Moreover, symmetric responses in the same potential range during both anodic charging and cathodic discharging processes are found between 0 and 1.4 V, although the perfect linear curves are not obtained

compared with the case of EDLCs on curve (a) in Fig. 7. The above results further support the statement that nanocomposite exhibited reversible characteristics in the potential region prior to the oxygen evolution reaction. Based on the Eq. (1), the average specific capacitance of 25 F/g is obtained over the whole potential range by dividing the unit cell capacitance by the total mass of both electrode active materials (nickel oxide + CNTs + binder). This larger pseudocapacitance indicates that the nickel oxide nanocomposite prepared by cathodic deposition is a potential candidate for EC supercapacitor. Fig. 8 – 10 presents the complex-plane plots for the CNTs, pure nickel oxide and nickel oxide/CNTs nanocomposite. The CNTs shows much lower impedance than the pure nickel oxide and nanocomposite electrode. The impedance spectra of the pure nickel oxide 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 nickel oxide is very large and the resistance increase notably at a higher electrode potential of 0.5 V (Fig. 9), which will result in the serious deterioration of the capacitance at high discharge current. Although the internal resistance of the CNTs/nickel oxide 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 nickel oxide. It can be seen from the Fig. 10 that the resistance of the

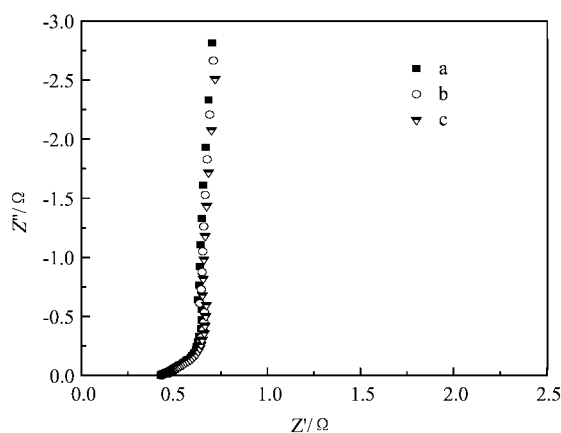


Fig. 8 The complex-plane impedance plots at ac amplitude of 5 mV for carbon nanotubes electrode  
The potential of electrode: a. 0 V, b. 0.5 V, c. 1 V.

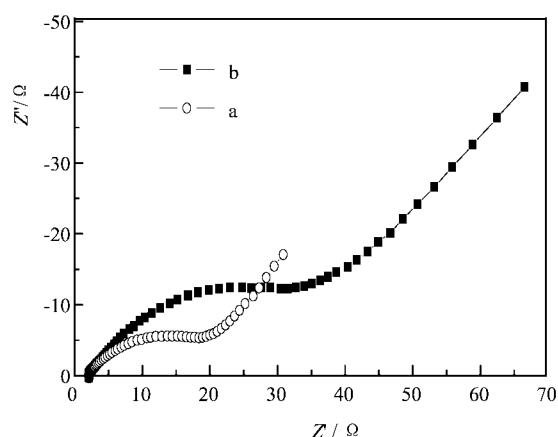


Fig. 9 The complex-plane impedance plots at ac amplitude of 5 mV for pure nickel oxide electrode  
The potential of electrode: a. 0 V, b. 0.5 V.

nanocomposite electrode is still very low even when the electrode potential is increased to 1.0 V. With the introduction of the carbon nanotubes into the nickel oxide, the phase angle of  $\tan(R_{\text{imag}}/R_{\text{real}})$  at the low frequency region is close to  $90^\circ$ , indicating a significant reduction of the internal resistance in the CNTs/nickel oxide nanocomposite electrode. All these data suggest that the carbon nanotubes obviously affect the specific capacitance and internal resistance in the composite electrode.

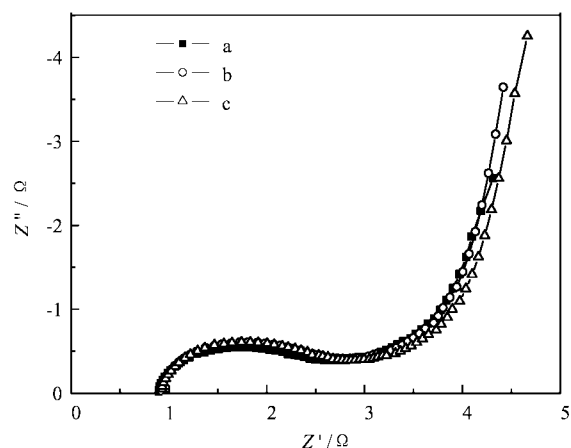


Fig. 10 The complex-plane impedance plots at ac amplitude of 5 mV for nanocomposite electrode  
The potential of electrode: a. 0 V, b. 0.5 V, c. 1 V.

The phenomenon of self-discharge of an electrochemical capacitor diminishes its performance characteristics (eg, power and energy density)

because there is a decline in voltage on open circuit after charging. This introduces an unreliability factor in energy storage by a capacitor, depending on the type of use to which it is put. The self-discharge characteristics of a capacitor device are important in evaluating its performance and commercial specifications. The CNTs and nanocomposite based capacitor were charged to 1 V and held at that voltage for 120 s, and then disconnected from the tester. The voltage of the device was then measured for 20 h as it self-discharged. The form of the potential decline on self-discharge over time in hours is shown in Fig. 11. The CNTs based capacitor shows the poor self-discharge characteristic: open potential of the capacitor dropped to 0.55 V within the period of 10 h. Compared with CNTs based capacitor, the nanocomposite based capacitor exhibits very favorable self-discharge characteristic. It is evident that the open potential of the nanocomposite based capacitor remains up to 0.8 V even after 16 h. The application of the CNTs/nickel oxide nanocomposite based electrochemical supercapacitor involves the use for standby power or photo-flash purposes where a low rate of self-discharge is desirable.

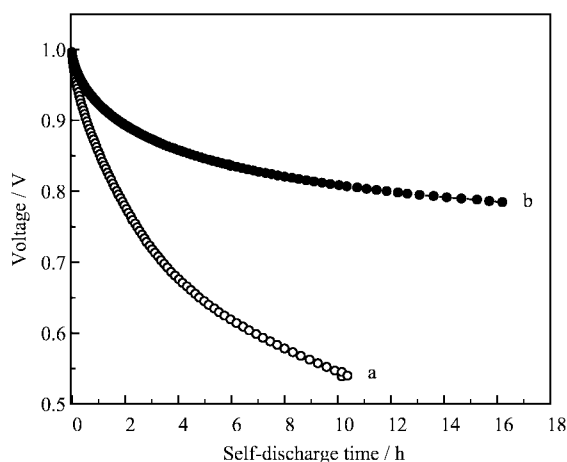


Fig. 11 The open-circuit potential decay of CNTs based and nanocomposite based supercapacitor over times  
a. The open-circuit potential of CNTs based capacitor,  
b. The open-circuit potential of nanocomposite based capacitor.

## 4 Conclusion

The CNTs/nickel oxide nanocomposite electrode

was introduced to improve the specific capacitance of the supercapacitor by combining the electric double layer and faradic redox reaction. Compared with pure nickel oxide and carbon nanotubes, the nanocomposite shows high specific capacitance. The high specific capacitance of the composite is due to the fact that the carbon nanotubes are uniformly covered with nano nickel oxide, and the carbon nanotubes increase the active sites on the nickel oxide particles. The introduction of carbon nanotubes in nickel oxide increased the capacitance by reducing the internal resistance of the electrode. The nanocomposite based capacitor exhibited very favorable self-discharge characteristic compared with the cell based on pure carbon nanotubes.

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