Effect of calcination methods on electrochemical performance of NiO used as electrode materials for supercapacitor

L WANG* and X Y QIN

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, 230031 Hefei, P. R. China

Abstract. Ni(OH)$_2$ precursors were prepared via the precipitation transformation method, which was originated from Na$_2$C$_2$O$_4$, NiSO$_4$·6H$_2$O and urea. NiO samples were successfully obtained by calcining Ni(OH)$_2$ precursor with different calcination methods. Some were calcination in a tube furnace under the nitrogen flow and others were calcination in a muffle furnace. The products were well-characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The influence of calcination methods on electrochemical performance of NiO samples were investigated. Moreover, the possible reason was proposed. The charge storage mechanism of NiO positive electrode in aqueous electrolyte was discussed. The electrochemical test showed that the as-prepared NiO prepared in a tube furnace can exhibit a good pseudocapacitance behaviour due to the higher utilization of active material.

Keywords. NiO; calcination methods; electrochemical performance; electrode materials; supercapacitor.

1. Introduction

Electrochemical capacitors (EC) have received great attention due to their high power capability, excellent reversibility and long cycle life (Conway 1991; Zhang *et al* 2009). Based on the different energy storage mechanism, EC could be classified into two categories: one is electric double-layer capacitors, mainly focusing on carbon materials with a high specific surface, whose capacitance arises from the charge separation at an electrode/electrolyte interface; The other is pseudocapacitors, mainly concentrating upon conducting metal oxides and polymers, which utilize the capacitance resulting from fast-faradaic redox reactions occurred within the active electrode materials (Chen *et al* 2008).

Nickel oxide (NiO), as an important functional material, has received an intensive attention recently due to their attractive applications in diverse fields, such as gas sensors (Lee *et al* 2007; Mattei *et al* 2007), magnetic materials (Parada and Morán 2006; He *et al* 2008; Kim *et al* 2010), catalysts (Park *et al* 2005), electrochromic films (Tenent *et al* 2010) and electrode materials (Wang *et al* 2006; Zheng *et al* 2009; Gillaspie *et al* 2010; Chai *et al* 2012). NiO has been extensively studied as a pseudocapacitor electrode material owing to its large surface area, high pseudocapacitance behaviour, and low cost with a good possibility of enhancing its performance by improving the preparative methods (Prasad and Miura 2004;

Zheng and Zhang 2007; Meher *et al* 2011). However, it is rarely discussed about the effect of calcination methods on electrochemical performance of NiO used as electrode materials for the supercapacitor.

This paper presents the results of an investigation into the effect of calcination methods on electrochemical performance of NiO used as electrode materials for supercapacitor. Two different calcination methods were studied and compared. In comparison with muffle furnace calcination, NiO obtained by tube furnace calcination showed the better electrochemical performance. And the possible reason was proposed.

2. Experimental

2.1 *Preparation of NiO*

All the chemicals were purchased and used as received without any purification. In a typical experiment, Na$_2$C$_2$O$_4$ (0·5 mol/L) was dipped into NiSO$_4$·6H$_2$O (0·25 mol/L) under vigorous stirring to get a green precipitate. The precipitate was aged in 70 °C water bath for 30 min, after that tween-80 was added under stirring for 30 min, followed by the addition of urea solution (1 mol/L). The above solution was placed in a 50 °C water bath for 1 h and then aged for 12 h. Ni(OH)$_2$ precursor was collected by filtration, washed with distilled water and absolute ethyl alcohol. The black powder NiO could be acquired by placing Ni(OH)$_2$ precursor in a tube furnace under the nitrogen flow (20 mL/min) with a linear heating rate

---

*Author for correspondence (wangling1172@126.com)

(5 °C/min) from room temperature to 450 °C for 2 h. In order to study the effects of calcination method, the other sample was obtained in muffle furnace at 450 °C for 2 h.

2.2 *Characterization*

Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 F1 thermogravimetric analyser with 40 mL/min of nitrogen flow from 50 to 550 °C at a heating rate 10 °C/min. Powder X-ray diffraction data were collected on a Rigaku D/MAX-rA diffractometer with CuKα radiation ($\lambda = 0.15418$ nm) being operated at 40 kV and 100 mA. The morphology and particle size were examined by the scanning electron microscope (SEM, JSM-5900LV, Japan).

2.3 *Electrochemical measurements*

Nickel oxide electrodes were prepared by pressing an active paste onto a nickel foam substrate. The paste contained 70 wt% as-obtained nickel oxide, 25 wt% acetylene black (AB) and 5 wt% polyvinylidene fluoride (PVDF), which were dissolved by *N*-methy-l-2-pyrrolidine (NMP). First, the paste was dried in vacuum at 60 °C for 12 h. Second, the active paste was pressed onto a nickel foam substrate that served as a current collector (surface was 1 cm^2) under a pressure of 20 MPa. Then NiO electrodes were dried in vacuum at 60 °C for 3 h. The charge/discharge test was performed with a two-electrode cell in which NiO electrode was used as positive electrode and a.c. electrode was used as negative electrode in 6 mol/L KOH aqueous solutions and it was carried out with Neware battery programme-control testing system. Cyclic voltammetry (CV) tests and electrochemical impedance spectra were performed with a three-electrode cell equipped with a working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE). CV tests were carried out with LK2005 electrochemical workstation system. The electrochemical impedance spectra (EIS) tests were performed with Potentiostat Galvanostat PGSTAT302 (The Netherlands) in 6 mol/L KOH aqueous solution. The frequency limits were set between 10 kHz and 0.05 Hz and amplitude of the signal is 5 mV. All the electrochemical tests were carried out at room temperature.

3. Results and discussion

3.1 *Thermal analysis*

TGA curve of Ni(OH)$_2$ precursor is shown in figure 1. The initial weight loss of about 4% between 50 and 200 °C was due to the removal of physically adsorbed water molecules and carbonaceous polysaccharide. The rapid weight loss of about 36% between 200 and 450 °C

corresponded to the removal of the intercalated water molecules and the decomposition of Ni(OH)$_2$. Beyond 450 °C, all the intercalated water molecules and organic species were completely removed from the interslab space of Ni(OH)$_2$ and NiO was formed as the final product. Based on the thermal analysis, NiO can be prepared by calcining the Ni(OH)$_2$ precursor at 450 °C for 2 h.

3.2 *XRD analysis*

XRD pattern of the NiO samples obtained by different calcination methods are presented in figure 2. The diffraction peaks at 37.2, 43.3 and 62.9° of 2θ are corresponding to (111), (200) and (220) planes, respectively which can be indexed perfectly to cubic NiO phase. These results are in good agreement with the data of
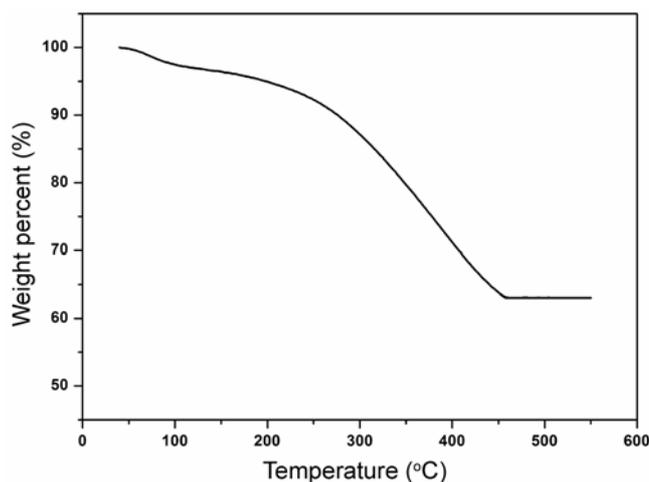

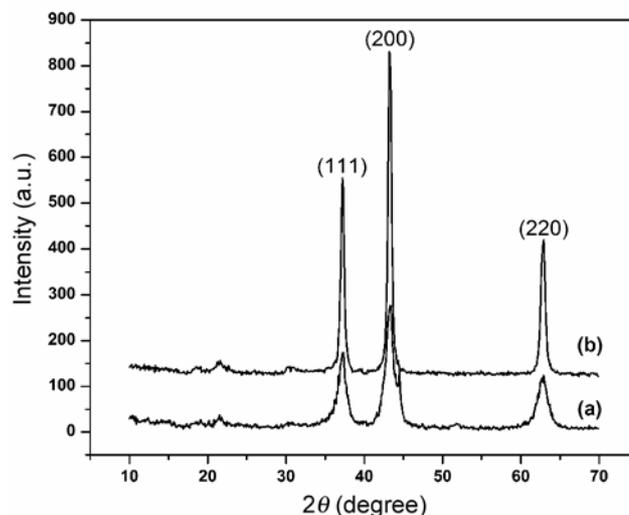**Figure 1.** TGA curve of Ni(OH)$_2$ precursor.

Figure 2. XRD patterns of NiO obtained by (a) muffle furnace calcination and (b) tube furnace calcination.
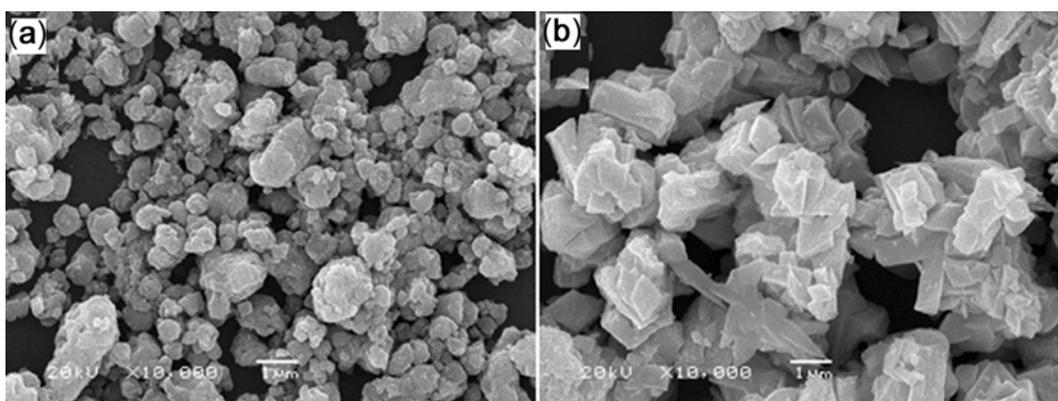
Figure 3. SEM images of NiO obtained by (**a**) muffle furnace calcination and (**b**) tube furnace calcination.

JCPDS file no. 47-1049. It is clear that the resulting sample possesses very good crystallinity after it was annealed at 450 °C for 2 h. No other peaks can be observed, indicating high purity of the as-prepared NiO samples. According to Scherrer formula based on all the diffraction peaks (the peak broadening effect aroused by the instrument was not taken out), the average particle size of the samples obtained by different calcination methods are about 20 nm (figure 2a) and 50 nm (figure 2b). Moreover, among the two NiO samples, the diffraction peaks of that prepared in a tube furnace under the nitrogen flow have stronger intensity and sharper shape, indicating that this sample has the better crystallization as shown in figure 2(b).

3.3 *SEM analysis*

SEM was used to observe the grain morphology and particle size of the prepared NiO samples. Figure 3 shows SEM images of the NiO samples obtained by different calcination methods. From figure 3(a), we can see that the morphologies of NiO samples obtained by muffle furnace calcination are particles with a wide range of size and the average particle size is about 100 nm. However, NiO samples obtained by tube furnace calcination exhibit sheet morphology. The sheets are about 300 nm in diameter and they aggregate into a cluster. In addition, it indicates that the product obtained by tube furnace calcination has a higher degree of crystalline character, which is consistent with results of XRD.

3.4 *Electrochemical performance of products*

To investigate the effect of different calcination methods of NiO on the electrochemical properties, their charge/discharge and cyclic voltammetry performances were measured.

NiO samples prepared by calcining $Ni(OH)_2$ precursor at 450 °C for 2 h were used as electrode material for charge/discharge test. Figures 4 and 5 show charge/discharge curves of the first and 800th for the NiO/a.c. supercapacitor at a constant current density of 100 mA/g in 6 mol/L KOH solution, respectively. As shown, a good linear potential variation vs time is observed for all charge/discharge curves, which is a typical characteristic of an ideal supercapacitor.

Based on the discharge curves, the discharge specific capacitance (C_s) of these hybrid supercapacitors were calculated by the following formula:

$$C_s = \frac{i \times \Delta t}{\Delta V \times m},\qquad(1)$$

where $i(A)$, $\Delta V(V)$, $\Delta t(s)$ and $m(g)$ are the discharge current, discharge potential range, discharge time consumed in the potential range ΔV, and the active mass of the single electrode, respectively. Based on the discharge curves in figures 4 and 5, the results of discharge specific capacitance for NiO/AC are listed in table 1 according to formula 1. The first cycle specific capacitance of a.c./NiO electrode NiO obtained by tube furnace calcination is 166·8 F·g^{-1} and the specific capacitance is 154·4 F g^{-1} after 800 cycles. The specific capacitance decreased by 7·4% after 800 cycles for a.c./NiO electrode. The first cycle specific capacitance of the a.c./NiO electrode which NiO obtained by muffle furnace calcination is 78 F·g^{-1} and the specific capacitance is 68·8 F·g^{-1} after 800 cycles. The specific capacitance decreased by 11·8% after 800 cycles.

Figure 6 presents the cycling performance of NiO/a.c. hybrid capacitor at a current density of 100 mA/g in 6 mol/L KOH solution. The data illustrate that these hybrid capacitors exhibited good capacity retention. As shown in figure 6 and table 1, it is obvious that sample (b) exhibited better electrochemical performance and had the higher discharge specific capacity between the two samples. The charge–storage mechanism of NiO for a pseudocapacitor electrode in alkaline solution has been represented as an invertible oxidation–reduction reaction

between Ni^{2+} and Ni^{3+}, which is described by following reaction (Srinivasan and Weidner 2000).

$$NiO + zOH^- \xrightleftharpoons[\text{discharge}]{\text{charge}} zNiOOH$$
$$+ (1 - z)NiO + ze^-, \qquad (2)$$
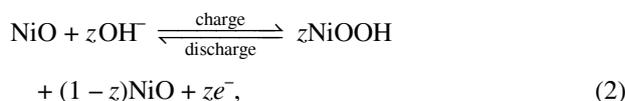
According to the chemistry defects, due to the existence of O_2 part of Ni^{2+} was oxidized into Ni^{3+}, generating the nonstoichiometric compounds $Ni_{1-x}O$ when the products were obtained by muffle furnace calcination. In this situation, the loss of Ni^{2+} led to the lower capacitance. When the products were obtained by tube furnace calcination, nonstoichiometric compounds $Ni_{1-x}O$ were fewer owing to N_2 for protection. So the utilization of active material
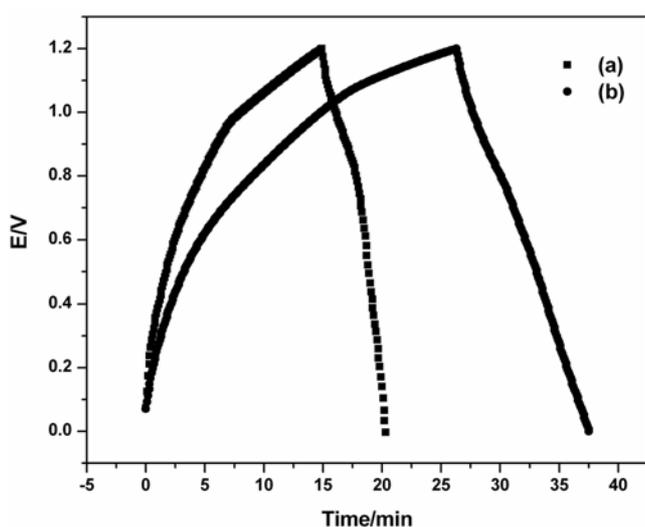

Figure 4. Charge/discharge curves of 1st cycle for a.c./NiO supercapacitor. NiO obtained by (a) muffle furnace calcination and (b) tube furnace calcination.
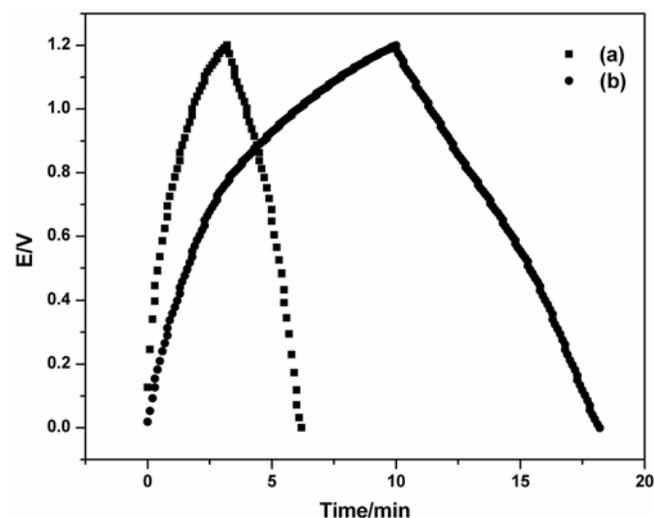

Figure 5. Charge/discharge curves of 800th cycle for a.c./NiO supercapacitor. NiO obtained by (a) muffle furnace calcination and (b) tube furnace calcination.

was higher when capacitor materials were gained by tube furnace calcination and gained a higher capacitance.

Figure 7 shows CV curves of NiO electrode in 6 mol/L KOH solution at a scan rate of 10 mV/s. In the potential range of $(-0\cdot1-0\cdot4)$ V, the appearance of two prominent symmetric redox peaks indicates the NiO electrode has good electrochemical reversibility and pseudocapacitance behaviour. CV curve of the NiO electrode obtained by muffle furnace calcination is similar to that of the NiO electrode obtained by tube furnace calcination, but there is larger area for CV curve of the NiO electrode obtained by tube furnace calcination. The discharge specific capacitance can be estimated from the voltammetric charge surrounded by CV curve according to the following formula (Hu and Tson 2003)

$$C = \frac{Q}{\Delta V \times w} = \frac{1}{2\Delta V} \int \frac{I}{vw} dI, \qquad (3)$$

where C is the specific capacitance of the electrode based on the mass of active materials (F/g), Q is the sum of anodic and cathodic voltammetric charges on positive and negative sweeps (C), I is the current during discharge process (A), ΔV is the potential window of $CV(V)$, v is the scanning rate (V/s) and w is the mass of active electrode
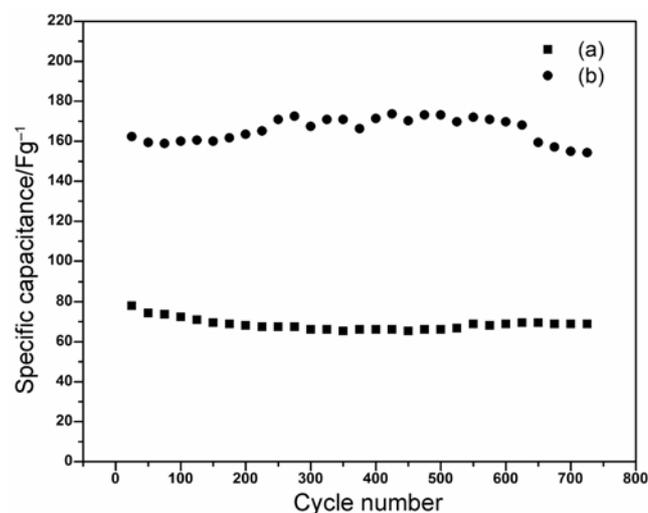

Figure 6. Cycling performance of a.c./NiO hybrid capacitor at a current density of 100 mA/g in 6 mol/L KOH.

Table 1. First cycle and 800th cycle discharge specific capacitance for NiO/a.c. supercapacitor: NiO obtained by (a) muffle furnace calcination and (b) tube furnace calcination.

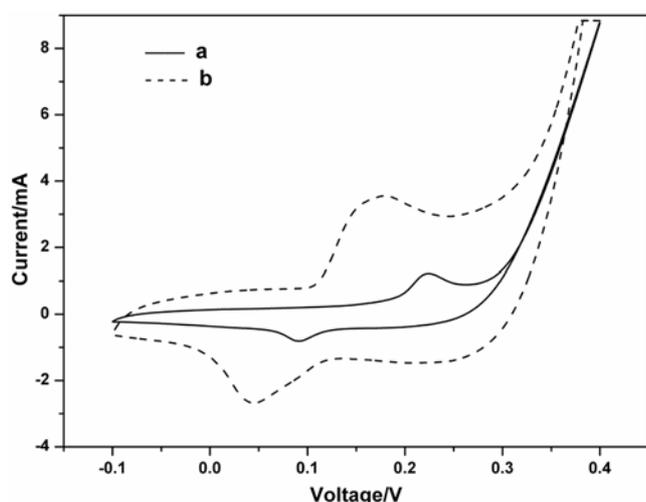|	Discharge specific capacitance $(Cs)/F \cdot g^{-1}$	
Samples	First cycle	800th cycle
a	78	68·8
b	166·8	154·4

Figure 7. CV curves of NiO electrode in potential range of (−0·1–0·4) V in 6 mol/L KOH solution at a scan rate of 10 mV/s. NiO obtained by (a) muffle furnace calcination and (b) tube furnace calcination.
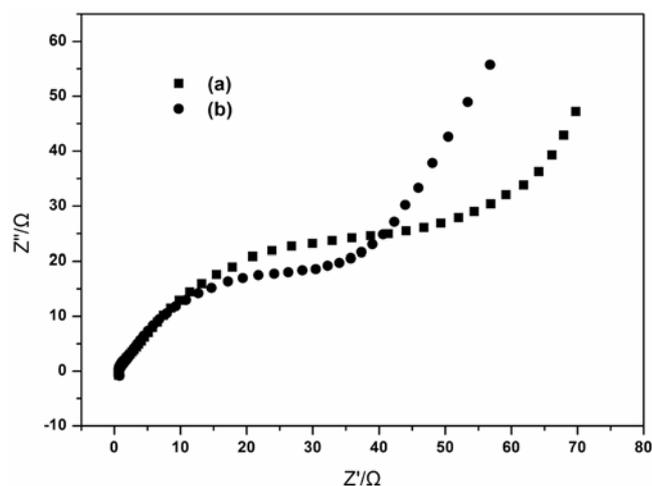

Figure 8. A.c. impedance spectra of NiO electrode in 6 mol/L KOH solution. NiO obtained by (a) muffle furnace calcination and (b) tube furnace calcination.

materials (*g*). According to formula 3, the discharge specific capacitance of NiO electrode obtained by different calcining way can be calculated from CV were 71·8 F/g (figure 7a) and 151·2 F/g (figure 7b), respectively. However, the values of the discharge specific capacitance are larger in comparison with that in table 1, which may be caused by different testing systems.

The electrochemical performance of the electrochemical impedance spectroscopy (EIS) for NiO electrode was further investigated at 0·25 V (vs SCE). The Nyquist plots of EIS spectra of NiO electrode obtained by different calcination methods are shown in figure 8, which shows the real part (Z') and the imaginary part (Z'') of the impedance. The semicircles in the high-frequency region

and the slopes of the straight line in the low-frequency range were different. Typically, the high-frequency semicircle is associated with two resistances: the solution or electrolyte resistance (R_e) and the particle resistance (R_p). The total resistance of NiO electrode obtained by different calcining ways are 40·2 Ω (figure 8a) and 30·1 Ω (figure 8b), respectively. Figure 8 shows that the electrolyte resistance is invariant. The particle resistance (R_p) of NiO electrode obtained by tube furnace calcination is smaller than that of muffle furnace calcination. It shows that the NiO electrodes obtained by tube furnace calcination have higher conductance and are more prone to electrochemical reaction.

Based on these results, it is believed that the NiO obtained by tube furnace calcination exhibits better electrochemical performance, which is a good way to acquire electrode material of supercapacitor field.

4. Conclusions

NiO samples were prepared via a precipitation transformation method through different calcination methods. NiO samples, which were obtained by different calcination methods, were used as the electrode material for cyclic voltammetry, charge/discharge test and electrochemical impedance spectra. The results showed that NiO samples obtained by tube furnace calcination displayed better electrochemical performance than that of the other products. Based on galvanostatic charge/discharge tests, the first cycle specific capacitance of a.c./NiO electrode which the NiO obtained by tube furnace calcination is 166·8 F·g^{-1} and the specific capacitance is 154·4 F·g^{-1} after 800 cycles. The specific capacitance decreased by 7·4% after 800 cycles for the a.c./NiO electrode. The first cycle specific capacitance of the a.c./NiO electrode which the NiO obtained by muffle furnace calcination is 78 F·g^{-1} and the specific capacitance is 68·8 F·g^{-1} after 800 cycles. The specific capacitance decreased by 11·8% after 800 cycles. The results show that NiO sample obtained by tube furnace calcination is better than that obtained by muffle furnace calcination for the specific capacitance and stability. It is causation that the loss of non-stoichiometric compounds Ni$_{1-x}$O under N$_2$ for protection increases the utilization of active material.

Electronic Supplementary Material

Supplementary material pertaining to this article is available on the Bulletin of Materials Science website (www.ias.ac.in/matersci).

References

Chai H, Chen X, Jia D Z, Bao S J and Zhou W Y 2012 *Mater. Res. Bull.* **47** 3947

Chen L M, Lai Q Y, Hao Y J, Huang J H and Ji X Y 2008 *Ionics* **14** 441

Conway B E 1991 *J. Electrochem. Soc.* **138** 1539

Gillaspie D, Norman A, Tracy C E, Roland Pitts J, Lee S H and Dillon A 2010 *J. Electrochem. Soc.* **157** H328

He J H *et al* 2008 *J. Magn. Magn. Mater.* **320** 3293

Hu C C and Tson T W 2003 *J. Power Sources* **115** 179

Kim J, Piao Y Z, Lee N, Il Park Y, Lee I H, Lee J H, Paik S R and Hyeon T 2010 *Adv. Mater.* **22** 57

Lee C Y, Chiang C M, Wang Y H and Ma R H 2007 *Sens. Actuators* **B122** 503

Mattei G, Mazzoldi P, Post M L, Buso D, Guglielmi M and Martucci A 2007 *Adv. Mater.* **19** 561

Meher S K, Justin P and Ranga Rao G 2011 *Nanoscale* **3** 683

Parada C and Morán E 2006 *Chem. Mater.* **18** 2719

Park J *et al* 2005 *Adv. Mater.* **17** 429

Prasad K R and Miura N 2004 *Appl. Phys. Lett.* **85** 4199

Srinivasan V and Weidner J W 2000 *J. Electrochem. Soc.* **147** 880

Tenent R C, Gillaspie D T, Miedaner A, Parilla P A, Curtis C J and Dillon A C 2010 *J. Electrochem. Soc.* **157** H318

Wang X, Li L, Zhang Y G, Wang S T, Zhang Z D, Fei L F and Qian Y T 2006 *Cryst. Growth Des.* **6** 2163

Zhang Y 2009 *Int. J. Hydrogen Energ.* **34** 4889

Zheng Y Z and Zhang M L 2007 *Mater. Lett.* **61** 3967

Zheng Y Z, Ding H Y and Zhang M L 2009 *Mater. Res. Bull.* **44** 403