Morphology-dependent electrochemical performances of nickel hydroxide nanostructures

KARTHIK S BHAT* and H S NAGARAJA

Department of Physics, National Institute of Technology Karnataka, P.O. Srinivasnagar, Surathkal, Mangaluru 575 025, India

*Author for correspondence (kasubhat@gmail.com)

MS received 15 October 2018; accepted 8 March 2019

Abstract. Electrochemical capacitors form part of the developing technologies in the field of alternative energy sources. In the present work, nickel hydroxide ($\text{Ni}(\text{OH})_2$) nanosheets and microflowers are hydrothermally prepared employing different chemical precursors. Structure, morphology and chemical analysis are conducted using powder X-ray diffraction, field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy measurements. Electrochemical performances as supercapacitor electrodes of the synthesized nanostructures are evaluated through cyclic voltammetry and galvanostatic charge–discharge measurements with three-electrode configurations. The results indicated the specific capacitance of 180 and 417 F g^{-1} at a scan rate of 5 mV s^{-1} for $\text{Ni}(\text{OH})_2$ nanosheets and microflowers, respectively. The higher specific capacitances for $\text{Ni}(\text{OH})_2$ microflowers could be attributed to the higher specific surface area, morphology, electronic conductivity and porosity. Both $\text{Ni}(\text{OH})_2$ nanostructures exhibited good capacitance retention for 1500 cycles.

Keywords. Hydroxides; nickel hydroxide; supercapacitors; nanosheets; microflowers.

1. Introduction

The rapid surge in the energy demand and insufficiency of fossil fuels have fascinated researchers for the improvement of viable energy devices [1]. Among which supercapacitors have gained prominence owing to their ease of fabrication, composition flexibility and other analytical factors such as high power density and energy density [2,3]. Supercapacitors store charges *via* two mechanisms: electrochemical double-layer capacitance (non-Faradaic) and pseudo-capacitance (Faradaic) processes [4,5]. The non-Faradic process can be ascribed to adsorption of ions at the electrode surface, while pseudo-capacitance is based on oxidation–reduction of the electrode material with the electrolyte. Graphene and their analogues exhibit electrochemical double-layer capacitance and on the other hand; materials such as metal oxides and metal hydroxides operate *via* redox reactions [6,7].

Various classes of nanostructures such as transition metal oxides [8], hydroxides [9], chalcogenides [10], carbon compounds [11] and conducting polymers [12] are used as electrode materials for supercapacitors. Among which transition metal hydroxides are emerged as promising electrode materials owing to their high specific surface area, redox structures and multivalent oxidation states [13]. So far, hydroxides of various transition metals such as cobalt hydroxide [14], copper hydroxide [15], lanthanum hydroxide [16], nickel hydroxide [17], manganese hydroxide [18], etc. are

evaluated as electrode materials for supercapacitors. Among which, nickel hydroxide nanostructures and their carbon composites [19–24] are fairly explored with their electrochemical properties. However, no effort has been made to study the effect of the nickel hydroxide morphology on their electrochemical performances. In this framework, we account for the synthesis of nickel hydroxide nanostructures of two different morphologies (nanosheets and microflowers) *via* a hydrothermal method. Both nickel hydroxide nanostructures were evaluated as electrodes for supercapacitor applications. The results indicate the microflower morphology could deliver the best specific capacitance of 417 F g^{-1} at 5 mV s^{-1} as compared with nanosheets (180 F g^{-1}) and also suggests nickel hydroxide nanostructures can be a suitable material for high-performance supercapacitor applications.

2. Experimental

2.1 Chemicals and reagents

Nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium solution (NH_4OH), urea ($\text{CH}_4\text{N}_2\text{O}$) and trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) of the analytical grade available were purchased from Loba Chemicals and were used as received. Deionized (DI) water from a Milli-Q ($18 \text{ M}\Omega \text{ cm}$) ultrapure system was used throughout the experiments.

Figure 1. Powder-XRD patterns and FESEM images of: (a, b) Ni(OH)_2 nanosheets, (c, d) Ni(OH)_2 microflowers. (a, b) Reprinted from Bhat and Nagaraja [17], with the permission of AIP Publishing.

2.2 Synthesis of Ni(OH)_2 nanosheets

The Ni(OH)_2 nanosheets are synthesized as described elsewhere [25,26]. In brief, 0.5416 g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in 70 ml of DI water to obtain a green solution under magnetic stirring. An opaque solution was obtained while adding 10.5 ml of 2 M NH_4OH . The mixture was continuously stirred for 20 min and then transferred to a 120 ml autoclave; the hydrothermal process was carried out at 180°C for 24 h. Next, the green precipitates were collected, washed and dried at 60°C .

2.3 Synthesis of Ni(OH)_2 microflowers

The Ni(OH)_2 microflowers are synthesized as per earlier reports [27]. In brief, 1.744 g of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and

0.728 g of $\text{CH}_4\text{N}_2\text{O}$ were dissolved in 80 ml of DI water to obtain a pale green solution under vigorous stirring. Then 0.024 g of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ were added to the resulting dispersion and stirred for 30 min. The final solution was transferred to a 120 ml autoclave and the hydrothermal process was carried out at 150°C for 24 h. Dark green precipitates were collected, washed and dried at 60°C .

2.4 Electrode preparation and supercapacitor characterization

The working electrodes for supercapacitors were fabricated by mixing the active material with conductive carbon black (acetylene black) and polyvinylidene fluoride in the 6:3:1 ratio, using *N*-methyl-2-pyrrolidone as the solvent. The above mixture is uniformly coated on a titanium foil substrate

Figure 2. EDS spectra of: (a) Ni(OH)₂ nanosheets and (b) Ni(OH)₂ microflowers.

on $\sim 1 \text{ cm}^2$ area and dried in an oven at 60°C for 6 h. Electrochemical performances of the fabricated electrodes were evaluated using Biologic SP-150 workstation with three-electrode configurations with the fabricated electrodes as working electrodes, saturated calomel electrode (SCE) as the reference and platinum (Pt) wire as the counter electrode. Electrochemical measurements with 1 M KOH as the electrolyte were conducted. The values of specific capacitance from the CV curves can be calculated using the equation:

$$C_s = \frac{\int I(V)dV}{vm\Delta V} (\text{F g}^{-1}), \quad (1)$$

where ' C_s ' represents the specific capacitance (F g^{-1}), integral represents the area under the CV curve, ' m ' is the active mass of the electroactive material (mg), ' v ' is the scan rate (mV s^{-1}) and ' ΔV ' is the potential window (V).

2.5 Structure, morphology and chemical analysis

Figure 1a and b shows powder-X-ray diffraction (PXRD) patterns and field emission scanning electron microscopy (FESEM) images of Ni(OH)₂ nanosheets and figure 1c and d shows PXRD patterns and FESEM images of Ni(OH)₂ microflowers.

Figure 1a shows the XRD patterns of the as-synthesized Ni(OH)₂ nanosheets with lattice constants $a = 2.12 \text{ \AA}$ and

Figure 3. (a, d) CV curves of Ni(OH)₂ nanosheets and microflowers at various scan rates; (b, e) effect of the scan rate on the specific capacitances of Ni(OH)₂ nanosheets and microflowers and (c, f) GCD curves of Ni(OH)₂ nanosheets and microflowers at different current densities. (a–c) Reprinted from Bhat and Nagaraja [17], with the permission of AIP Publishing.

Table 1. Specific capacitance values at different scan rates of Ni(OH)₂ nanosheets and microflowers.

Scan rate (mV s ⁻¹)	Specific capacitance (F g ⁻¹)	
	Nanosheets	Microflowers
5	180.2	417.4
10	142.1	391.0
20	105.6	339.1
50	62.1	250.2
100	39.7	185.3

$c = 4.60$ Å with a hexagonal crystal structure, which are commensurate with standard JCPDS files 014-0117 [28]. On the other hand, figure 1c represents the XRD patterns of Ni(OH)₂ microflowers indicating the rhombohedral crystal structure with lattice constants $a = b = 3.08$ Å and $c = 23.4$ Å, which are consistent with reference JCPDS file 038-0715 [29]. Further, FESEM measurements confirm the two-dimensional hexagonal sheet-like morphology of Ni(OH)₂ nanosheets (figure 1b) and the interconnected three-dimensional flower-like network of Ni(OH)₂ microflowers (figure 1d), respectively.

Next, energy-dispersive X-ray spectroscopy (EDS) measurements were performed to determine the elemental

composition of the structures as shown in figure 2a and b. Both Ni(OH)₂ nanosheet and microflower morphologies indicate the elemental peaks corresponding to Ni and O, confirming their purity. Surprisingly, the EDS measurements on Ni(OH)₂ microflowers also indicate the peaks corresponding to nitrogen, which could be due to the use of a urea precursor during the synthesis process. Since the presence of nitrogen is in considerable quantities, one can assume the nitrogen doping in the Ni(OH)₂ microflower system. Further, the atomic and weight percentages obtained from EDS measurements are provided as insets of figure 2a and b, respectively.

2.6 Electrochemical measurements

The electrochemical performances of fabricated Ni(OH)₂ supercapacitor electrodes are evaluated using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. All electrochemical measurements are performed in three-electrode configurations with 1 M KOH as the aqueous electrolyte. CV and GCD curves were recorded in the voltage window range of 0–0.5 V vs. SCE at various scan rates (5–100 mV s⁻¹) and different applied current densities (2, 4 and 6 A g⁻¹), respectively. Further, EIS measurements were performed in the frequency range of 0.2 Hz–100 kHz to

Figure 4. Comparison of (a) CV curves and (b) GCD curves of Ni(OH)₂ nanosheet and microflower electrodes at a scan rate of 10 mV s⁻¹ and a current density of 4 A g⁻¹ respectively.

study the interface behaviour of the electrode material with the electrolyte.

Figure 3a and d shows CV curves of Ni(OH)₂ nanosheets and microflowers at various scan rates, figure 3b and e shows the effect of a scan rate on the specific capacitances of Ni(OH)₂ nanosheets and microflowers and figure 3c and f shows GCD curves of Ni(OH)₂ nanosheets and microflowers at different current densities.

Figure 3(a and d) represents the CV curves of the fabricated Ni(OH)₂ nanosheets and microflowers in the voltage window range of 0–0.5 V. The CV curves differ from the ideal rectangular behaviour of the supercapacitor, suggesting the redox-type charge storage behaviour of the electrodes. In other words, both nanostructures exhibit pseudo-capacitive characteristics [30]. Also, it is important to consider that the Ni(OH)₂ microflowers exhibit prominent oxidation and reduction peaks in contrast to Ni(OH)₂ nanosheets, suggesting the good reversibility and higher specific capacitances of the electrodes. Further, the values of specific capacitances at different scan rates as estimated from CV curves using equation (1) are tabulated in table 1.

The steady decrease in the specific capacitance at a higher scan rate can be attributed to the inadequate time for adsorption and diffusion of electrolyte ions at the electrode surface. The variation in specific capacitances of Ni(OH)₂ nanosheets and microflowers with respect to scan rates is shown in figure 3b and e, respectively. It is worth noting that even at higher scan rates (100 mV s⁻¹) Ni(OH)₂ microflowers retain about ~44% of the initial capacitance (417 F g⁻¹ at a scan rate of 5 mV s⁻¹) suggesting the prominent electrochemical stability of the electrodes.

The value of the specific capacitance of Ni(OH)₂ microflower electrodes is comparatively higher as compared with Ni(OH)₂ nanosheet electrodes. For instance at a scan rate of 5 mV s⁻¹, the obtained value of the specific capacitance

Figure 5. Cyclic stability of Ni(OH)₂ nanosheet and microflower electrodes.

for Ni(OH)₂ microflowers is 417 F g⁻¹, which is more than a twice as compared with Ni(OH)₂ nanosheets (180 F g⁻¹). The large difference in the specific capacitance maybe attributed to the higher specific surface area and pore size of the Ni(OH)₂ microflowers, which in turn enhances the adsorption and diffusion of electrolyte ions during the cyclic process.

Further, figure 3c and f depicts the GCD curves of Ni(OH)₂ nanosheets and microflowers. The deviation from the typical triangular charge–discharge profile confirms the pseudocapacitive nature of the electrodes. It can also be noted that the charge–discharge time of Ni(OH)₂ microflowers is higher as compared with Ni(OH)₂ nanosheets, which once again confirms the higher values of specific capacitances of the Ni(OH)₂ microflower electrodes as estimated from CV curves. For better comparison of the electrochemical performances, CV

Figure 6. (a, c) Nyquist plots of $\text{Ni}(\text{OH})_2$ nanosheets and microflowers and their corresponding Bode phase angle plots (b, d). (a, b) Reprinted from Bhat and Nagaraja [17], with the permission of AIP Publishing.

Table 2. Parameters obtained from the Nyquist plots of the electrodes.

EIS values	Nanosheets	Microflowers
R_S (Ω)	2.58	0.68
R_{CT} (Ω)	10.42	0.42

curves at a scan rate of 10 mV s^{-1} and GCD curves at a current density of 4 A g^{-1} are shown in figure 4a and b, respectively.

The cycle lifespan is one of the important parameters of supercapacitor applications. We have examined the electrochemical stability of the fabricated both $\text{Ni}(\text{OH})_2$ nanosheets and microflower-based electrodes through CV measurements at a scan rate of 50 mV s^{-1} for 1500 cycles. As shown in figure 5, the results indicate the specific capacitance retention of 76 and 82% for $\text{Ni}(\text{OH})_2$ nanosheets and microflowers, respectively, indicating the promising stability of the electrodes.

Finally, the interface behaviour of the $\text{Ni}(\text{OH})_2$ supercapacitor electrodes is characterized with the help of EIS measurements. EIS measurements were performed in the frequency range of 0.2 Hz–100 kHz, with the applied bias of 10 mV. Supercapacitors behave as resistors at high frequencies, drawing a kinetic arc and capacitive behaviour at low frequencies [31], presenting a vertical straight line [32]. The vertical straight line also indicates the prominent capacitance response and good electronic conductivity of the materials [33]. Figure 6a and c represents the recorded Nyquist plots and figure 6b and d depicts the Bode phase angle plot of $\text{Ni}(\text{OH})_2$ nanosheet and microflower electrodes.

The parameters extracted from the Nyquist plots consist of electrode resistance (R_S) and charge transfer resistance (R_{CT}). The lower R_S value indicates the better contact of electrodes with the electrolyte and the lower R_{CT} indicates the higher electronic conductivity and higher rate of adsorption/diffusion of electrolyte ions through the electrodes [34]. The value of R_{CT} is as low as 0.42Ω for $\text{Ni}(\text{OH})_2$ microflowers and the value of R_S is about three times

lower as compared with Ni(OH)₂ nanosheets, once again supporting the higher values of specific capacitances. The parameters extracted from the Nyquist plots are tabulated in table 2.

Further, the Bode phase angle is also the important parameter of the supercapacitors. Ideal capacitors display the phase angle of -90° , while the phase angle varies for pseudocapacitors [35]. The obtained phase angles are -75° and -85° for Ni(OH)₂ nanosheets and microflowers, which also confirm the pseudocapacitive charge storage mechanism of the electrodes.

3. Conclusion

In summary, Ni(OH)₂ nanostructures of two different morphologies (nanosheets and microflowers) were synthesized employing a hydrothermal method. When used as the electrodes for supercapacitors, the Ni(OH)₂ microflowers could deliver the enhanced specific capacitance of 417.4 F g^{-1} at a scan rate of 5 mV s^{-1} , which is more than twice as compared to Ni(OH)₂ nanosheets with a specific capacitance of 180 F g^{-1} . Both morphologies of Ni(OH)₂ exhibited good capacitance retention capability for 1500 CV cycles. The superior electrochemical performance of the nanostructures opens up interesting possibilities for the design and development of high-performance energy storage devices.

References

- [1] Serrano E, Rus G and García-Martínez J 2009 *Renewable Sustainable Energy Rev.* **13** 2373
- [2] Wang H, Feng H and Li J 2014 *Small* **10** 2165
- [3] Hu Y and Fisher T S 2018 *Bull. Mater. Sci.* **41** 124
- [4] Zhi M, Xiang C, Li J, Li M and Wu N 2013 *Nanoscale* **5** 72
- [5] Bhat K S and Nagaraja H S 2019 *Electrochim. Acta* **302** 459
- [6] Li W and Yang Y J 2014 *J. Solid State Electrochem.* **18** 1621
- [7] Gao Y, Wu J, Zhang W, Tan Y, Gao J, Tang B *et al* 2015 *J. Appl. Electrochem.* **45** 541
- [8] Periasamy P, Krishnakumar T, Sathish M, Chavali M, Siril P F and Devarajan V P 2018 *J. Mater. Sci.: Mater. Electron.* **29** 6157
- [9] Sichumsaeng T, Chanlek N and Maensiri S 2018 *Appl. Surf. Sci.* **446** 177
- [10] Bhat K S, Shenoy S, Nagaraja H S and Sridharan K 2017 *Electrochim. Acta* **248** 188
- [11] Chen C, Fan W, Ma T and Fu X 2014 *Ionics* **20** 1489
- [12] Tamai H, Hakoda M, Shiono T and Yasuda H 2007 *J. Mater. Sci.* **42** 1293
- [13] Kiran S K, Padmini M, Das H T and Elumalai P 2017 *J. Solid State Electrochem.* **21** 927
- [14] Aghazadeh M, Karimzadeh I, Ahmadi A and Ganjali M R 2018 *J. Mater. Sci.: Mater. Electron.* **29** 14567
- [15] Ghasemi S, Jafari M and Ahmadi F 2016 *Electrochim. Acta* **210** 225
- [16] Rajagopal R and Ryu K-S 2018 *J. Ind. Eng. Chem.* **60** 441
- [17] Bhat K S and Nagaraja H S 2018 *AIP Conf. Proc.* **1943** 020057
- [18] Anandan S, Gnana Sundara Raj B, Lee G-J and Wu J J 2013 *Mater. Res. Bull.* **48** 3357
- [19] Kovalenko V L, Kotok V A, Sykchin A A, Mudryi I A, Ananchenko B A, Burkov A A *et al* 2017 *J. Solid State Electrochem.* **21** 683
- [20] Chen Y, Zhang Z, Sui Z, Liu Z, Zhou J and Zhou X 2016 *Int. J. Hydrogen Energy* **41** 12136
- [21] Qu R, Tang S, Qin X, Yuan J, Deng Y, Wu L *et al* 2017 *J. Alloys Compd.* **728** 222
- [22] Wang H, Shi X, Zhang W and Yao S 2017 *J. Alloys Compd.* **711** 643
- [23] Zeng Z, Sun P, Zhu J and Zhu X 2017 *Surf. Interfaces* **8** 73
- [24] Ghosh D, Giri S, Mandal A and Das C K 2013 *Chem. Phys. Lett.* **573** 41
- [25] Bhat K S, Barshilia H C and Nagaraja H S 2017 *Int. J. Hydrogen Energy* **42** 24645
- [26] Karthik S B and Nagaraja H S 2018 *Mater. Res. Express* **5** 105504
- [27] Guan B, Li Y, Yin B, Liu K, Wang D, Zhang H *et al* 2017 *Chem. Eng. J.* **308** 1165
- [28] Bhat K S and Nagaraja H S 2018 *Int. J. Hydrogen Energy* **43** 19851
- [29] Kim S-I, Kang K-N, Kim S-W and Jang J-H 2014 *RSC Adv.* **4** 59310
- [30] Bu I Y Y and Huang R 2015 *Mater. Sci. Semicond. Process.* **31** 131
- [31] Portet C, Taberna P L, Simon P, Flahaut E and Laberty-Robert C 2005 *Electrochim. Acta* **50** 4174
- [32] Aurbach D 1998 *J. Electrochem. Soc.* **145** 3024
- [33] Musiani M M 1990 *Electrochim. Acta* **35** 1665
- [34] Zhu J, Xiang L, Xi D, Zhou Y and Yang J 2018 *Bull. Mater. Sci.* **41** 54
- [35] Biswal M, Banerjee A, Deo M and Ogale S 2013 *Energy Environ. Sci.* **6** 1249