

Electrochemical characteristics of nickel hydroxide/activated carbon nano composite for supercapacitors

Mok-Hwa Kim^a, Jae-Won Lee^b, Sun-Min Park^a and Kwang Chul Roh^{a,*}

^aEnergy Materials Center, Korea Institute of Ceramic Engineering & Technology, 233-5, Gasan-dong, Geumcheon-gu, Seoul 153-801, Korea

^bDepartment of Energy Engineering, Dankook University, Cheonan 330-714, Korea

Nickel hydroxide/activated carbon nanocomposite electrode material was successfully synthesized by a precipitation method. The activated carbon was prepared from isotropic pitch with chemical and electrochemical activation. Structural and morphological characterizations were performed using X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HR-TEM). The capacitive properties were evaluated by cyclic voltammetry (CV), charge/discharge, and electrochemical impedance spectroscopy (EIS) in 6M KOH aqueous electrolyte. The results showed that nano-sized nickel hydroxide was loaded on the surface of activated carbon. A specific capacitance of 277.8 Fg⁻¹ was obtained at a constant current of 1 mAcm⁻², indicating that the nickel hydroxide/activated carbon nanocomposite is a promising electrode material for supercapacitors.

Key words: Supercapacitor, Activated carbon, Nickel hydroxide, Nanocomposite.

Introduction

Supercapacitors are considered a promising candidate for energy storage due to high power performance, long cycle life, and low maintenance cost [1-3]. However, compared to rechargeable battery systems, supercapacitors still present a very significant drawback (i.e., the amount of energy density is relatively low) and preclude the extensive industrial utilization in energy storage [4-6]. Recently, asymmetric or hybrid supercapacitors, regarded as a trend in electrochemical capacitors, have been reported on. Asymmetric supercapacitors can be fabricated with one electrode of a double layer carbon material, and the other of a pseudocapacitance material [7]. Pseudocapacitive materials, such as hydroxides, oxides, and polymers, are being explored for producing supercapacitors with increased specific capacitances and a high energy density [8]. Noble metal-oxide based materials (e.g., ruthenium oxide) exhibiting Faradaic pseudo capacitance have also been identified as the ideal electrode materials for supercapacitors [9]. However, although the capacitive performance of ruthenium oxide is excellent, it is too expensive for commercialization. Most of the attention is, therefore, focused on alternative electrode materials that are inexpensive and exhibit capacitive behavior similar to that of ruthenium oxide [10-12]. Nickel

hydroxide is a good alternative material, which is cheap, easily synthesized, and exhibits good pseudo capacitive behavior, similar to that of the state-of-the-art supercapacitor material, ruthenium oxide [13].

Activated carbon is a feasible porous material for energy storage and electrochemical purposes because of its unique surface characteristics. The microstructure of activated carbon is expected to significantly affect the properties of the electric double layer formed on the surface between the electrode and the electrolyte solution. However, activated carbon has a limitation in terms of energy density [19].

In this work, the activation by potassium hydroxide was applied to the soft carbon derived from isotropic pitch to prepare a moderate surface area. In order to increase the energy density, nickel hydroxide/activated carbon nanocomposite was prepared by precipitation method. The well-distributed, nano-sized nickel hydroxide was loaded on the surface of activated carbons. The use of nanocomposite in high energy-density aqueous asymmetric supercapacitors has been demonstrated.

Experimental

Preparation of the activated carbon

The activated carbon (AC, Anshan Chemical Co. Ltd., China) was prepared from isotropic pitch. The pitch was carbonized at 600 °C for 1 hr in an N₂ atmosphere to prepare graphitizable carbon (soft carbon). The resulting soft carbon was mixed with small flakes of potassium hydroxide (KOH). KOH activation was carried out at 900 °C for 1 hr under an

*Corresponding author:
Tel : +82-2-3282-2463
Fax: +82-2-3282-2475
E-mail: rkc@kicet.re.kr

Ar flow, and the soft carbon/KOH ratio was at one to four by weight. The alkali-rich residual carbon was neutralized with hydrochloric acid (HCl) solution, filtered, and washed with distilled water until pH value reached 6-7. The resulting KOH-activated carbon was dried by heating in a vacuum.

Synthesis and characterization of the nickel hydroxide/activated carbon nanocomposite

Ni(OH)₂/AC nanocomposite was prepared by precipitation method. Firstly, activated carbon was treated in 1M nitric acid (HNO₃) solution for 4 hrs at room temperature. In typical synthesis, a stoichiometric amount of nitrate hexahydrate (Ni(NO₃)₂ · 6H₂O) was dissolved in distilled water to form a green homogeneous solution (1M). Predetermined amounts of Ni(NO₃)₂ solution were added to the activated carbon in HNO₃ solution. After stirring for 5 hrs, the pH of the mixture was slowly adjusted to 9 by a dropwise addition of 1M LiOH at room temperature. The obtained suspension was stirred at the same temperature for an additional 18 hrs and then filtered, washed with distilled water, and air-dried at 80 °C for 24 hrs.

The obtained products were characterized by X-ray diffraction (XRD) measurements (Rigaku, Dmax2500, Japan), high resolution-transmission electron microscope (HR-TEM, Jeol, JEM-2000EX, Japan) and field emission-scanning electron microscope (FE-SEM, Jeol, JSM-7000F, Japan).

Electrochemical activation and measurement

A beaker-type electrochemical cell was used for the electrochemical measurement and equipped with a working electrode, a platinum plate counter electrode, and a saturated calomel electrode (SCE) reference electrode. Working electrodes were prepared by mixing the active materials with 10 wt% carbon black, and 10 wt% polyvinylidene fluoride (PVDF) of the total electrode mass. A small amount of N-Methyl-2-pyrrolidone was added to this composite to make a more homogenous mixture, which was coated on titanium foil (area for 1 cm²). All the measurements were carried out in 6M KOH aqueous solution as electrolyte. For confirmation of the electrochemical activation formed in electrode under the initial charging state, we tried a charge-discharge cycle test by increasing the voltage from 0.6 V to 1.0 V with 0.1 V steps. The cyclic voltammetry (CV) behavior of the electrodes was measured by means of electrochemical analyzer systems, VSP (Biologic, France). Electrochemical impedance spectroscopy measurements were performed in an a.c. frequency ranging from 100 mHz to 100 kHz with an excitation signal of 5 mV. All the electro-chemical experiments were carried out at room temperature and the potentials were recorded to SCE.

Results and Discussion

Characterization of materials

The crystal structures of AC and Ni(OH)₂/AC nanocomposite were characterized using an X-ray diffractometer. The pure activated carbon (Fig. 1 (a)) shows the major diffraction peak at $2\theta = 20.1$ and 43.4° . The diffraction peaks of the Ni(OH)₂/AC nanocomposite appeared at $2\theta = 15.7, 33.1, 38.6,$ and 59.4° . It is well-known that Ni(OH)₂ has two types of polymorphs, α - and β -Ni(OH)₂. β -Ni(OH)₂ is clearly identified by the diffraction peak at $2\theta = 19.2^\circ$ and α -Ni(OH)₂, because of the disordered structure of this species, is more difficult to characterize but should show a broader peak between $2\theta = 15$ - 20° , as shown in Fig. 1(b).

Fig. 2 shows the FE-SEM images of Ni(OH)₂/AC nanocomposite with the energy-dispersive X-ray spectra (EDS). The FE-SEM images of Ni(OH)₂/AC nanocomposite (Fig. 2(a)-(b)) clearly show that the Ni(OH)₂ is distributed homogeneously on the surface of the activated carbon, and that some particles fill the inner big pores of activated carbon. The EDS taken on the square area in Fig. 2(b) gives proof of the existence of Ni, O, and C elements. The content of carbon is 79.8 wt.%, calculated according to the EDS result.

A HR-TEM image of the Ni(OH)₂/AC nanocomposite is given in Fig. 3(a), in which inhomogeneous distribution of small dark dots are clearly discernible. The Ni(OH)₂ nanocrystals are distributed over the whole observed area, although their concentration varies remarkably. The size of the individual nanocrystals ranges from 5 to 20 nm. Fig. 3(b) shows NiO nanoparticles formed by the electron beam around a very thin edge of Ni(OH)₂ during TEM observation. These nanoparticles are 5-10 nm in size. The d-spacing was calculated to be 2.078 Å, corresponding to the (200) planes of a NiO structure.

Electrochemical characterization of Ni(OH)₂/AC nanocomposite

Electrochemical activation discharge profiles while increasing the voltage with a Ni(OH)₂/AC nanocomposite

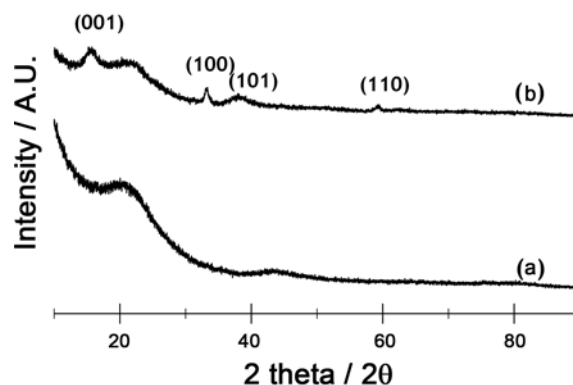


Fig. 1. X-ray diffraction patterns of (a) activated carbon and (b) nickel hydroxide/activated carbon nanocomposite.

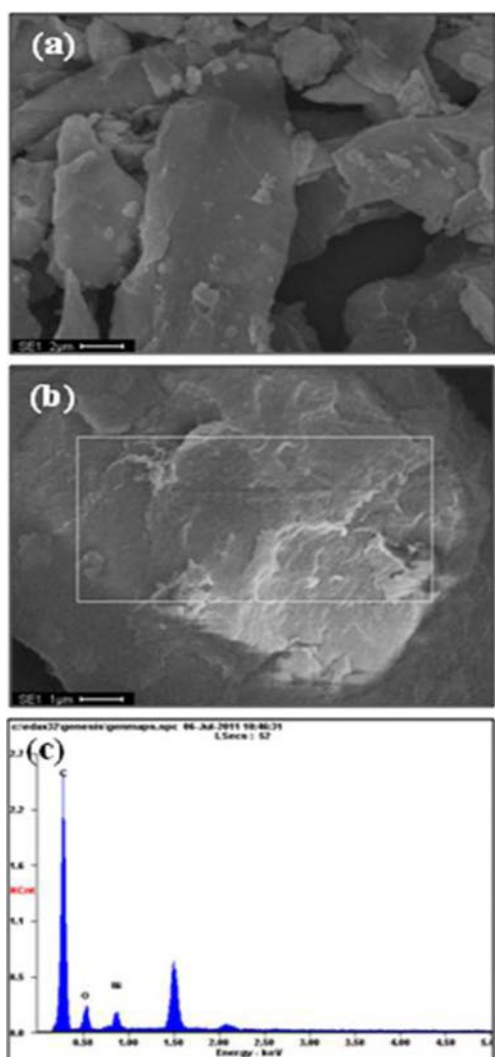


Fig. 2. FE-SEM images and EDX spectrum of nickel hydroxide/activated carbon nanocomposite. (a, b) FESEM images of nickel hydroxide/activated carbon sample, (c) EDX spectrum taken from the square area in (b).

electrode are shown in Fig. 4. Sequential test was conducted by changing the applied voltage, in 0.1 V steps, from 0.6 V to 1.0 V with 1 mAcm^{-2} current density at room temperature. During the sequential charge-discharge procedure, the discharging time increased in proportion to the increasing voltage (from 0.6 V to 0.8 V). In contrast, the discharging time rose to 0.9 V, and then increased very rapidly to 1.0 V. Such a profile may suggest a structural change in activated carbon at above 0.9 V. The phenomenon observed on the activated carbon has been explained by electrochemical activation. The ions in the electrolyte were intercalated during the charging process into the interlayer of partially graphitized carbon structure; and during the discharging process, the excess ions were de-intercalated. The capacitance increases irreversibly as the charging-discharging cycles are repeated. After that, the potential capacitance of material is realized.

Fig. 5 shows the CV curves of the $\text{Ni}(\text{OH})_2/\text{AC}$

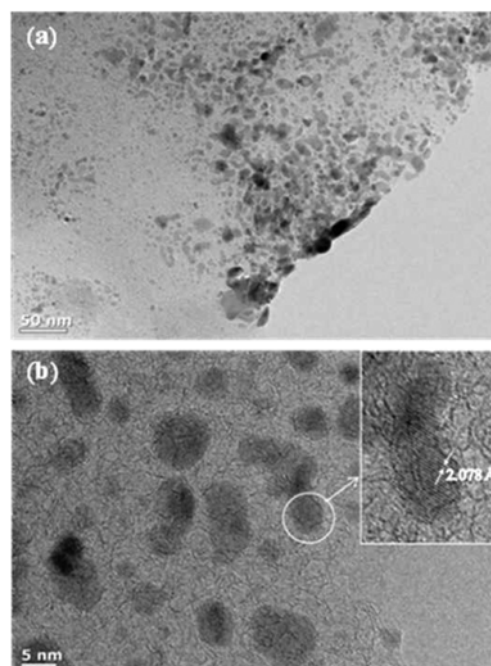


Fig. 3. HR-TEM images of nickel hydroxide/activated carbon nanocomposite. (a) HR-TEM image taken from a very thin edge after irradiation with an intense 400 kV electron beam and (b) NiO nanoparticles formed by electron beam during TEM observation.

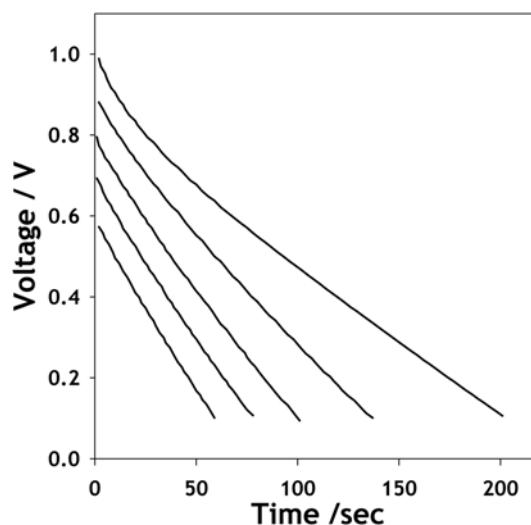


Fig. 4. The electrochemical activation discharge profile. Sequential test by charging the applied voltage (0.1 V) step, from 0.6 V up to 1.0 V, with 1 mAcm^{-2} current density.

nanocomposite electrode at different scan rates in 6 M KOH electrolyte solution. As can be seen in Fig. 5, the redox peaks were observed at a wide range of voltage. The two redox reaction peaks are responsible for the pseudo capacitance. One peak is anodic (positive current density) during the oxidation reaction of Ni^{2+} to Ni^{3+} , and the other is cathodic (negative current density) during the reverse process. These peaks represent fast and reversible redox processes that occur at the interface of $\text{Ni}(\text{OH})_2$ and the electrolyte. This indicates that the capacitance characteristics are

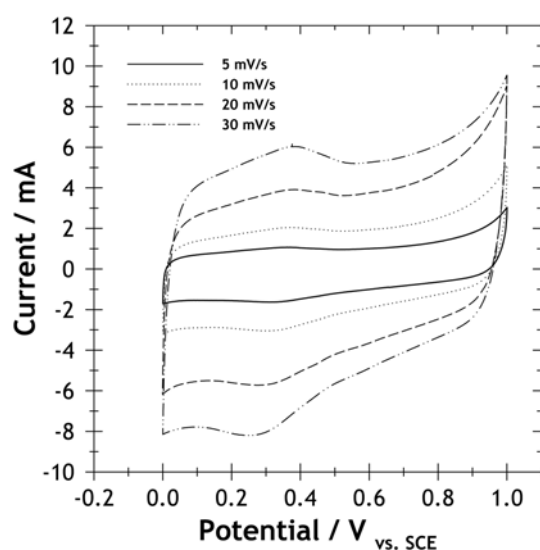


Fig. 5. Cyclic voltammograms of nickel hydroxide/activated carbon nanocomposite electrode within a potential window of 0.0–1.0 V (vs. SCE) at a different scan rate (5, 10, 20, and 30 mVs⁻¹).

Table 1. Summaries of specific capacities of the nickel hydroxide/activated carbon nanocomposite based on total weight.

Sample	Specific capacitance (Fg ⁻¹)	Specific capacitance (Fg ⁻¹) Scan rate (mVs ⁻¹)				
		1	5	10	20	30
Ni(OH) ₂ /AC	277.8	265.8	231.1	217.4	210.8	188.2

mainly governed by Faradaic reactions and not only by electric double layer capacitance. Since solution and electrode resistance can distort current response at the switching potential, and this distortion is dependent upon the scan rate, the shape of the CV changed appreciably with the scan rate increase. However, the CV of Ni(OH)₂/AC nanocomposite indicated that the composite shows excellent electro-chemical behavior as an electrode of super-capacitor. The specific capacitances (calculated based on the total weight of the active materials in the supercapacitor) for Ni(OH)₂/AC nanocomposite are listed in Table 1. At scan rates of 1, 5, 10, 20, and 30 mVs⁻¹, the composite electrodes showed 265.8, 231.1, 217.4, 210.8, and 188.2 Fg⁻¹ of specific capacitance, respectively. With the scan rate increasing to 30 mVs⁻¹, the specific capacitance decreases. Since current must pass in the cell to accomplish this work, the resistance of the solution to charge movement (i.e., current) will be responsible for a potential drop between the electrodes in the cell, called the Ohmic drop. This phenomenon may be explained by referring to OH⁻ ion diffusion processes during the charging/discharging for the electrode. When the electrode at high sweep rates corresponds to a high current density, massive OH⁻ ions are required to redox reaction swiftly at the interface of the electrode/electrolyte. However, relatively low

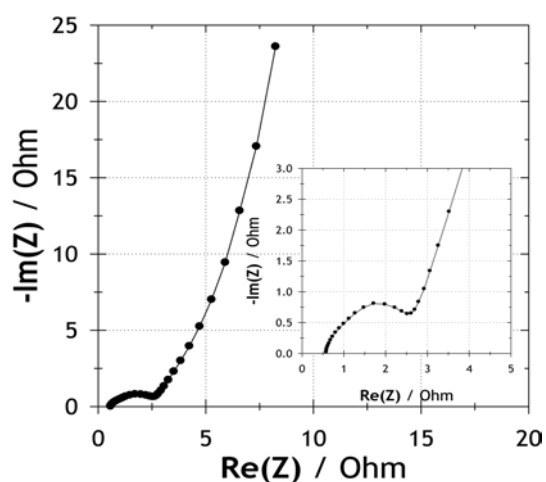


Fig. 6. The complex plane impedance plot of nickel hydroxide/activated carbon nanocomposite electrode (the insert presents the high frequency region of the plot).

concentration of OH⁻ ions could not meet this demand, and the processes would be controlled by the ion diffusion [7].

In order to investigate the electrochemical characteristics at the electrode/electrolyte interface in detail, a.c. impedance spectroscopic measurements were performed. Figure 6 shows the Nyquist plots for the composite electrode, where Re(Z) and -Im(Z) are the real and imaginary parts of the impedance, respectively. For the nanocomposite of Ni(OH)₂/AC, its impedance showed two overlapping semicircles. The higher-frequency semicircle would be primarily associated with pure AC (taking into account the fact that lower-frequency semicircle corresponds to Ni(OH)₂ nanoparticles on the surface of AC). This shows that Ni(OH)₂/AC nanocomposite electrodes in the present study are highly electronic conductive. At low frequencies, the slope of the impedance plot increases and tends to become purely capacitive, which demonstrates that the electrochemical capacitance of this material is higher.

Conclusions

The precipitation method for preparing the nickel hydroxide/activated carbon nanocomposite electrode materials for supercapacitors was investigated. The XRD analysis indicated that amorphous particles of α -Ni(OH)₂ were loaded on the activated carbon. The FE-SEM and HR-TEM studies reveal that activated carbon was loaded with 5–20 nm nanocrystals of nickel hydroxide. Electrochemical tests demonstrate that the nickel hydroxide/activated carbon nanocomposite electrodes have good electrochemical capacitance of 277.8 Fg⁻¹. Considering low cost of the starting materials, simple preparation method, and the high specific capacitance, α -Ni(OH)₂/activated carbon nanocomposite electrode materials are believed to be promising material for supercapacitor applications.

Acknowledgements

This work was supported by the Energy Efficiency and Resources R & D program (No.20112020100070) and the Advanced Technology Center program (No.10035919) under the Ministry of Knowledge Economy, Republic of Korea.

References

1. P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845.
2. R. Kotz., M. Carlen, *Electrochim. Acta.* 45 (2000) 2483.
3. A. Burke, *J. Power Sources.* 91 (2000) 37.
4. J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.
5. D. Michell, D.A.J. Rand, R. Woods, *J. Electroanal. Chem.* 89 (1978) 397.
6. J.K. Park, O.O. Park, K.H. Shin, C.S. Jin, J.H. Kim, *Electrochem. Solid St.* 5 (2002) H7.
7. J.Q. Lang, L.B. Kong, M. Liu, Y.C. Luo, L. Kang, *J. Solid State Electr.* 14 (2010) 1533.
8. H. Wang, H.S. Casalongue, Y. Liang, K. Dai, *J. Am. Chem. Soc.* 132 (2010) 7472.
9. Q. Huang, X. Wang, J. Li, C. Dai, A. Gambia, P.J. Sebastian, *J. Power Sources.* 164 (2007) 425.
10. F. Portemer, A. Delahaye-Vidal, M. Fidlaz, *J. Electrochem. Soc.* 139 (1992) 671.
11. A. Audemer, A. Delahaya, R. Farhi, N. Sac-Epee, J.M. Tarascom, *J. Electrochem. Soc.* 144 (1997) 2614.
12. M. Oshitani, K. Takashima, S. Tsuji, *J. Appl. Electrochem.* 16 (1986) 403.
13. J. Zhang, L.B. Kong, J.J. Cai, H. Li, Y.C. Luo, L. Kang, *Micropor. Mesopor. Mat.* 132 (2010) 154.
14. Y.G. Wang, L. Yu, Y.Y. Xia, *J. Electrochem. Soc.* 153 (2006) A743.
15. H. Li, Y. Li, R. Wang, O. Cao, *J. Alloy Compd.* 481 (2009) 100.
16. N.W. Duffy, W. Balasin, A.G. Pandolfo, *Electrochim. Acta.* 54 (2008) 535.
17. J.Q. Lee, J.M. Ko, J.D. Kim, *J. Phys. Chem. C.* 115 (2011) 19445.
18. M. Takeuchi, T. Maruyama, K. Koike, A. Mogami, T. Oyama, K. Kobayashi, *Electrochemistry.* 69 (2001) 487.
19. S. Mitani, S.I. Lee, S.H. Yoon, Y. Korai, I. Mochida, *J. Power Sources.* 133 (2004) 298.