

Synthesis and electrochemical properties of mesoporous nickel oxide

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Abstract

Mesoporous Ni(OH)₂ is synthesized using sodium dodecyl sulfate as a template and urea as a hydrolysis-controlling agent. Mesoporous NiO with a centralized pore-size distribution is obtained by calcining Ni(OH)₂ at different temperatures. The BET specific surface area reaches 477.7 m² g⁻¹ for NiO calcined at 250 °C. Structure characterizations indicate a good mesoporous structure for the nickel oxide samples. Cyclic voltammetry shows the NiO to have good capacitive behaviour due to its unique mesoporous structure when using a large amount of NiO to fabricate the electrode. Compared with NiO prepared by dip-coating and cathodic precipitation methods, mesoporous NiO with a controlled pore structure can be used in much larger amounts to fabricate electrodes and still maintain a high specific capacitance and good capacitive behaviour.

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1. Introduction

With increasing interest in high-power devices, especially for hybrid electric vehicles, electrochemical capacitors (ECs) have been studied extensively in recent years. Capacitance can arise from two processes, i.e., electrical double-layer capacitance and interfacial redox capacitance (pseudocapacitance or faradaic capacitance). Traditionally, carbon materials with high surface areas have been used to increase the electrical double-layer capacitance [1–3]. As alternatives to carbon materials, however, most metal oxides operate via the latter mechanism. An amorphous phase of RuO₂·xH₂O formed by a sol–gel method at low temperatures shows a specific capacitance more than 700 F g⁻¹ in an acidic electrolyte, but its high cost limits commercial application [4]. Hence, much effort has been aimed at searching for alternative electrode materials (nickel oxide [5–10], cobalt oxide [11–13] and manganese oxide [14,15]), which are inexpensive and exhibit pseudocapacitive behaviour similar to that of RuO₂ and IrO₂ [16]. Among them, nickel oxide is easily available and possesses a high specific capacitance that is comparable with carbon materials.

Generally, two methods have been used to obtain NiO electrodes for capacitors, namely, the sol–gel dip-coating method and the cathodic precipitation method. Liu and Anderson [5] used the sol–gel method to fabricate a porous NiO electrode. In this process, nickel foil was withdrawn from the prepared Ni(OH)₂ sol and then heated at 300 °C to convert Ni(OH)₂ to NiO. The prepared NiO layer was ~0.4 μm thick. The structure of this type of NiO is however uncontrollable and disordered. In addition, only a small amount of Ni(OH)₂ can be attached to the current-collector. In order to control the coating mass of the active material, Srinivasan and Weidner [6] applied an electrochemical precipitation method to fabricate NiO electrodes. The prepared NiO film was 0.1–1 μm thick and 7.0–70.0 μg in weight. The average capacitance of a 35 μg nickel oxide film was ~168 F g⁻¹ during the first several decades of measurement. In more recent work [7] these authors reported that the specific capacity reaches 104 and 155 F g⁻¹ when cycling a 350 μg NiO film over a 0.35 and 0.5 V range, respectively. Although the precipitated amount of Ni(OH)₂ can be controlled by using this method, the structure of precipitated Ni(OH)₂ is less porous than that obtained by the sol–gel method and the mass of precipitated materials is still much less than 1 mg. From the results of these groups of workers, it can be concluded that the capacitance decreases dramatically with an increased mass of nickel oxide on the electrode,

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even though the total mass of active material is still much less than 1 mg. This means that the sol–gel dip-coating method and cathodic precipitation method will inevitably encounter a serious fall in capacitance during scaling-up. This is considered to be due to the uncontrollable pore structure of NiO prepared by the methods resulting in a poor contact between the pore surface and the electrolyte as the NiO film thickens. NiO with a controlled pore structure will improve the contact and, thereby, will probably maintain high capacitance during scaling-up. This will assist meeting the demands of commercialization.

Since electric double-layer capacitance and pseudocapacitance are interfacial phenomena, the materials for electrochemical capacitors should possess a high specific surface area with a suitable pore-size distribution to enhance the charge-storage capability. Thus, control of the surface morphology of electrode materials is one of the most important design parameters for making an electrochemical capacitor. In this work, a mesoporous nickel oxide with a very high surface area is developed by an anionic template according to Banerjee's method [17]. The unique mesopore system and large surface area of the NiO samples are expected to favour ion transfer in the pore system and increase the NiO–electrolyte interfacial area, respectively. In addition, the unique mesoporous structure of the NiO is expected to help maintain its high specific capacitance when using a large amount of NiO to fabricate an electrode.

2. Experimental

2.1. Synthesis of mesoporous nickel oxide

The Ni(OH)₂ samples were prepared using NiCl₂·6H₂O (AR grade; AJAX Chemicals, Australia), sodium dodecyl sulfate (SDS) (>99% pure; Sigma Chemicals, USA), urea (AR grade; AJAX Chemicals, Australia), and distilled water. The mixtures were stirred at room temperature for 2 h to yield a transparent solution, and then transferred to an oven for heating at 80 °C for 6 h. The resulting precipitate was cooled down and separated by centrifugation. Then, the Ni(OH)₂ products were dried, without washing, at 100 °C overnight to stabilize the structure. The resulting solid was washed with ethanol extensively, and then dried in air. The samples were calcined at different temperatures, viz., 250, 300, 350 °C.

2.2. Structure characterization of mesoporous nickel oxide

Nitrogen adsorption and desorption experiments were carried out at 77.3 K by means of a Nova 1200 (Quantachrome) analyzer. The surface area was calculated using the BET equation. Pore-size distributions were calculated by the BJH (Barrett, Joyner and Halender) method using the desorption branch of the isotherm. Infrared spectra were recorded on a

PE2000 Fourier transform infrared (FTIR) spectrophotometer using KBr pellets that contained 1 wt.% of the sample in KBr. Thermogravimetric analysis (TGA; Shimadzu TGA 50H) was performed at a heating-rate of 2 °C min⁻¹. X-ray diffraction (XRD) measurements were performed at a speed of 0.01 ° s⁻¹ by a Bruker Axs diffractometer (Germany) with Cu Kα radiation generated at 40 kV, 30 mA. A scanning electron microscope (JEOL 6400) was used to image samples at high resolution.

2.3. Electrochemical tests

The electrode materials were ground with 10 wt.% PTEF as binder and 20 wt.% carbon black as conducting agent. The ground products was then pressed between two pieces of nickel foam under 300 kg cm⁻². Each electrode contained about 10 mg of active material. The electrode was dried overnight at 100 °C under vacuum. Before electrochemical tests, the electrodes were vacuum-impregnated with electrolyte to guarantee that the electrode material was thoroughly wetted by electrolyte. Afterwards, the wetted electrode was characterized electrochemically in 3 wt.% KOH solution using a Ag|AgCl reference electrode and a platinum counter electrode. Cyclic voltammetry and galvanostatic charge–discharge experiments were conducted with a Solartron 1480 potentiostat/galvanostat.

3. Results and discussion

3.1. TGA analysis

Thermogravimetric analysis was conducted for as-synthesized Ni(OH)₂ in air atmosphere to examine the conversion process during calcination. The TG curve and its differential curve (DTG) are shown in Fig. 1. A very sharp peak is present between 250 and 350 °C on the DTG curve. This corresponds to a weight loss via the following

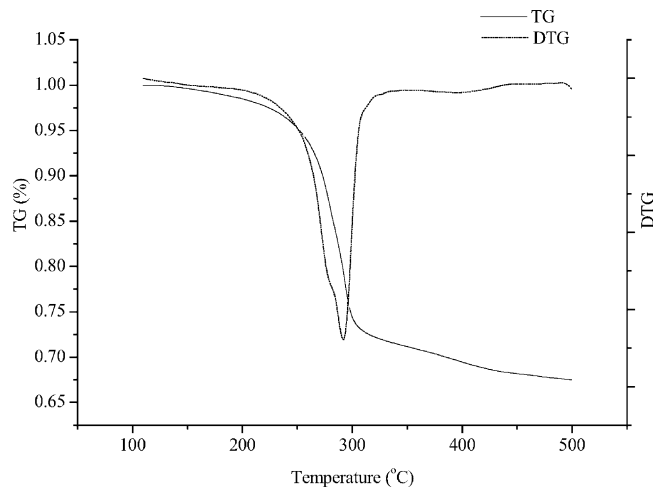


Fig. 1. TG–DTG plots of as-synthesized Ni(OH)₂.

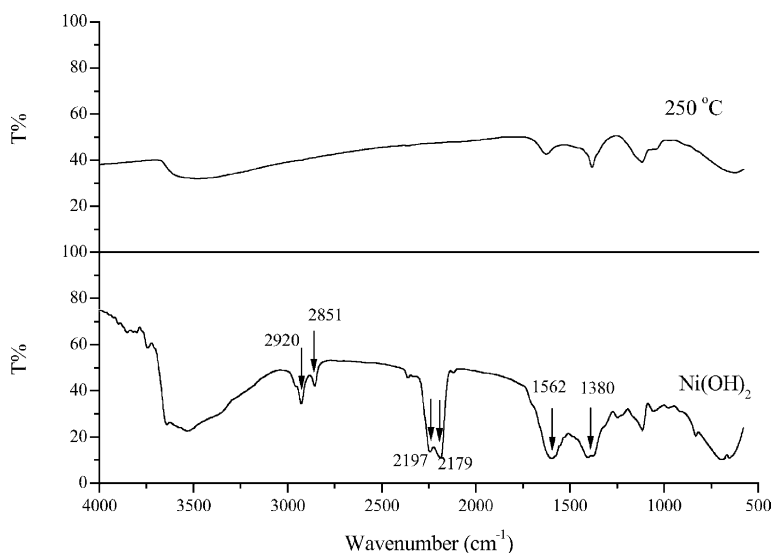


Fig. 2. FTIR spectra of Ni(OH)₂ and NiO calcined at 250 °C.

reaction:



This is the reason why calcining temperatures at 250, 300 and 350 °C were chosen in this study. With the hydroxyl groups removed from Ni(OH)₂, the NiO crystal phase is expected to be formed, which is confirmed by the following XRD results. At the same time, the pore structure of the samples will undergo major changes. From 110 to 250 °C, the sample weight decreases slowly. This is expected to be due mainly to the removal of chemically adsorbed H₂O. Nevertheless, the conversion of Ni(OH)₂ to NiO is still at an early stage during this step. When the temperature is above 350 °C, the weight decreases slowly because of the removal of a small amount of hydroxyl-group residue during development of the NiO phase. When the temperature reaches 500 °C, a weight loss of 35% is observed, which is very close to the stoichiometric weight loss, 36.7%, calculated from reaction (1).

3.2. Structure characterization of mesoporous nickel oxide

The FTIR spectra of as-synthesized Ni(OH)₂ and NiO calcined at 250 °C are presented in Fig. 2. In the spectrum of Ni(OH)₂, the prominent bands at 2850–2950 and 1380 cm⁻¹ are typical of C–H symmetric stretching and bending vibrations, respectively. This confirms incomplete removal of surfactant, even after extensive washing with ethanol. The peaks at 2197 and 2179 cm⁻¹ are also assigned to surfactant residues. After calcination at 250 °C, almost all the peaks from the surfactant have disappeared, and the broad peak at around 3500 cm⁻¹, corresponding to –OH, is also decreased in intensity. This means that the surfactant is almost removed after calcination and that the samples still contain some hy-

droxyl groups after calcination at 250 °C. As a result, the surfactant can be removed effectively by calcination at temperature around 250 °C. Thereby, the calcining temperature selected in this experiment is suitable for surfactant removal.

Surface area and pore-size distribution analysis were conducted using N₂ adsorption. As seen from Table 1 and Fig. 3, the as-synthesized Ni(OH)₂ possesses a narrow mesoporous distribution at around 3–4 nm and has a high surface area of 431.7 m² g⁻¹. This means that an anionic-sulfate-based surfactant is very effective to control and maintain the mesopore structure of nickel hydroxide. The hydrolysis rate of nickel chloride is well controlled by urea hydrolysis at 80 °C, which contributes to the stable skeleton of the mesoporous nickel hydroxide. After calcination at 250 °C for 3 h, the pore skeleton of the sample is well sustained. In addition, some surfactant residues and hydroxyl groups are removed from the pore system during calcination and, thereby, the specific surface area, pore volume and average pore size increase dramatically to 477.7 m² g⁻¹, 0.60 cm³ g⁻¹ and 5.0 nm, respectively. At this temperature, NiO crystallites develop due to the slow removal of hydroxyl species from the Ni(OH)₂, which is confirmed by the following XRD analysis. The slow removal of hydroxyl species at this temperature provides one reason to account for the stability of the pore skeleton

Table 1
Surface properties of nickel hydroxide and its calcined products

Samples	BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter ^a (nm)
Ni(OH) ₂	431.7	0.39	3.6
NiO (250 °C) ^b	477.7	0.60	5.0
NiO (300 °C) ^b	297.1	0.43	5.8
NiO (350 °C) ^b	217.0	0.40	7.4

^a Calculated by $4V(\text{pore volume})/S(\text{BET})$.

^b Samples were kept at calcination temperature for 3 h.

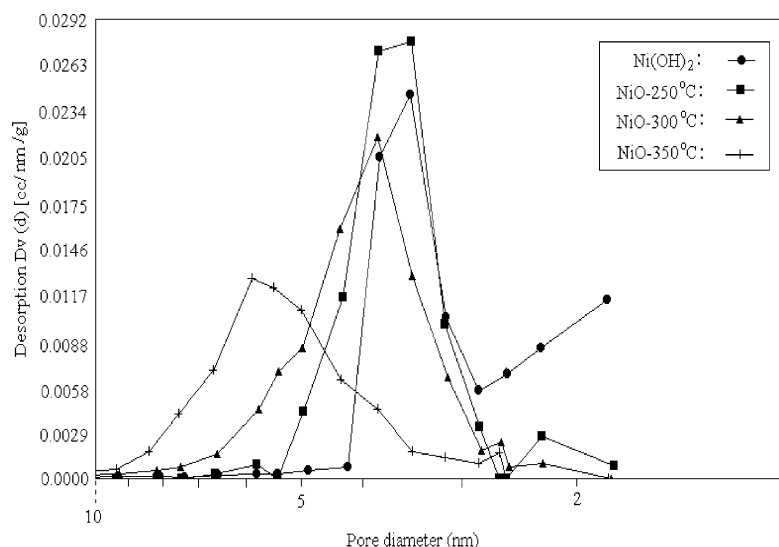


Fig. 3. Pore-size distribution plots of as-synthesized $\text{Ni}(\text{OH})_2$ and its calcined products. Data calculated using desorption curve by BJH method.

during calcination at this temperature. Further, calcination at 300 and 350 °C results in fast removal of hydroxyl species and the pore walls collapse, which causes the BET surface area and pore volume to decrease dramatically. The average pore size is enlarged, however, because of the sintering of the small pores. It can be concluded that the calcination temperature is an important factor to control the surface area and pore-size distribution of NiO.

The XRD patterns of the as-synthesized $\text{Ni}(\text{OH})_2$ and nickel oxide produced by heating the $\text{Ni}(\text{OH})_2$ at different temperatures are shown in Fig. 4. Small-angle X-ray scattering (SAXS) investigations show peaks at small angles, which indicate the existence of a size-controlled porosity. For the calcined samples, the peak positions shift to low angles with increase in the calcination temperature, which indicates an enlargement of mesopore size with temperature increase. This trend coincides with the average pore-size val-

ues listed in Table 1, which have been obtained by the N_2 adsorption method. The deviation in the peak position for $\text{Ni}(\text{OH})_2$ is probably due to the differences in composition and crystal structure between $\text{Ni}(\text{OH})_2$ and NiO.

The wide-angle XRD pattern of the as-synthesized $\text{Ni}(\text{OH})_2$ corresponds to the layered $\alpha\text{-Ni}(\text{OH})_2$ structure [18]. The strong peaks indicate a high degree of crystallization for this mesoporous $\text{Ni}(\text{OH})_2$, which is much higher than observed for cathodic precipitated $\text{Ni}(\text{OH})_2$ in previous work [8,9]. The first peak (001) appears at about $2\theta = 10.8^\circ$, and it shows that the inter-sheet distance (C-spacing) of $\alpha\text{-Ni}(\text{OH})_2$ is 0.82 nm. At temperatures higher than 250 °C, the XRD patterns exhibit the characteristic peaks of rock salt NiO at $2\theta = 37, 43$ and 63° , which first appeared at 250 °C. Therefore, when heated at or above 250 °C, $\text{Ni}(\text{OH})_2$ is converted to NiO with a crystalline structure. With increase in calcination temperature, the peak density

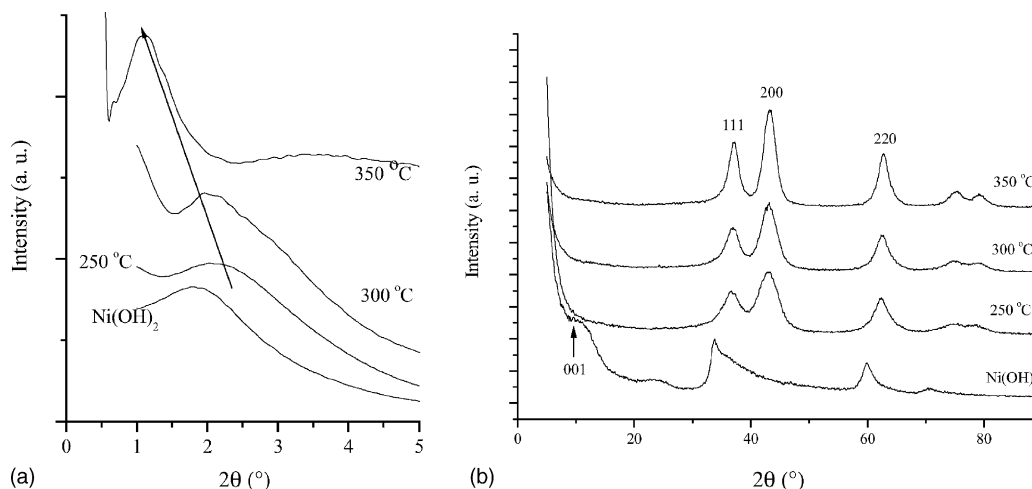


Fig. 4. XRD spectra of as-synthesized $\text{Ni}(\text{OH})_2$ and NiO calcined at different temperatures: (a) small-angle XRD spectrum; (b) XRD spectrum.

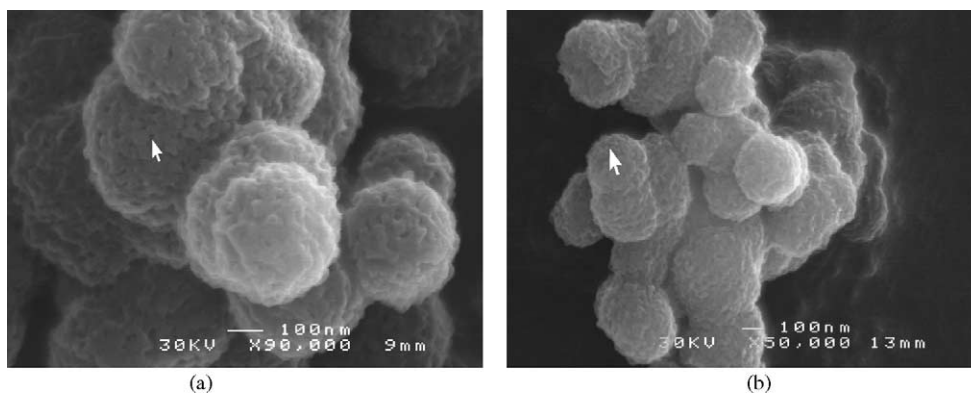


Fig. 5. Scanning electron micrographs of (a) as-synthesized $\text{Ni}(\text{OH})_2$ and (b) NiO calcined at 350°C .

increases as well. This indicates that degree of crystallization of NiO increases with calcination temperature, and suggests that the latter is an important factor for controlling the properties of NiO .

Scanning electron micrographs of mesoporous $\text{Ni}(\text{OH})_2$ and NiO calcined at 350°C are shown in Fig. 5(a) and (b), respectively. The micrographs reveal a sub-micron ball shape with a porous structure. The diameter of the balls is around 300 nm. The mesopores can be observed in the micrographs and are indicated by white arrows. Clearly, calcination at 350°C neither damages the ball shape nor destroys the pore system dramatically, although the crystal phase and sample weight change markedly during calcination.

3.3. Electrochemical properties of mesoporous nickel oxide

Cyclic voltammetry (CV) and galvanostatic techniques were used to determine the electrochemical properties of

mesoporous nickel oxide as a function of the calcination temperature. The CV experiments within a 0.0–0.5 V range were conducted with $\text{Ni}(\text{OH})_2$ and NiO calcined at different temperatures. The characteristic shapes of the CV curves for mesoporous nickel hydroxide dried at 100°C and nickel oxide calcined at three different temperatures (250, 300 and 350°C) are shown in Fig. 6. For $\text{Ni}(\text{OH})_2$ electrode material, it is well-accepted that the surface faradaic reactions will proceed according to the following reaction [19]:



For calcined samples, it has been shown that the reaction of Ni^{2+} to Ni^{3+} occurs at the surface of NiO according to (3):

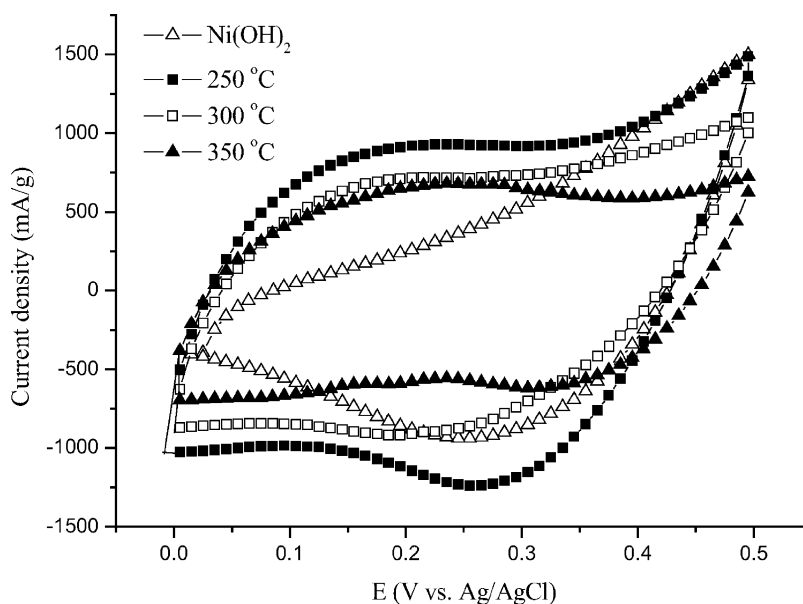
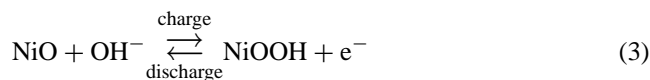


Fig. 6. Cyclic voltammograms of $\text{Ni}(\text{OH})_2$ and NiO calcined at three different temperatures. Curves are normalized to current response for 1 g of active material; voltammograms measured in 3 wt.% KOH at a sweep rate of 10 mV s^{-1} .

The CV curve of mesoporous Ni(OH)₂ shows a special triangular shape that is distorted from a rectangular shape; there are no sharp peaks. Srinivasan and coworkers [6,7,10] and Nam et al. [9] have reported very sharp anodic and cathodic peaks at around 0.37 and 0.20 V, respectively, on the CV curve for a cathodic precipitated Ni(OH)₂ electrode. These sharp peaks are attributed to reactions between bulk Ni(OH)₂ and the electrolyte. This means that bulk Ni(OH)₂ prepared by cathodic precipitation reacts more readily with the electrolyte, probably, due to its low degree of crystallization [8,9]. The mesoporous Ni(OH)₂ prepared in this work possesses a higher degree of crystallization and thus has a more stable crystal structure. Compared with cathodic precipitated Ni(OH)₂, the bulk phase of mesoporous Ni(OH)₂ is expected to be more inert to the electrolyte, which accounts for the absence of sharp peaks on its CV curve.

After calcination, the CV changes to a distorted rectangular shape, which indicates good capacitive behaviour over the 0.5 V range. NiO calcined at 250 °C displays the most distorted rectangular shape with the highest anodic and cathodic peak currents, while NiO calcined at 350 °C has the most normal rectangular shape with the lowest peak currents. It is well known that the more rectangular the CV shape, the better is the capacitive behaviour of the material. Therefore, it can be concluded that NiO calcined at 250 °C exhibits the worst capacitive behaviour among the calcined NiO samples and that the capacitive behaviour improves with increases in calcination temperature. According to the XRD results, the degree of crystallization of NiO increases with the calcination temperature. It is expected that the NiO crystal phase becomes inert to the electrolyte with increasing degree of crystallization. In the CV test, the faradiac reactions are more strictly confined to the surface of NiO with the higher degree of crystallization, which explains why the

capacitive behaviour of NiO samples improves with increase in calcination temperature.

Compared with previous work, the NiO electrode mass used in this work is 30–300 times more than that employed in previous work [5–10]. Nevertheless, the NiO electrode still displays good capacitive behaviour due to its unique mesoporous structure that favours easy transfer of OH⁻ to the NiO surface.

Constant-current discharge was also conducted to obtain the specific capacitance of mesoporous Ni(OH)₂ and NiO samples. The electrodes were charged to 0.5 V at the same current density before discharge. All the curves appear linear (Fig. 7), except that for Ni(OH)₂, which exhibits a curved line because of its poor capacitive behaviour. The linear discharge curves indicate good capacitive behaviour for the calcined samples. The corresponding specific capacitance of the NiO samples is calculated from the following expression:

$$C = \frac{I \Delta t}{m \Delta V} \quad (4)$$

where I is the discharge current, Δt the total discharge time, m the mass of active material, ΔV the potential drop during discharging and C the specific capacitance. The specific capacitance of NiO samples calcined at 250, 300 and 350 °C is calculated to be 124, 106 and 68 F g⁻¹, respectively. The calculated capacitances decrease with decrease in the BET specific surface area of the NiO samples. It is well known that the electric double-layer capacitance and the pseudo-capacitance are both interfacial phenomena. Accordingly, materials with high specific surface areas should have high charge-storage capabilities. The intrinsic capacitance of NiO calcined at 250, 300 and 350 °C is calculated to be 26.0, 35.7 and 31.3 μF cm⁻², respectively. NiO calcined at 300 °C possesses the highest capacitance, it has the highest surface

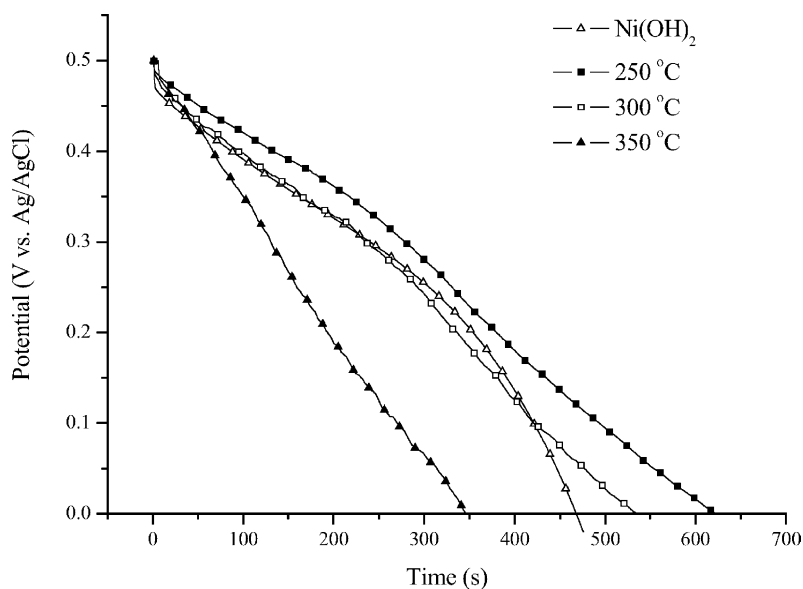


Fig. 7. Effect of calcination temperature on constant-current discharge curves of mesoporous Ni(OH)₂ and NiO electrodes measured with a current density of 100 mA g⁻¹ in 3 wt.% KOH.

redox reactivity. This observation is in agreement with the results of other researchers [5–10]. It can also be concluded that the capacitance of NiO is determined by two factors, namely, surface area and surface reactivity. Taking these two factors into consideration, calcination at 250 °C gives the highest capacitance. Compared with previous work [5–10], the mesoporous NiO samples possess similar capacitance when using 30–300 times more NiO material to fabricate the electrode, which is expected to be due to the unique mesoporous structure that provides OH⁻ accessible pores and a very high surface area for charge storage. In the previous work [5–10], however, the capacitance value was found to decrease dramatically with increased mass of the NiO electrode, even though the total mass of NiO was still much less than in the present work. This discrepancy is considered to be due to the uncontrolled pore structure of the NiO samples prepared in those studies.

4. Conclusion

A novel mesoporous nickel hydroxide with very high surface area has been synthesized with an anionic sulfate template. The BET surface area of NiO calcined at 250 °C reaches 477.7 m² g⁻¹. Nitrogen adsorption and XRD analysis show that Ni(OH)₂ and calcined NiO have good mesoporous structures. Cyclic voltammetry indicates a good capacitive behaviour for mesoporous NiO samples and that this behaviour improves with increase in calcination temperature. Galvanostatic discharge indicates that the capacitance of NiO is determined by two factors, namely, surface area and surface reactivity. Taking these two factors into consideration, calcination at 250 °C gives the highest capacitance, i.e., 124 F g⁻¹. On the other hand, NiO calcined at 300 °C possesses the highest surface redox reactivity. Compared with NiO prepared by dip-coating and cathodic deposition methods, mesoporous NiO can be used

to fabricate electrodes for capacitors in a much larger mass and, at the same time, maintain a high value of specific capacitance and good capacitive behaviour.

Acknowledgements

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