

Highly Porous Carbon Materials Filled with Nickel Hydroxide Nanoparticles; Synthesis, Study, Application in Electrochemistry

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PCM – porous carbon matrix;

XRD – X-ray diffraction;

XRF – X-ray fluorescence;

SEM – scanning electron microscope;

EDL – electrical double layer;

NC – nanostructured composite.

Abstract

Nickel hydroxide was deposited on the surface of the porous carbon to obtain a cathode material for supercapacitors. This work is the first part of the study of Ni(OH)₂/C composite, which considers the conditions of its synthesis using two types of porous carbon matrices with a highly developed specific surface area (1000–3000 m²/g) and two types of precursors (NiCl₂·6H₂O and Ni(N₃)₂). The morphology of the systems, in particular the shape and size characteristics of the hydroxide filler particles, was examined using the scanning electron microscopy, X-ray diffraction, and nitrogen adsorption-desorption at 77 K. The measurements of capacity of the Ni(OH)₂/C-electrodes were made in 6 M KOH using an asymmetric two-electrode cell (a porous carbon material with known electrode characteristics was employed as the counter electrode). The capacity was shown to decrease by 22–56% with increasing the scanning rate from 10 to 80 mV/s. A maximum capacity of the composite was obtained at a scanning rate of 10 mV/s was 346 F/g.

1. Introduction

There is an ever growing interest in the development of new nanostructured composite materials for the electrodes for energy storage devices, in particular supercapacitors [1–3]. Nickel hydroxide is a promising material for chemical current sources because it has a high theoretical capacity [4], but macrocrystalline nickel hydroxide has some drawbacks [5]. To overcome these drawbacks, small size Ni(OH)₂ crystallites were deposited on graphene [6, 7], foamed graphite [8], foamed nickel [9] and other electroconductive substrates, which makes it possible to obtain electrode materials with high specific characteristics (specific capacity, specific power, and cyclability) due to enhanced ionic transport to the surface of active substance from the bulk of electrolyte, development of the electrode surface, an increased cell conductance, etc. [10]. The formation of nickel hydroxide crystallites as lamellar particles with thickness less than 10 nm on the highly developed surface (for example, on graphene [11])

facilitates electrode processes in the bulk of active material. Thus, the synthesis of carbon materials combining high specific surface areas and porous 3D structure and the use of such material as the supports for electrochemically active nanoparticles (in particular Ni(OH)₂) are quite a promising line in the creation of materials for reversible (Faraday) electrodes.

2. Experimental

2.1. Materials and matrices

NiCl₂·6H₂O (99%) or Ni(N₃)₂, which were obtained by two-stream crystallization from aqueous solutions of sodium azide (99.5%) and nickel chloride, were used as the nickel hydroxide precursors. An alkali was represented by NaOH (99%). The corresponding salts were dissolved in distilled water.

Two types of porous carbon matrices (PCM) were employed: 1) natural oxidized carbon (coal mine Shestaki, Russia) was deashed [12], mechanically mixed with an alkali (KOH, 99%) in a ball

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mill at the alkali/carbon ratio equal to 2/1, and subjected to high-temperature activation [13] to obtain the so-called Carbonizat; 2) a hydroquinone/furfural mixture (1/1) was carbonized with simultaneous high-temperature activation of the alkali [14] to obtain the so-called Kemerit.

2.2. Composite materials preparation

A PCM sample was impregnated with an aqueous solution of nickel salt with a specified concentration and dried to a constant mass. After that, the impregnated PCM was placed in an aqueous solution of alkali heated to 80 °C and held at this temperature for 30 min. The samples were then washed to neutral pH and dried in a vacuum drying oven for 8 h. The composites that were synthesized by the indicated procedure from a chloride precursor on Carbonizat matrix are denoted as HNi-HI/Carbonizat (HNi is nickel hydroxide; HI or Az is the chloride or azide precursor, respectively; Carbonizat or Kemerit is the corresponding carbon matrix). The concentration of nickel hydroxide in all the samples was (40 ± 1) wt. %.

2.3. Composite materials characterization

X-ray diffraction analysis of the composites was carried out on a DIFRAY-401 X-ray diffractometer with iron radiation. Positions of the reflections were determined using the PDF database. Sizes of nickel hydroxide crystallites were calculated using the

Scherrer-Selyakov method with approximation of reflection profiles by the Cauchy function [15]. The morphology and elemental composition were studied on a Jeol JSM 6390 scanning electron microscope equipped with a jed 2300 attachment for X-ray fluorescence analysis. Pore structure of the composites and PCM was examined on a Micromeritics ASAP-2020 instrument using nitrogen adsorption-desorption at 77 K. Electrode characteristics were measured on a Parstat 4000 device using an asymmetric two-electrode cell (a porous carbon material with known electrode characteristics was employed as the counter electrode) in a 6 M KOH solution at a potential window (−1;1) V. Capacity was calculated from the area of CV curves according to [16].

3. Results and Discussion

3.1. Data of the SEM and XRD characterization

As follows from typical micrographs of the composites (Fig. 1a), nickel hydroxide covers quite uniformly the carbon matrix surface. At a x10000 magnification (Fig. 1b) one can see that the hydroxide has a developed pore structure, which should facilitate the penetration of electrolyte into the bulk of the composite. The XRF data (Fig. 1c) indicate a high purity of the produced composites (the total content of impurities does not exceed 1 wt.%), although Carbonizat matrix was obtained from inexpensive natural feedstock.

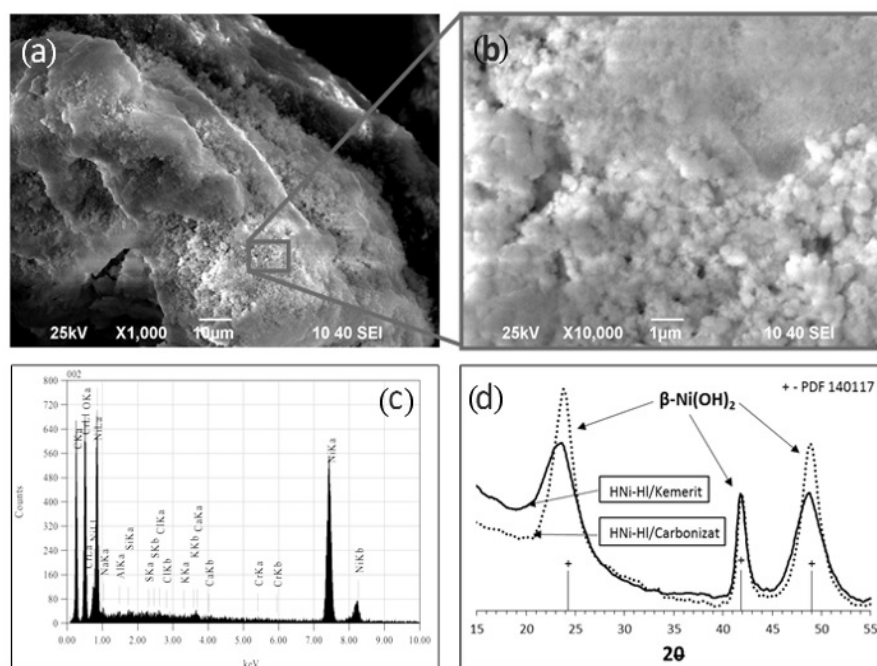


Fig. 1. Surface of the HNi-HI/Kemerit sample at a x1000 magnification (a); a section of the surface at a x10 000 magnification (b); X-ray fluorescence spectrum of the HNi-Az/Carbonizat sample (c); diffraction patterns of the HNi-HI/Kemerit and HNi-HI/Carbonizat samples (d).

Diffraction patterns of the composites synthesized on different matrices (Carbonizat or Kemerit) are shown in Fig. 1d. Anisometricity of nickel hydroxide reflections points to the lamellar structure of the crystallites. Positions of the reflections correspond to the PDF 140117 standard for β -Ni(OH)₂ [17]. Crystallite sizes calculated from the broadening of main reflections are listed in Table 1. It is seen that the thickness of nickel hydroxide nanocrystallites is 3–5 nm; so, these materials are promising for the use as the electrodes in high-power chemical sources of electric energy. The ratio of length (along the 100 face) to thickness (along the 001 face) of nickel hydroxide crystallites characterizes the degree of lamellation. This ratio is greater for the crystallites that formed on the surface of Kemerit matrix as compared to those on Carbonizat matrix. A possible reason is the difference in specific surface areas of the matrices. The difference is more pronounced for the hydroxide obtained from the “chloride” precursor.

Table 1

Parameters of nickel hydroxide crystallites in NC

Specimen	D ₀₀₁ , nm	D ₁₀₀ , nm	D ₁₀₀ /D ₀₀₁
HNi-HI/Carbonizat	4.7	22.0	4.7
HNi-Az/Carbonizat	4.1	25.0	6.1
HNi-HI/Kemerit	3.2	24.0	7.5
HNi-Az/Kemerit	4.5	30.0	6.7

3.2. Parameters of the porous structure

Figure 2 shows the nitrogen adsorption-desorption isotherms for the matrices and corresponding composites. The data were normalized to PCM mass in a sample to exclude the effect of sample weighting due to addition of a denser Ni(OH)₂.

The hysteresis loops for Carbonizat and Kemerit matrices have different shapes, which are related to different shapes of the matrix pores. Composites derive the loop shape from their matrices. A loop for

Carbonizat matrix is of type B, and that for Kemerit matrix is of type C according to the De Boer classification [18]. Thus, the Carbonizat matrix and its composites have predominantly the slit-like pores, while the Kemerit matrix and its composites have mostly the wedge-like pores with open ends. The adsorption isotherms for Carbonizat matrix belong to type I of the IUPAC classification, which indicates a developed microporosity, whereas those for Kemerit matrix belong to type IV indicating a developed mesoporosity. The pore structure parameters of the composites are listed in Table 2.

The volume of nickel hydroxide introduced into the composite is 0.16 cm³/g at its density of 4.15 g/cm³, which is equal to the density of macrocrystalline Ni(OH)₂. Data of Table 2 show that the volume of hydroxide introduced into Kemerit matrix is several times smaller than the total decrease in the matrix pore volume. This may be caused by blocking the pores with nickel hydroxide crystallites, which makes a part of the pores inaccessible to nitrogen as was noted in our work [19]. In the composites with Carbonizat matrix, this effect is less pronounced and is observed only when the hydroxide content is below 10 wt.%. It seems reasonable to attribute this observation to the difference in pore shapes because the wedge-like pores (having a narrow neck) are blocked more readily than the slit-like ones. There-with, blocking of small pores occurs mainly on Carbonizat matrix, which shows up as an increase in the average pore size of the composite with respect to the matrix. On the contrary, blocking of larger pores occurs mainly on Kemerit matrix, which leads to a decrease in the average pore size.

For the samples synthesized from azide precursors, the blocking effect is more pronounced as compared to the composites obtained from chloride precursors. This may be related to the crystallite sizes of respective hydroxides (Table 1). Crystallites of the “azide” nickel hydroxide have somewhat greater dimensions along the developed face, which allows a stronger blocking of the pores.

Table 2

Pore structure parameters of composites and matrices. Data are normalized to PCM mass in a sample.

Specimen	Pore Volume (BJH), cm ³ /g	Micropore Volume, cm ³ /g	Surface Area (BET), m ² /g	Average Pore Size, nm
Carbonizat	0.43	0.31	1113	2.7
HNi-HI/Carbonizat	0.33	0.28	850	2.9
HNi-Az/Carbonizat	0.34	0.16	670	3.0
Kemerit	3.94	0.13	3064	5.3
HNi-HI/Kemerit	1.91	0.07	2267	4.7
HNi-Az/Kemerit	1.30	0.10	1352	4.1

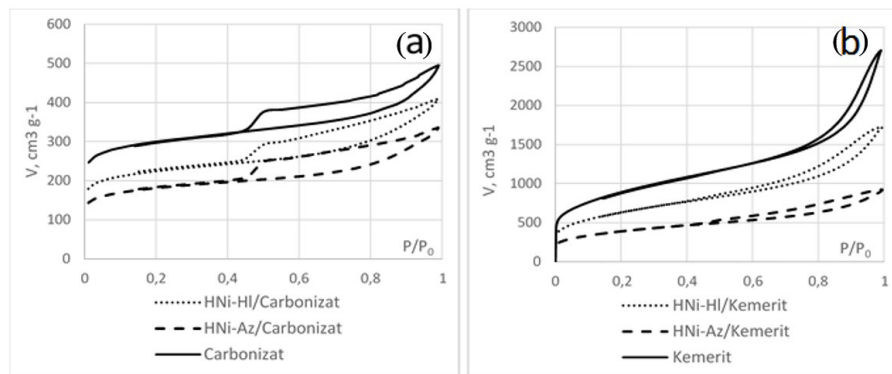


Fig. 2. Nitrogen adsorption-desorption isotherms for: (a) Carbonizat matrix and its composites; (b) Kemerit matrix and its composites.

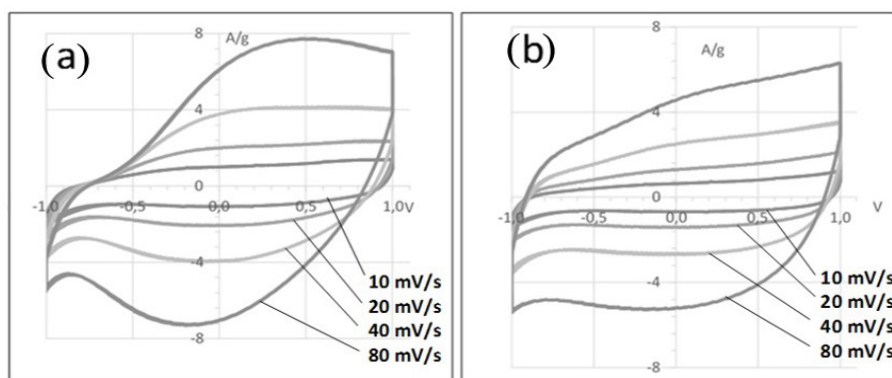


Fig. 3. CV curves for the HNi-HI/Kemerit (a) and HNi-HI/Carbonizat (b) samples.

3.3. Investigation of the electronic properties

The CV curves obtained at a scanning rate of 10 to 80 mV/s (Fig. 3, a-b) for the composite samples synthesized on Carbonizat and Kemerit matrices are characterized by the presence of a current peak in the region of minus 0.55 to plus 0.45 V. Thus, shape of the curve deviates from the rectangular one, which is typical of the EDL formation. This is a manifestation of the Red-Ox processes characterizing the Ni (II) \leftrightarrow Ni(III) transition.

The curves of capacity versus scanning rate (Fig. 4) showed different behavior for the samples synthesized on different matrices. A likely reason is the accessibility of the active substance to electrolyte solution. Capacity of the samples obtained on Kemerit matrix depends mostly on the scanning rate. This may be caused by a stronger blocking of the pores, which hinders the transport of electrolyte ions to the active substance. When the scanning rate was increased from 10 to 80 mV/s, a decrease in capacity was 50.1% for the HNi-HI/Kemerit sample and 56.5 % for HNi-Az/Kemerit. The samples synthesized on Carbonizat matrix showed a more stable

behavior at different scanning rates, especially the HNi-HI/Carbonizat sample whose capacity decreased only by 22.1%.

A maximum capacity for the systems under consideration (346 F/g) was obtained on the HNi-HI/Kemerit sample, which makes it a promising material for supercapacitor electrodes that are synthesized with the matrices made from available and inexpensive raw materials.

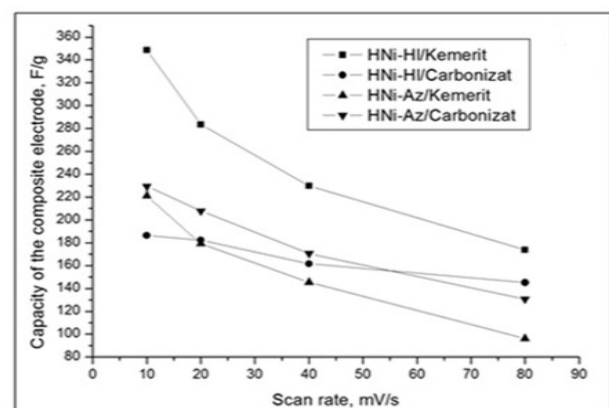


Fig. 4. Curves of capacity versus scanning rate.

4. Conclusions

The Ni(OH)₂/C composites synthesized with two types of matrices and two different precursors of the hydroxide have been studied. The lamellation of nickel hydroxide crystallites was shown to depend on the type of carbon matrix (Carbonizat or Kemerit). Nickel hydroxide covers the PCM surface with a porous “film” but blocks a part of the pores, thus hindering the access of electrolyte to the bulk of active substance. Nevertheless, capacity of the synthesized materials is as high as 346 F/g. This makes promising the further studies aimed to obtain composites with a greater filling with Ni(OH)₂ crystallites and without pore blocking; capacity of such composites should exceed the implemented values.

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