Journal of Vasyl Stefanyk Precarpathian National University
http://jpnu.pu.if.ua
Vol. 3, No. 1 (2016), 23-28

UDC 541.1, 5367, 621.794
PACS numbers: 75.75.Cd, 76.80.+y
doi: 10.15330/jpnu.3.1.23-28

THE STRUCTURE OF THE ELECTRODE MATERIAL BASED ON $Ni(OH)_2$/C COMPOSITE FOR ENERGY STORAGE DEVICES

O.M. KHEMIY, L.S. YABLON, I.M. BUDZULYAK, O.V. MORUSHKO

Abstract. The paper presents the results of studies of the structure β-$Ni(OH)_2$/C composite. It is shown that the XRD-pattern of heated composite β-$Ni(OH)_2$/C has a broad diffraction peak at 23°, which can be attributed to the activated carbon in addition to peaks characteristic for NiO.

Keywords: nickel hydroxide, activated carbon, thermogravimetry, X-ray analysis, galvanostatic and potentsiodynamic methods, the accumulation of charge.

1. INTRODUCTION

The specific capacitance of electrochemical capacitors (ECs) is one of the basic characteristics that define the area of their use. Therefore, the main efforts of researchers are focused at finding new methods and materials that facilitate the achievement of this goal. The idea of using hybrid systems and materials for electrodes that provide fast reversible Faradaic reactions is the most promising. It can be used in EC with pseudocapacitance accumulation of energy [1]. Currently ECs are formed from such oxides as ruthenium and iridium, but they are not used commercially due to the high cost.

Among the cheap and available electrode materials, nickel hydroxide ($Ni(OH)_2$) is of particular interest. There are two polymorphs of the nickel hydroxides [2], which are denoted as α-$Ni(OH)_2$ and β-$Ni(OH)_2$, respectively. β-phase $Ni(OH)_2$ is isostructural with brucite $Mg(OH)_2$. Since this material has trigonal symmetry, it should be noted that the a- and b-axis in Fig. 1 is not orthogonal, and the angle between them is 120°.Although α - phase has a higher theoretical capacitance, but it is unstable in alkaline and fast becomes more stable β-$Ni(OH)_2$ [3].

In addition to the two fundamental phases of nickel hydroxide there are several possible types of structural disorder, including the incorporation of foreign ions, defects in the crystal lattice and others [4]. The effects of structural disorder can have very important practical implications, particularly, well-crystallized β-$Ni(OH)_2$ has a lower electrochemical activity than disordered β-$Ni(OH)_2$ [5]. Nowadays these materials are widely used, particularly in supercapacitors [6], photocatalysis [7] and electrochemical sensors [8].

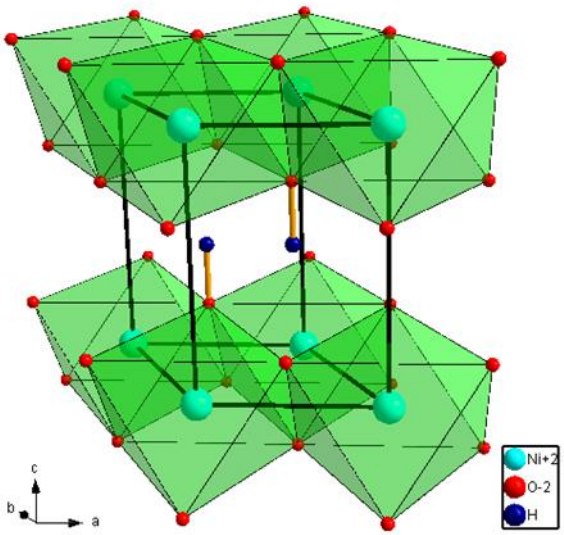

Fig. 1. The crystal structure of β-Ni(OH)₂.

2. METHODS AND MATERIALS

Nickel hydroxide and its composite with nanoporous carbon as electrode material of energy storage devices are studied. In this composite activated carbon reduces specific resistance and increases the power density. Activated carbon and β-Ni(OH)₂ was thoroughly mixed and then was heated at 50°C / min. in air to a temperature of 325°C, which was kept for 30 minutes. The choice of the temperature was determined that at this temperature the decomposition of β-Ni(OH)₂ to nickel oxide and water occurs [9]. Cooling of composite was carried out in mode excluded oven. The crystal structure of nickel hydroxide and Ni(OH)₂/C composite was studied using X-ray diffraction analysis (CuKα - radiation) in the range of angles $10° < 2\theta < 90°$. The method of thermogravimetry was used for the above given samples during their heated in the temperature range 20 - 800°C in air with a heating rate of 10°C / min. This method was used to understand the change of mass and heat, and, accordingly, the optimum temperature of forming the composite. Researches were conducted simultaneous thermal analyzer STA 449 F3 Jupiter. Empty crucible of Al_2O_3 was used as a comparative standard. The sample was heated with a reference sample and current temperature of the sample and difference of the temperature between the sample and standard were recorded. This allows to fix processes associated with absorption or release of energy.

3. RESULTS AND DISCUSSION

Fig. 2 shows XRD pattern of the initial Ni(OH)₂ and Ni(OH)₂/C composite. It can be seen from Fig. 2 that all of the diffraction peaks can be indexed to a pure hexagonal structure of β-Ni(OH)₂ ($P\bar{3}m1$), no diffraction peaks from impurities are found in the sample. According to the Debye-Scherrer formula, the calculated grain sizes are 14.9 nm, which is in accordance with the reported values [10]. In the case of composite, diffraction peaks are wider and have lower intensity, which indicates the presence of amorphous activated carbon.

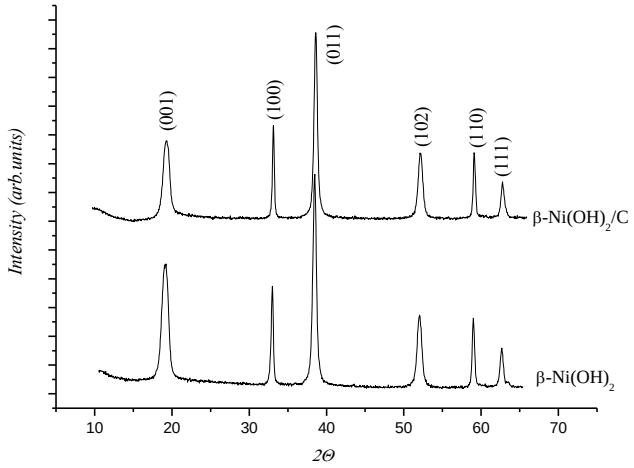

Fig. 2. XRD pattern of the initial $Ni(OH)_2$ and $Ni(OH)_2$/C composite.

Thermal behavior of β-$Ni(OH)_2$ was investigated using thermogravimetric (TG) and differential thermal analysis (DTA). As shown in Fig. 3 (curve TG) weight of β-$Ni(OH)_2$ decreases rapidly at temperatures of 285 - 325°C, with a 22% weight loss. It is known [9] that the decomposition of β-$Ni(OH)_2$ to NiO and water occurs in the range of temperature 298 - 340°C. As a result, residue can reasonably be ascribed to NiO. The DTA curve (Fig. 3) showed endothermic peak with a maximum located at 320°C, which is consistent with the weight loss of the material.

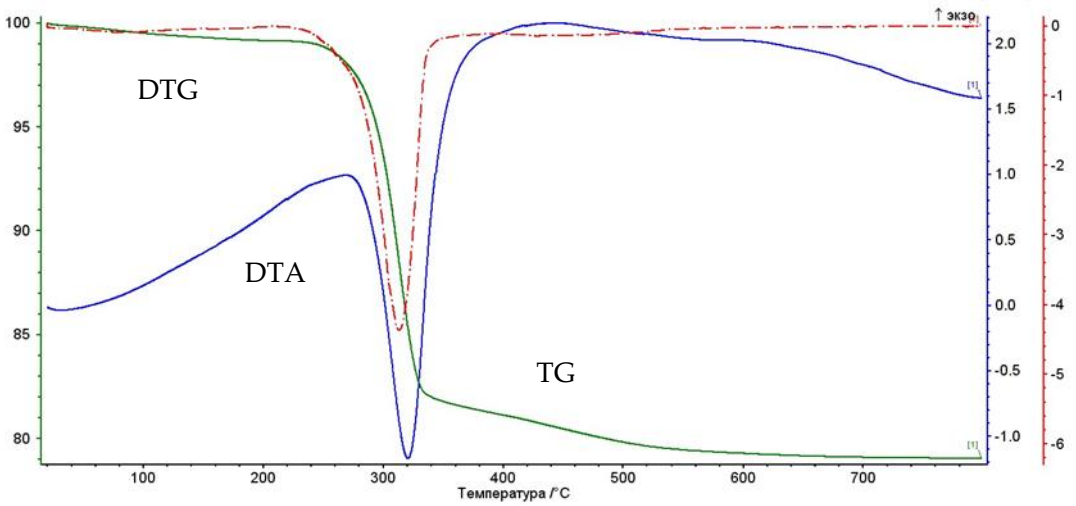

Fig. 3. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) curves of β-$Ni(OH)_2$.

The composition and phase purity of β-$Ni(OH)_2$, heated at 325°C was investigated using X-ray diffraction analysis (Fig. 4). According to XRD pattern, after heating only face-centered cubic structure NiO was formed ($Fm\bar{3}m$). Thus β-$Ni(OH)_2$ is completely converted to NiO after heating to 325°C.

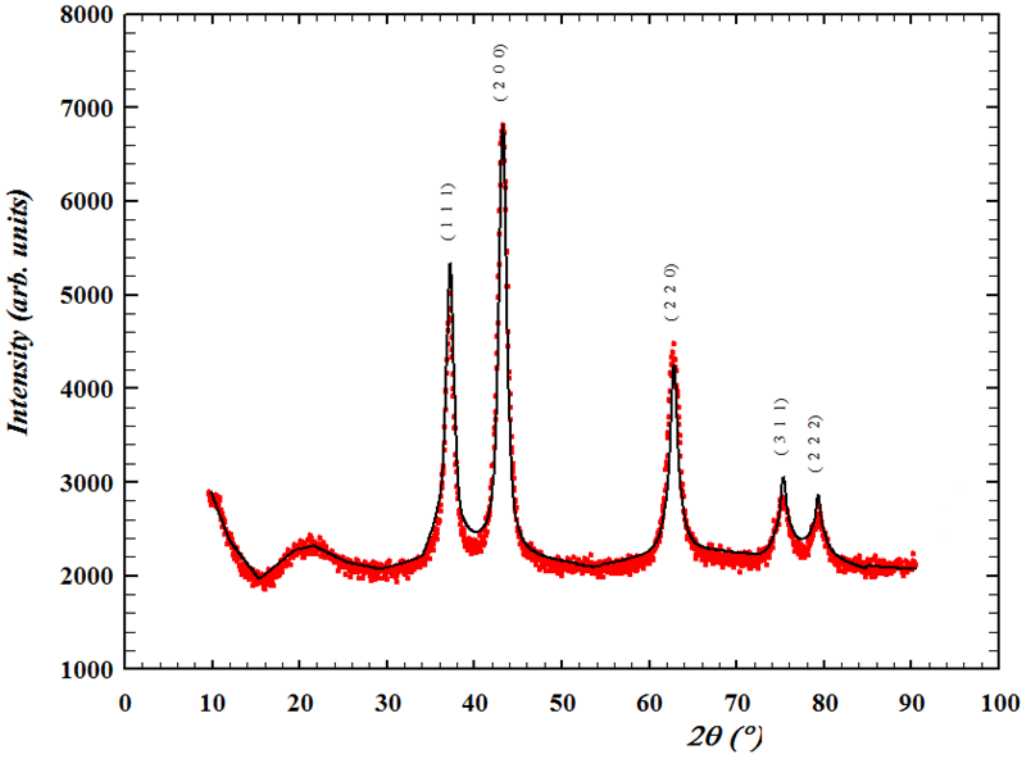

Fig. 4. XRD pattern of the β-Ni(OH)₂ heated to a temperature of 325°C (phase NiO).

β-Ni(OH)₂/C composite underwent a two-step weight loss due to dehydration and decomposition (Fig. 5). The two endothermic peaks at 130 and 325°C on the DTA curve are indicative of two successive stages of these physical-chemical changes during the heat treatment. The initial weight loss to 140°C is attributed to the loss of surface adsorbed water. The weight loss in the range of 140 - 280°C is due to the removal of the crystalline water molecules.

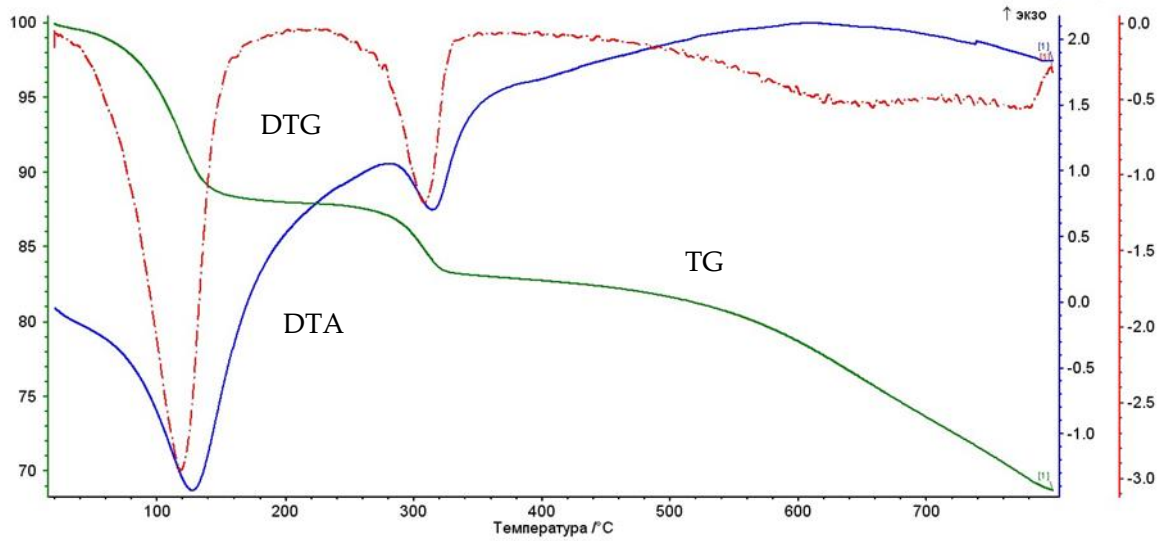

Fig. 5. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) curves of β-Ni(OH)₂/C composite.

There is a broad diffraction peak at 23° (Fig. 6) in XRD-pattern of heated composite, which can be attributed to activated carbon.

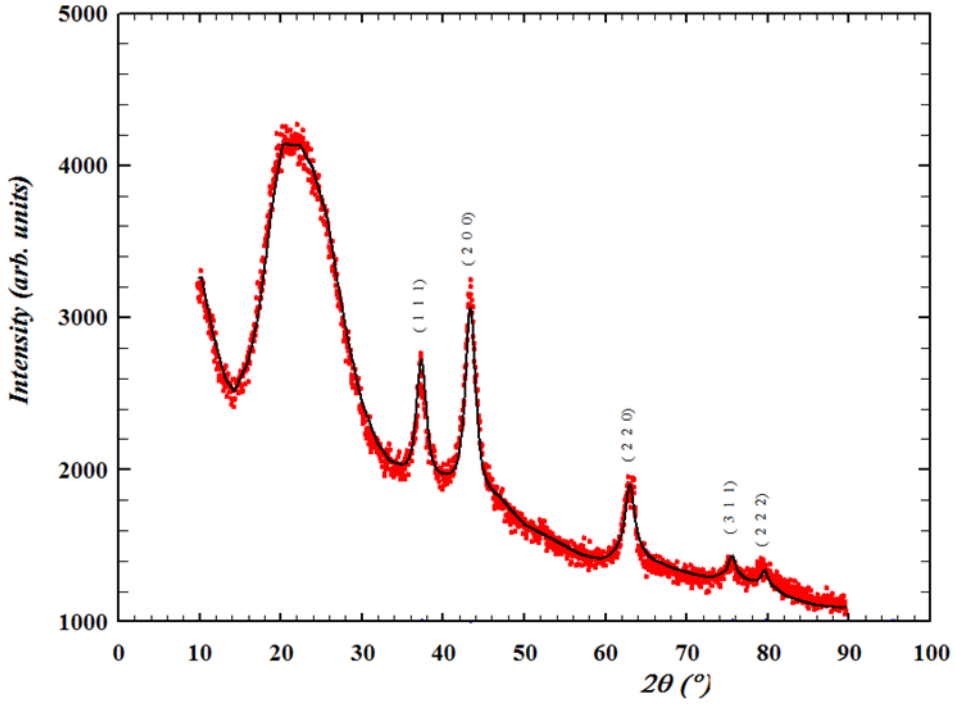

Fig. 6. XRD pattern of the β-Ni(OH)₂ / C composite heated to a temperature of 325 ° C.

Based on DTA and TG curves was found that the original weight of β-Ni(OH)₂ and the composite material decreases rapidly in the temperature range 285 - 325°C, which is associated with the formation of a stable residue of NiO. This is confirmed by X-ray diffraction analysis. XRD pattern heated Ni(OH)₂/C composite shows that there is a broad diffraction peak at 23°, which can be attributed to the activated carbon, besides the peaks characteristic of NiO.

4. CONCLUSIONS

It is assumed that the weight loss of nickel hydroxide and composite β-Ni(OH)₂/C decreases rapidly in the temperature range 285-325°C, due to the decomposition β-Ni(OH)₂ and the formation of a stable nickel oxide. It is shown that the XRD-pattern of heated composite β-Ni(OH)₂/C has a broad diffraction peak at 23°, which can be attributed to the activated carbon in addition to peaks characteristic for NiO.

REFERENCES

[1] Khomenko V., Raymundo-Piñero E., Frackowiak E., Béguin F. High-voltage asymmetric supercapacitors operating in aqueous electrolyte. *Applied Physics A.*, **82** (4) (2006), 567-573. doi: 10.1007/s00339-005-3397-8

[2] McEwen R.S. Crystallographic studies on nickel hydroxide and the higher nickel oxides. *Journal of Physical Chemistry*, **75** (12) (1971), 1782–1789. doi: 10.1021/j100681a004

[3] Oliva P., Leonardi J., Laurent J.F., Delmas C., Braconnier J.J., Figlarz M., et al. Review of the structure and the electrochemistry of nickel hydroxides and oxy-hydroxides. *Journal of Power Sources*, **8** (2) (1982), 229-255. doi: 10.1016/0378-7753(82)80057-8

[4] Hall D.S., Lockwood D.J., Poirier S., Bock C., MacDougall B.R. Raman and Infrared spectroscopy of α and β phases of thin nickel hydroxide films electrochemically formed on nickel. *Journal of Physical Chemistry*, **116** (25) (2012), 6771–6784. doi: 10.1021/jp303546r

[5] McBreen J. *Nickel hydroxides*. In: Daniel C., Besenhard J.O. (Eds.) Handbook of battery materials. 2011, 149–168. doi: 10.1002/9783527637188.ch5

[6] Aghazadeh M., Ghaemi M., Sabour B., Dalvand S. Electrochemical preparation of α-$Ni(OH)_2$ ultrafine nanoparticles for high-performance supercapacitors. *Journal of Solid State Electrochemistry*, **18** (6) (2014), 1569–1584. doi: 10.1007/s10008-014-2381-7

[7] Ran J., Yu J., Jaroniec M. $Ni(OH)_2$ modified CdS nanorods for highly efficient visible-light-driven photocatalytic H2 generation. *Green Chemistry*, **13** (10) (2011), 2708–2713. doi: 10.1039/C1GC15465F

[8] Fan Y., Yang Z., Cao X., Liu P., Chen S., Cao Z. Hierarchical macro-mesoporous $Ni(OH)_2$ for nonenzymatic electrochemical sensing of glucose. *Journal of. Electrochemical Society*, **161** (10) (2014), B201–B206. doi: 10.1149/2.0251410jes

[9] Shangguan E., Chang Z., Tang H., Yuan X.Z., Wang H. Synthesis and characterization of high-density non-spherical $Ni(OH)_2$ cathode material for Ni-MH batteries. *International Journal of Hydrogen Energy*, **35** (18) (2010), 9716-9724. doi:10.1016/j.ijhydene.2010.06.096

[10] Rifaya Nowsath M., Theivasanthi T., Alagar M. Chemical Capping Synthesis of Nickel Oxide Nanoparticles and their Characterizations Studies. *Nanoscience and Nanotechnology*, **2** (5) (2012), 134-138. doi: 10.5923/j.nn.20120205.01

Address: O.M. Khemiy, L.S. Yablon, I.M. Budzulyak, O.V. Morushko, Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano- Frankivsk, 76018, Ukraine.
E-mail: olchuk1991@mail.ru; yablon_lyubov@ukr.net; ivan-budzulyak@ukr.net; morushko@rambler.ru.
Received: 12.02.2016; **revised:** 10.04.2016.

Хемій О.М., Яблонь Л.С., Будзуляк І.М., Морушко О.В. Структура електродного матеріалу на основі композиту гідроксид нікелю / вуглець для пристроїв накопичення заряду. *Журнал Прикарпатського університету імені Василя Стефаника*, **3** (1) (2016), 23–28.

У роботі представлено результати досліджень структури композиту β-$Ni(OH)_2$/C. Показано, що на дифрактограмах спеченого композиту β-$Ni(OH)_2$/C крім піків характерних для NiO, спостерігається широкий дифракційний пік на 23°, який може бути віднесений до активованого вугілля.

Ключові слова: гідроксид нікелю, активований вуглець, термогравіметрія, Х-променевий аналіз, гальваностатичний та потенціодинамічний методи, накопичення заряду.