Materials

Electrochemical performance of nickel oxide/KOH/active carbon super-capacitor

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Abstract: The fabrication and characterization of new type Nickel oxide/KOH/Active carbon super-capacitor have been described. Porous nickel oxide was prepared by hydrolysis of nickel acetate and heated in air at 300 °C. The resulting nickel oxide behaved as an electrochemical capacitor electrode with a specific capacitance (50-70 F/g) superior to most active carbon electrodes. This kind of nickel oxide maintained high utilization at high rate of discharge (*i.e.*, high power density) and had excellent cycle life more than 1 000 times, while the capacitance of the cell composed of two identical nickel oxide electrodes was poor at high discharge current density and the maximum operational voltage of this type capacitor was limited to 0.5 V. A new type super-capacitor was designed in which the nickel oxide and the active carbon were applied to the positive and negative electrodes respectively. The breakdown voltage of this type super-capacitor was improved effectively to 0.8 V and excellent characteristic of high power discharge was attained in this way. The Nickel oxide/KOH/Active carbon super-capacitor has promising potentials in portable telecommunications, uninterruptable power supplies and battery load leveling applications.

Key words: nickel oxide; active carbon; super-capacitor; pseudo-capacitance

1 Introduction

Electrochemical capacitors have promising potentials in portable telecommunications, uninterruptable power supplies, and battery load leveling applications. For these applications, high energy density and high power density are required. Two types of electrochemical capacitors may be considered for these applications: ultra-capacitors and super-capacitors.

The electrochemical "ultra-capacitors" store charge electrostatically in the electric double layer at the surface of porous carbon electrodes in either aqueous or nonaqueous electrolytes. This type of electrochemical capacitor has been known for over 40 years. Its energy density is fundamentally limited by the surface areas of the carbon electrodes.

Electrochemical "super-capacitors ", on the other hand, store charge *via* topotactic insertion reactions into oxide. The super-capacitors store charge three-dimensionally as solid solutions of ions in the bulk crystal structure of the host lattice. A change in oxidation state (of the host cation) takes place to compensate the charge of ion as it enters/exits the lattice. This process is also known as "redox pseudo-capacitance"[1, 2] and

it can accommodate a much higher volumetric energy density than it is possible with carbon ultra-capacitors.

Initially, super-capacitors utilized crystalline RuO_2 or IrO_2 electrodes in aqueous acidic electrolytes. However, the diffusion of protons into crystalline RuO_2 and IrO_2 is kinetically slow and only the surface unit cells accommodate the protons during the typically fast charge /discharge cycles which are characteristic of super-capacitor applications. In these early super-capacitors, the capacitance was proportional (kinetically) to the surface area of the oxide electrodes. Recently, however, Jow and Zheng [3, 4] have overcome this diffusion limitation of the proton insertion reaction by utilizing amorphous hydrated ruthenium oxide electrodes. The open structure of the amorphous $RuO_2 \cdot xH_2O$ permits the fast diffusion of protons and allows for the volumetric utilization of RuO_2. A concomitant 2-fold improvement of the gravimetric energy density is achieved with this new material. The cost of ruthenium, however, limited the widespread utilization of this technology.

Conway has pointed out that other nonprecious metal oxides also exhibit redox pseudo-capacitance [1]. These materials include Co_3O_4 [5], MoN_2 [6]. Certain

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polymers [7] and sulfides also exhibit redox pseudo-capacitance. Liu and Anderson have attempted to utilize NiO_x as super-capacitor electrodes [8], Passerini et al. propose V_2O_5 aerogel electrodes and Fauteux et al. propose to use $LiMn_2O_4$ and $LiCoO_2$. However, none of these alternate materials has been developed into commercial super-capacitor.

In contradistinction to RuOx capacitors possessing wide window of potentials in anode and cathode areas, the difference between potentials of discharged electrode—$Ni(OH)_2$ and charged electrode—NiOOH is not significant (~100-200 mV). Thus, it's not expediently to create "pure" pseudo-capacious systems, such as $[+NiOOH/KOH/Ni(OH)_2-]$. On the other hand, while using NiO_x electrode in low changeable window of potential of charge, the window of potential change of the second electrode can be widened if carbon electrode e. g. capacity of double electric layer is used. This electrochemical system can be written as [+NiOOH/KOH/ C−]. The charge principle of NiO_x is based on charge transferring throughout the interface of phase. During the charge process of negative carbon electrode, a double electric layer is being created. The electrodes in the system are notable for their reversibility. The discharge process for this new type super-capacitor is a process of protonization of crystal grid NiOOH and destruction of layer of hydrated ions on a negative carbon electrode.

The study of combined system "Double layer capacitance-Pseudo-capacitance" and the designing and testing of capacitors based on the principle mentioned above are descriped in detail in this paper .

2 Experimental

2.1 Preparation methods of nickel oxide electrode

The nickel oxide/nickel composite was prepared from nickel acetate in the way described by Liu [4]. Nickel acetate tetrahydrate was dehydrated at (100 ± 10) ℃ for more than 6 h,about 10 g of this dehydrated powder was added to 100 mL distilled water and stirred for about one day. The precipitate was separated by centrifugation and resuspended in water with the volume ratio 1 ：1. This fresh opaque solution was used to make sample on 0.3 mm porous nickel foil by dripping with a burette. The area of electrode is about 0.3 cm in diameter. The film was fired at 300 ℃ for about 100 min with different ramp rate and allowed to cool for additional 5 h. The amount of material can be controlled flexibly in this way. The amount of active material coated on the foil was obtained by subtracting the mass of clean foil from the mass of fired sample.

2.2 Preparation methods of active carbon electrode

The approaches to forming a porous active carbon material involve two steps-chemical activation techniques and physical activation techniques in turn. The petroleum coke was immersed in KOH melt and kept at 400 ℃ for about 3 h in inert N_2 atmosphere. The ratio of the melt was 1 ：3. Then the melt temperature was kept at 900 ℃ for about 2 h with a ramp rate of 5 ℃/min and stirred vigorously. The product of chemical activation techniques was washed with distilled water and then maintained at 900 ℃ for 2 h under water vapor flow. The specific surface of the active carbon prepared in this way was about 1500 m^2/g. The active carbon electrode was made by mixing active carbon powder with 5% Teflon binder and 20% carbon black and then rolling out a film with a thickness of 100-200 μm. The film was pressed on porous nickel collector under pressure of 10 MPa. The electrode was dried in vacuum at 80 ℃ for about 4 h finally.

## 2.3 Capacitance measurements of NiO_x/KOH/NiO_x test super-capacitor

Heated NiO_x samples were characterized electrochemically in a 1 mol/L KOH solution using an Ag/AgCl reference electrode. A platinum grid was used as counter electrode. The size of the counter electrode was about 100 times larger than that of working electrode. Cyclic voltammetry was conducted on the samples using an EG&G M 273 potentiostat/galvanostat. The average capacitance of the nickel oxide samples was estimated from cyclic voltammetry. The specific capacitance can be calculated from cyclic voltammetry curves by $C = i/s$, where i and s are current response at 0.2 V(vs Ag/AgCl) and the potential sweep rate (dv/dt) respectively.

Two electrodes fixed in a parallel position were immersed in 1 mol/L KOH solutions. An Arbin battery testing system was used to recorder the capacity of this cell at different discharge current, the specific energy of the capacitor was obtained from the following equation:

$$E = \frac{1}{2}CV^2 \qquad\qquad (1)$$

2.4. Capacitor design of NiO_x/KOH/Active carbon super-capacitor

Figure 1 shows the structure of the cell designed for the measurement of capacitance of the NiO_x/KOH/Active carbon super-capacitor. The NiO_x electrode and active carbon electrode were pre-wetted by back filling 1 mol/L KOH alkaline solution in vacuum. Two different electrodes were separated by a porous paper separator with thickness of 100 μm. The porous membrane was
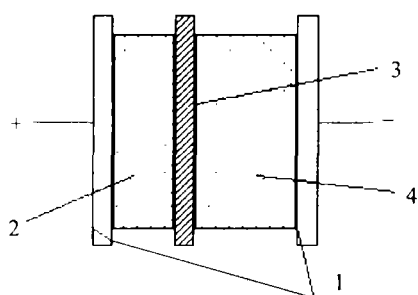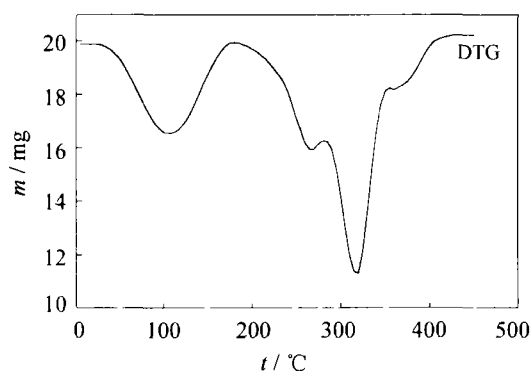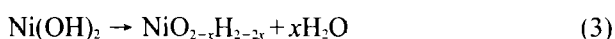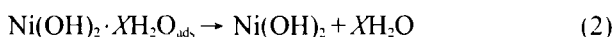
Figure 1 Cross section of the NiO$_x$/KOH/ carbon capacitor, 1 —porous nickel collector; 2—NiO$_x$ electrode; 3—paper separator; 4—plarizable electrode, activated carbon.

impregnated in 1 mol/L KOH alkaline solution. The capacitance of the active carbon in anode is in excess of NiO$_x$ capacitance used in the cathode for the convenience of test of NiO$_x$ capacitance. The capacitor was tested by discharge at different values of current on Arbin Instrument for super-capacitors.

3 Results and discussion

Thermogravimetric analysis (figure 2) was conducted on nickel hydroxide. About 50% of the mass was lost when the sample was heated to 300 ℃. This behavior is attributed to the loss of hydration and absorbed water at 200 ℃ and further by the conversion of hydroxide to the oxide at about 300 ℃ according to reactions (2) and (3):

$$Ni(OH)_2 \cdot XH_2O_{ads} \rightarrow Ni(OH)_2 + XH_2O \tag{2}$$

$$Ni(OH)_2 \rightarrow NiO_{2-x}H_{2-2x} + xH_2O \tag{3}$$

Figure 2 Thermal analysis curve of nickel oxide samples.

The change in electrochemical response of the sample resulting from the loss of water at different temperatures is seen in figure 3. In this figure, reduction currents are positive. The anodic and cathodic peaks in cyclic voltammetry of nickel hydroxide freshly prepared correspond to oxidation and reduction of the material according to the reaction:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e \tag{4}$$
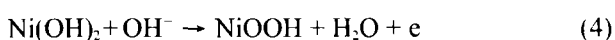
Heating the sample to 200 ℃ did not significantly affect the electrochemical response of the material which
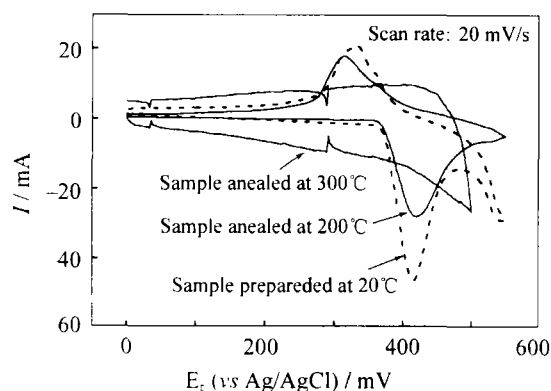

Figure 3 Cyclic voltammetry of NiO$_x$ treated at different temperatures.

was consistent with the statement that only absorbed water was lost when Ni(OH)$_2$ was heated to 200 ℃. In contrast, when the sample was heated to 300 ℃, a fundamentally new structure with significantly less capacity than the fresh sample was formed, the cyclic voltammogram reveal that the samples heated to 300 ℃ resembles a capacitor (figure 3). In figure 3, CV curve shows an approximately constant current response to the applied voltage in the range of 0-0.4 V vs Ag/AgCl. The redox reaction of nickel oxide is thought to be:

$$NiO_{2-x}H_{2-2x} + OH^- \rightarrow NiO_{3-x}H_{3-2x} + e \tag{5}$$
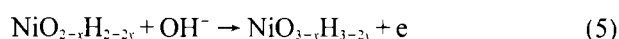
Figure 4 shows the average capacitance in the potential range of 0-0.4 V vs Ag/AgCl as a function of temperature exceeding 300 ℃. It can be seen that the capacitance decreases with temperature increasing. It is assumed that on increasing annealing temperature, more material become crystalline and the crystalline size increase (figure 5). At 300 ℃, the porous NiO$_x$ was formed. The capacitance is over 5 times larger than that of samples prepared at 500 ℃. This result clearly indicated that the Ni ions involved in the redox reaction with proton should not only from the surface but also from the bulk of the NiO$_x$ sample.
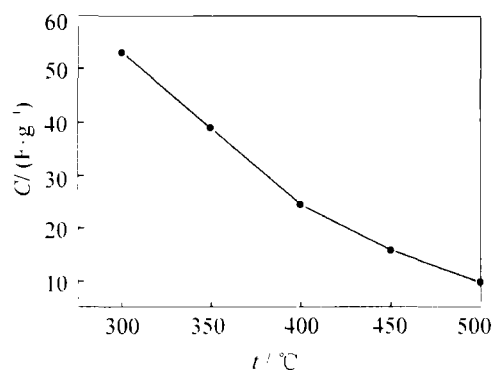
Figure 4 Effect of the calcination temperature on the capacitance of the sample.

According to the way described above, the average specific capacitance of a device consisting of two 1.5 mg nickel oxide electrodes is 50-70 F/g (i.e., excluding
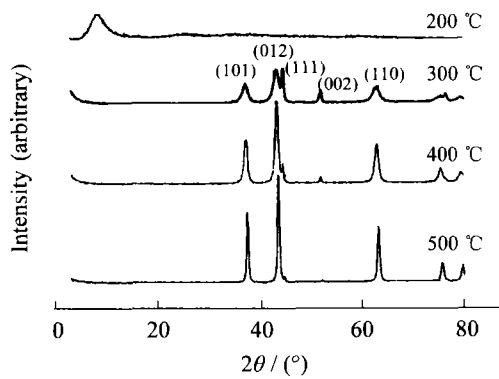
Figure 5 X-ray diffraction diagram of NiO$_x$ materials.

the mass of the electrolyte, current collector or device packing), the nickel oxide samples exhibit a specific capacitance superior to most activated carbon material. While the data in **table 1** demonstrate that the capacity of this type capacitor reduced unsatisfactorily at high current density. The capacitance of NiO$_x$ electrode at a current density of 0.3 A/g is only about 56% of that at low current densities. Moreover, the breakdown voltage of this type super-capacitor composed of two identical NiO$_x$ electrodes is only 0.5 V.

Table 1 The data of the tests for the NiO$_x$/KOH/ NiO$_x$ type super-capacitor

Discharge current/(A·g⁻¹)	Capacity for NiO$_x$ electrode/(F·g⁻¹)
0.030	64
0.150	50
0.300	36

Figure 6 shows the dc discharge characteristic of capacitor. The average capacitance could also be calculated by multiplying the current by the time duration of the discharge process and then dividing by the maximum applied voltage, the total energy store could be obtained by equation (1) where C and V are the capacitance and the maximum applied voltage, respectively. Here, it is assumed that the capacitance is independent of the voltage. The energy density of capacitor was calculated to be 35 kJ/kg at discharge current of 0.030 A/g
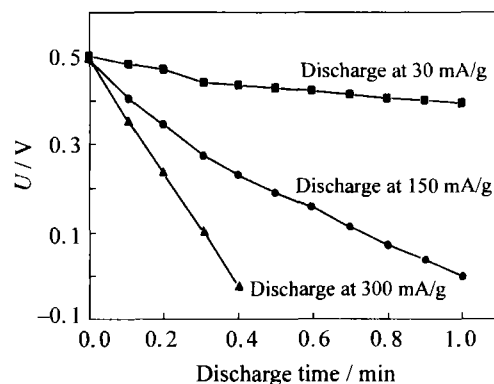

Figure 6 Discharge curve of NiO$_x$ super capacitor at different currents.

based on the NiO$_x$ material only.

In **figure 7**, the stability of NiO$_x$ as an electrode for capacitors was studied. The single cell capacitor was charged and discharged at constant current of 150 mA/ g. The capacitor was cycled about 1 000 times. The capacitance decayed 5% during the first 50 cycles and afterward the capacitance was much more stable and only decayed another 5% until the 1 000th cycle was measured. The efficiency of the capacitor was higher than 94% based on computing the charge/discharge time at a current of 0.15 A/g.
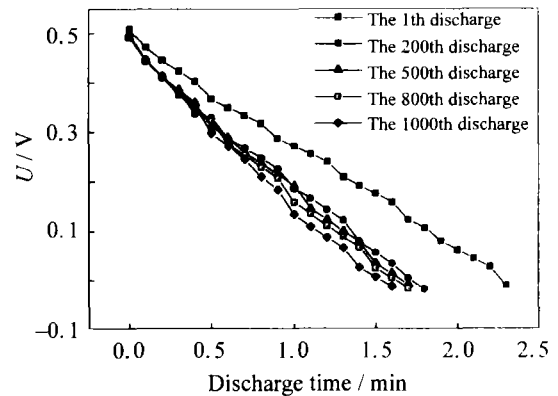

Figure 7 Stability and cycle life studies of the NiO$_x$ cell.

Existing need for super-capacitor possessing higher energy density and higher power density inspires world to create combined system "Double Electric Layer-Pseudo-capacity". The new type NiO$_x$/KOH/C super-capacitor combines the best features of both chemical battery and double layer capacitors by using a battery cathode and a double layer capacitor anode. The Cyclic votammogramms of the NiO$_x$ cathode and Carbon anode of this new type super-capacitor were displayed in **figure 8**. The super-capacitor employing an active carbon anode is able to withstand high breakdown voltages up to 0.8 V compared with 0.5 V for NiO$_x$/KOH/ NiO$_x$ type capacitor. **Figure 9** shows the dc charge/discharge characteristic of new type NiO$_x$/KOH/C super-capacitor. The discharge curves at different discharge currents are given in **figure 10**. The capacitance as a
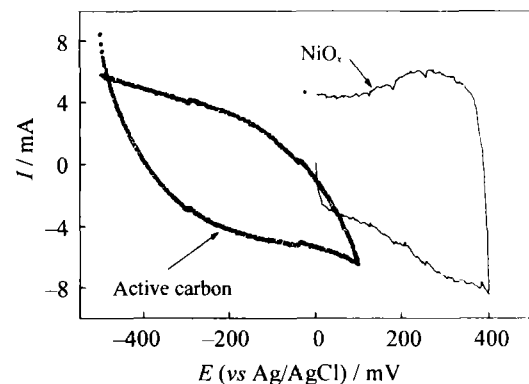

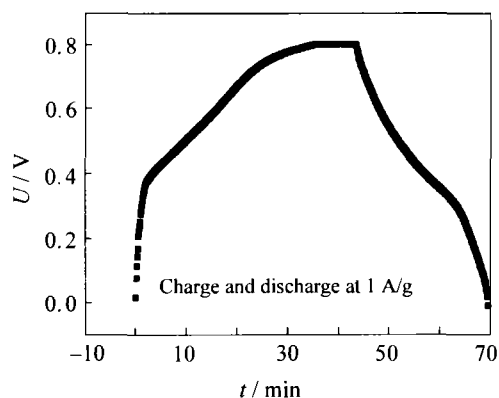**Figure 8 Cyclic votammogramms of the NiO$_x$/KOH/C super-capacitor.**

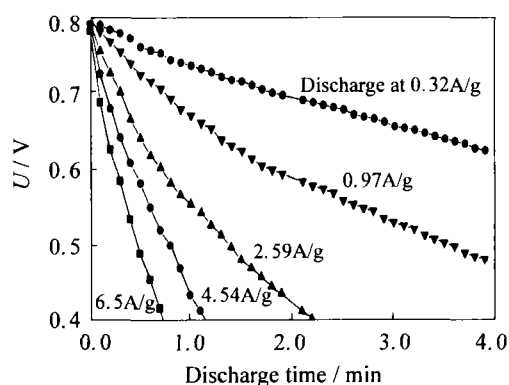**Figure 9 Charge / discharge curve of the NiO$_x$/KOH/C cell.**

Figure 10 Discharge curve of the NiO$_x$/KOH/C cell at different discharge currents.

function of current density was measured and generalized data of the tests are given in **table 2**. It can be seen that the capacitance reduced slightly at higher current densities. The capaci tance of NiO$_x$ electrode at a current density of 6.5 A/g was still about 72% of that at low current densities. The energy density of capacitor was calculated to be 140 kJ/kg at current density of 6.5 A/g based on the NiO$_x$ material only. The data demon-

Table 2 Generalized data of the tests for NiO$_x$/KOH/active carbon super-capacitor

Discharge current/(A·g^{-1})	Capacity for NiO$_x$ electrode/(F·g^{-1})
0.32	140
0.97	122
2.59	120
4.54	112
6.50	100

strates that the new type NiO$_x$/KOH/active carbon super-capacitor is capable of high power performance.

4 Conclusions

(1) A capacitor made with NiO$_x$ electrode and KOH electrolyte delivered a capacity of 50-70 F/g based on the NiO$_x$ only. About 1 000 charge /discharge cycles were achieved from NiO$_x$/KOH/NiO$_x$ super-capacitor.

(2) A new type super-capacitor composed of different electrodes could deliver a high capacitance at high power density.

(3) The breakdown voltage of 0.8 V was attained by use of active carbon as anode in this type super-capacitor. The new type Nickel oxide/KOH/Active carbon super-capacitor combines the best features of both chemical battery and double layer capacitors by using " double layer capacitance—pseudo-capacitance" system.

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