

Electrochemical behavior of nickel deposited on reticulated vitreous carbon

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Abstract

The electrochemical performance of nickel deposited on reticulated vitreous carbon (RVC) has been investigated in solutions of KOH. For comparison, the study of sintered nickel and nickel deposited on gold wire behavior were also included. Our results indicate that the RVC covered with nickel is a good carrier for Ni(OH)₂/NiOOH—an electrode material, used in rechargeable batteries. Ni/RVC saturated with Ni(OH)₂ shows behavior similar or even better than that of sintered Ni saturated with Ni(OH)₂. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Reticulated vitreous carbon (RVC); Nickel; RVC modified with nickel; Ni(OH)₂/NiOOH electrode; Rechargeable nickel batteries

1. Introduction

Reticulated vitreous carbon (RVC), invented 20 years ago [1], has been widely applied as an electrode material [2]. RVC is characterised by an open-pore structure with relatively large void volume (> 90%). The void volume and the real surface area depend on the respective porosity grade of material. In electrochemistry, RVC has been mostly used in electroanalysis. From RVC covered with a thin layer of metal, it was possible to prepare high surface area metallic electrodes with the minimum consumption of expensive and precious metals. It was found that RVC covered with a thin layer of platinum group metals and their alloys shows behavior analogous to the usually electrodeposited metal which is not affected by carbon background [3].

Recently, we demonstrated that such electric conductor as RVC can be easily modified (covered) with lead and lead oxide [4,5]. We found [4,5] that RVC covered with lead and/or PbO₂ is a very good electrode material. Its surface behavior in basic and acidic solutions is almost identical to that of metallic (pure) lead and lead dioxide. Our conclusion was that RVC modified with lead and lead

dioxide can be used as an electrode material in lead-acid batteries [6]. The preliminary tests of a Pb/RVC–PbO₂/RVC cell (without any special Pb and PbO₂ active material preparation) showed that its electrical capacity (A h/kg) is comparable to that of commercial lead-acid cells [7].

In our previous paper, it was shown that a thin layer of nickel deposited on a gold matrix is suitable for the study of its electrochemical behavior [8]. This kind of thin layer electrode, also called a limited volume electrode (LVE) [8,9], is very convenient for use in electrochemical experiments where the surface of studied metal can be refreshed before each experiment. In this paper, we describe the electrochemical performance of RVC substrates covered with Ni. The resulting electrodes show virtually identical electrochemical performance to that of solid nickel. The behavior of Ni/RVC electrode is also compared with sintered nickel, which is widely used as a carrier for nickel hydroxides (Ni(OH)₂/NiOOH-couple)—the material of the positive electrode in Ni–Cd, Ni–Fe or Ni–MeH rechargeable batteries. Also the electrical capacity of positive electrode materials Ni/RVC–NiOOH and Ni–NiOOH has been compared.

Traditional sintered electrodes in nickel–cadmium and nickel–hydride cells in modern devices are now more

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frequently replaced by other materials. Among them are polymer fibres with deposited nickel [10–12]. The active material is uniformly distributed around the fibre. The fibre structure plaque which can be found in commercial products, is formed by the reduction and sintering of fibres extruded from a mixture of nickel oxide and binder agents [13–15] or of organic fibres, followed by nickel electrode-

position [16–18]. The nickel-coated fibres are then pyrolyzed and sintered under special conditions.

Reticulated vitreous carbon plated with nickel seems to be an alternative carrier that can give new advantages in preparation of electrode materials and their exploitation. Perspectives of practical use of Ni/RVC strongly depend on the results of future research.

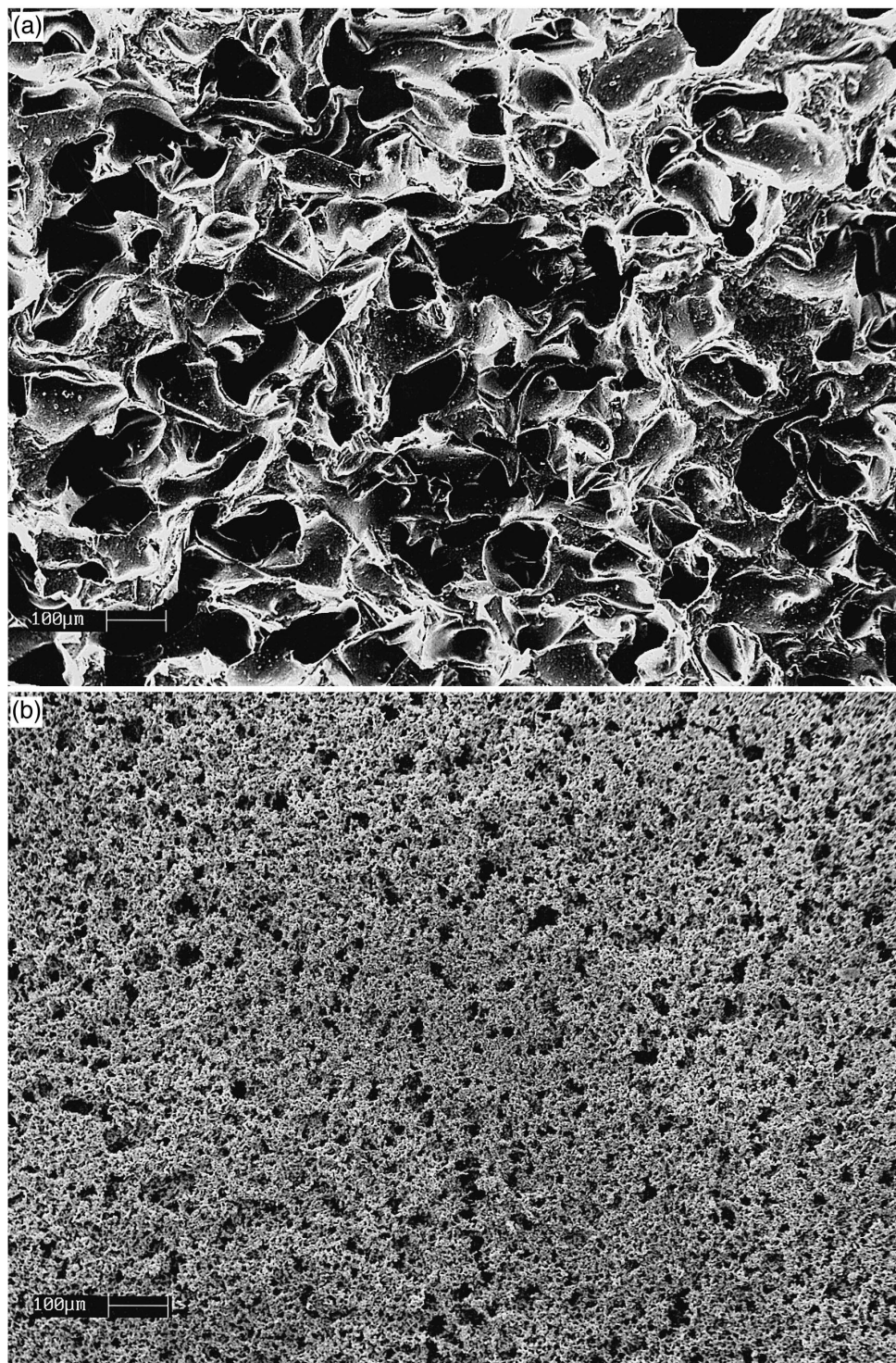


Fig. 1. Scanning electron microscope picture of Ni deposited on RVC (a) and sintered Ni (b). Magnification approximately $100\times$.

2. Experimental

2.1. Apparatus

Current–potential curves were recorded using a potentiostat–galvanostat CHI-604 (Cordoba, USA) controlled by an IBM compatible Pentium computer. The curves were recorded with a HP DJ 690 printer.

Micrographs of modified RVC surfaces were obtained with a Scanning Electron Microscope LEO 435 VP.

The structure and crystal sizes of Ni/RVC and sintered Ni were investigated by X-ray diffraction using Philips 1710 APD Diffractometer (Cu-K α radiation).

2.2. Electrode holder construction

Our electrode holder assembly and electrochemical cell were similar to that constructed previously to study Pb/RVC and PbO₂/RVC [4,5]. Nickel wire was used to provide good electrical contact.

2.3. Chemicals and materials

All chemicals were reagent grade quality and were used without further purification. Cyclic voltammograms of Ni/RVC electrodes were recorded in 1 M KOH solutions and compared to the cyclic voltammograms obtained for Ni deposited on Au and Ni wire (99.99%) in the same solution. The charging/discharging behavior of Ni/RVC–Ni(OH)₂/NiOOH and sintered Ni–Ni(OH)₂/NiOOH electrodes were performed in 6 M KOH (the solution used in batteries). The solutions were prepared using an ultrapure water (Millipore). During the experiments, the solutions were deaerated with pure argon.

RVC (ERG, Materials and Aerospace, 94% of porosity with $4 \cdot 10^3$ pores per meter (ppm), pore diameter approximately 130–180 μm , according to our calculations) was used in cyclic voltammetry experiments (sweep rate = 0.1 V s⁻¹) to avoid stronger electrode polarisation effects. Contrary to sintered nickel carrier, which is composed from the pores with the wide range of various radii, RVC is uniform in porous size and the mentioned porosity ($4 \cdot 10^3$ ppm) is large enough to avoid the diffusion polarisation at our experimental conditions. According to the manufacturer' data, the real surface area of RVC was approximately 66 cm²/cm³. For the experiments where Ni/RVC after saturation with Ni(OH)₂ was tested as a positive electrode in rechargeable cell, RVC with $56 \cdot 10^3$ ppm of 54% porosity (calculated pore diameter is approximately 8–10 μm) has been studied. The volume of RVC samples used in the experiments was approximately 0.25 cm³ (about 20%) and the geometric area was 16.5 cm². The volume of sintered nickel in the experiments was 0.065 cm³ and the geometric area was 0.319 m²/g. The porosity of sintered nickel ranged between 70%–74%.

Sintered nickel was prepared according to the procedure used for the production of Ni–Cd rechargeable batteries. Nickel paste consisted of nickel powder (200 g), sodium carboxymethylcellulose (CMC) (7 g), glycerol (12 g) and distilled water (140 cm³) was mechanically deposited on nickel wire net (current collector) and dried at temperature 150°C and heated in reducing atmosphere at 940–960°C.

2.4. Electrodes

A saturated calomel electrode, SCE (Mineral-Poland), and a platinum foil (2×2 cm²) were used as reference and auxiliary electrodes, respectively. The Ni/RVC system served as a working electrode. To verify the results obtained with Ni/RVC, nickel deposited on Au wire was used as Ni standard. The voltammograms of these Ni electrodes were taken under the same conditions as those of Ni/RVC. The measurements were taken in various regions of potential. Most cyclic voltammograms were recorded in the full oxygen–hydrogen range of potentials (from –1.20 V to +0.60 V). Also, the 'nickel hydroxide generation' region (from –0.20 V to +0.60 V) was investigated.

2.5. Preparation of Ni electrodes

Cathodic plating of Ni on RVC was accomplished in borate bath (83 g/dm³ Na₂SO₄, 83 g/dm³ NiSO₄ · 7H₂O, 10 g/dm³ H₃BO₃). The current, recorded during electrolysis at ambient temperature, was 1.5–2.0 mA/cm². The thickness of a deposit was approximately 1 μm and was calculated from the surface area and the amount of de-

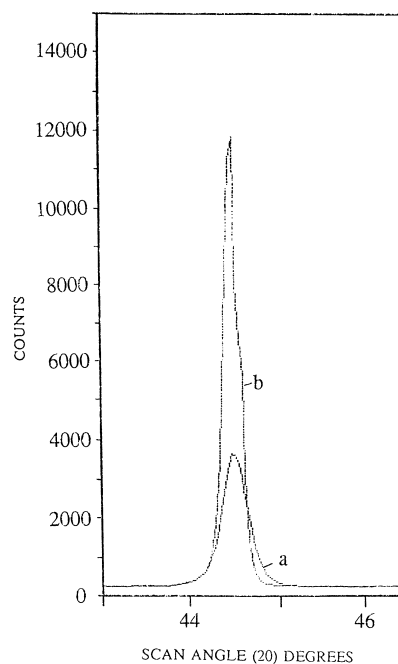


Fig. 2. X-ray structural analysis of Ni/RVC (a) and sintered Ni (b) surfaces. Calculated dimensions of Ni crystallites are $D_{111} = 490 \text{ \AA} \pm 10\%$ for Ni/RVC and $D_{111} = 3570 \text{ \AA} \pm 10\%$ for sintered Ni.

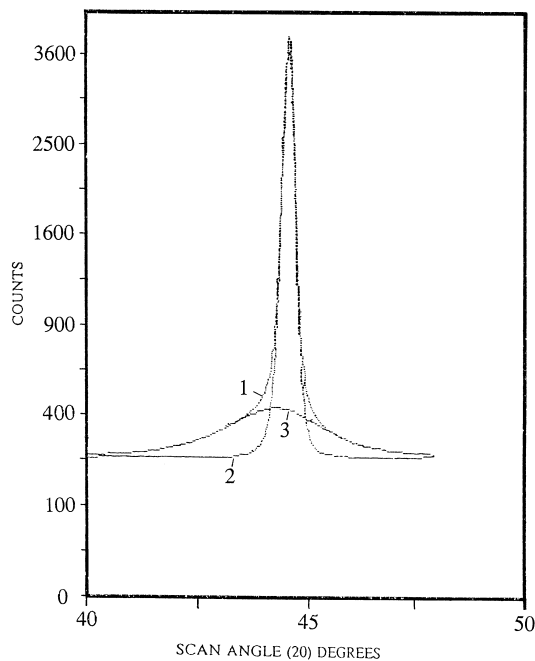


Fig. 3. X-ray structural analysis of Ni/RVC surface. Curve 1—real diffraction line which is distributed on line related to pure nickel (curve 2) and pure RVC (curve 3). Curves 2 and 3 were withdrawn from curve 1.

posited nickel. The efficiency of the nickel deposition, as estimated in separate experiments and based upon the mass of the electrodes before and after electrolysis, was between 90% and 95%.

Ni/RVC and sintered Ni were saturated with $\text{Ni}(\text{OH})_2$ according to the following procedure which was repeated a few times (till the electrode total weight was stabilised):

- porous material (Ni/RVC or sintered Ni) was saturated in melted $\text{Ni}(\text{NO}_3)_2$
- dried at 100°C
- dipped in hot 6 M KOH
- washed with water

3. Results and discussion

The SEM picture of Ni, which was deposited on RVC is shown in Fig. 1a. Also the SEM picture of sintered nickel (at the same magnification approximately $200\times$) is shown in Fig. 1b. It can be seen in these pictures that the structures of the two nickel matrices are markedly different. This result is supported by X-ray analysis, shown in Fig. 2, which indicated that the sizes of nickel crystallites deposited on RVC ($D_{111} = 490 \text{ \AA} \pm 10\%$) and sintered nickel ($D_{111} = 3570 \text{ \AA} \pm 10\%$) are different.

The X-ray structural analysis of Ni/RVC surface indicated that after Ni deposition on RVC, the latter influences the surface composition only slightly. The diffraction curve obtained for Ni/RVC (1) is presented in Fig. 3. Curves 2 (for pure Ni) and 3 (RVC) were calculated from curve 1 obtained using computer fitting (program APD).

After larger magnification of the SEM of Ni/RVC images, greater than $1500\times$ (Fig. 4), the uniform and complete nickel coating on carbon surface is demonstrated.

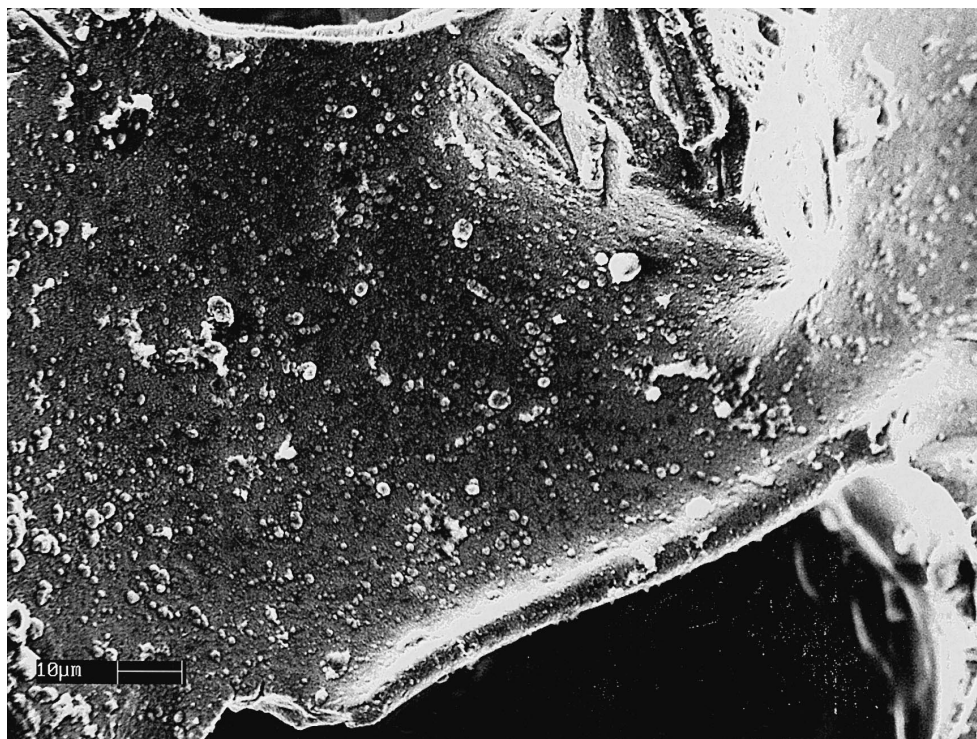


Fig. 4. Scanning electron microscope picture of Ni deposited on RVC. Magnification approximately $2000\times$.

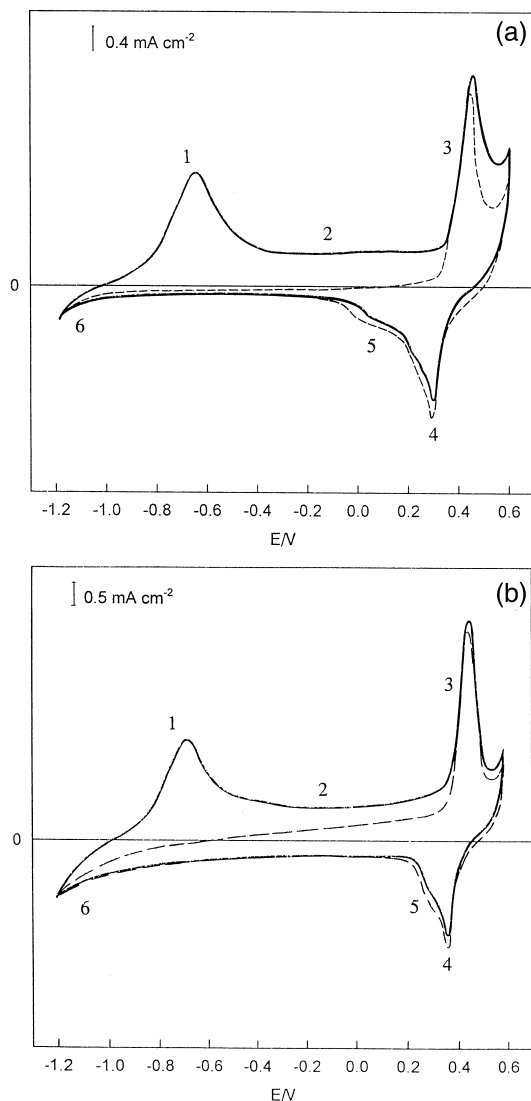
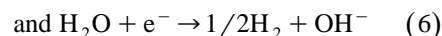
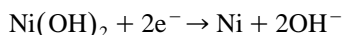
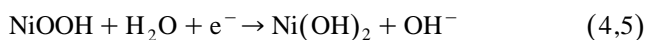
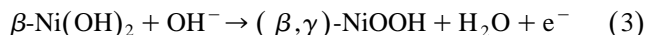
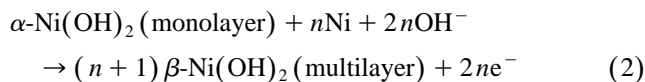
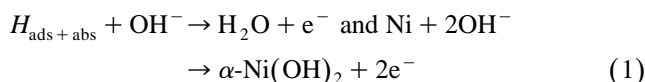


Fig. 5. Cyclic voltammetry of Ni/RVC (a) and Ni deposited on Au (b) in 1 M KOH in potential range from -1.20 V to 0.60 V vs. SCE at sweep rate 100 mV s^{-1} ; (1—solid line) first sweep, (2—dashed line) second sweep. The reactions are described in the text.

Cyclic voltammograms of Ni/RVC (a) and Ni/Au (b) electrodes are presented in Fig. 5a,b.

The shape of the cyclic voltammograms obtained on a Ni/RVC electrode is almost the same as the voltammograms for a LVE nickel electrode described in literature [8,19], i.e., no influence of matrix on deposited nickel was observed. The same result for Ni (99.99%) wire was also obtained in our laboratory. The cyclic voltammogram of sintered nickel was similar to those demonstrated in Fig. 5a and b. The scan rate used for RVC and sintered nickel was the same as chosen for solid nickel electrodes (wire or foil) and reported in the literature [8,19,20]. The current waves can be attributed to the following reactions [8,19–21]:



On the basis of the CV curves (Fig. 5a and b), it is difficult to conclude which parts of peak (peak C) correspond to β - or γ -NiOOH, generated according to Eq. (3). Therefore, we assume that peak C corresponds to the mixture of two phases of NiOOH. Composition of higher nickel oxides is still under discussion in the literature. The participation of nickel on a higher than III oxidation level (i.e., Ni(IV)) and full reaction pathways are still not clear [19–24]. Following the recent data [22], we assume that in the first polarisation cycles the amount of γ -NiOOH is negligible ($< 1\%$) in comparison with β -NiOOH. It has to be noted that in the second cycle the peak of α -Ni(OH)₂ generation is not observed. The reason is that β -Ni(OH)₂, formed from α -Ni(OH)₂ on the fresh nickel surface at these experimental conditions, is not transformed back to α -Ni(OH)₂ [8]. Such a behavior of a nickel electrode is the effect of an irreversible transition from α - to β -Ni(OH)₂ [19,25,26] (aging effect).

Ni/RVC electrode has been studied also as a matrix and current conductor for the NiOOH/Ni(OH)₂-redox couple working in batteries as a positive electrode. The pores of Ni/RVC were filled with Ni(OH)₂ in the same way as applied for the sintered nickel. This process is part of a routine Ni–Cd rechargeable batteries' production pathway. After charging, the Ni/RVC–Ni(OH)₂/NiOOH and sintered Ni–Ni(OH)₂/NiOOH electrodes with charging rate 0.1 C (current equal to 0.1 of total capacity in

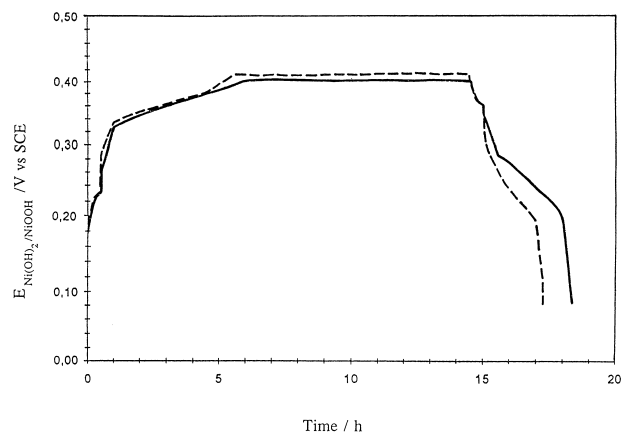


Fig. 6. Charging and discharging curves of Ni(OH)₂/NiOOH electrodes deposited on RVC (solid line) and sintered porous nickel (dashed line) in 6 M KOH. The charging process was held at current 0.1 C (4 mA/g for sintered nickel and 9 mA/g for Ni/RVC) per 14 h. Discharging was held at current rate 0.2 C (8 mA/g for sintered nickel and 18 mA/g for Ni/RVC) and finished at potential 0.08 V.

Table 1

Comparison of specific energy capacities for different types of nickel positive electrodes

Electrode	Ni/RVC–NiOOH	Sintered Ni–NiOOH
mA h/g (electrode)	88.70	43.35
mA h/cm ³ (electrode)	99.30	480.00

ampere hour, i.e., if the cell has capacity of 10 A h the current 0.1 C is equal to 1 A) the electrodes were discharged with current 0.2 C. The plots of E vs. time during charging and discharging processes obtained for Ni/RVC–Ni(OH)₂/NiOOH and sintered Ni–Ni(OH)₂/NiOOH systems are shown in Fig. 6.

The plots obtained for both electrodes studied (Ni/RVC–Ni(OH)₂/NiOOH and sintered Ni–Ni(OH)₂/NiOOH), have very similar shapes. The plots for discharging process show that Ni(OH)₂/NiOOH electrode deposited on Ni/RVC has better behavior as an electrode material for batteries. From the charging–discharging data, the total and specific energy capacities (in A h/g and A h/cm³, respectively) of studied electrodes have been calculated. In Table 1 are presented specific energy capacities obtained for Ni/RVC–Ni(OH)₂/NiOOH and sintered Ni–Ni(OH)₂/NiOOH electrodes.

It can be seen that the sintered Ni–Ni(OH)₂/NiOOH matrix has better volume capacity than Ni/RVC. However, it should be pointed out that when the low weight of battery plays an important role, Ni/RVC matrix can be used as a substrate for the Ni(OH)₂/NiOOH electrode.

4. Conclusions

(1) The electrochemical behavior of Ni/RVC was found the same as that of Ni solid electrodes.

(2) No significant influence of investigated RVC matrix on the electrochemistry of the deposited nickel layer was observed.

(3) The plots of discharging curves (E vs. t) of Ni/RVC–Ni(OH)₂/NiOOH and sintered Ni–NiOOH electrodes are similar to each other.

(4) The results of energy capacity calculation led us to the conclusion that the batteries supplied with Ni/RVC–NiOOH electrodes, when compared with the sintered Ni–NiOOH electrodes have much better weight specific energy (approximately 2 times). Sintered Ni–NiOOH electrodes, however, have better volume specific energy.

(5) The Ni/RVC seems to be a good matrix for Ni(OH)₂/NiOOH electrodes for the future studies with the

focus on the possibility of using these electrodes in rechargeable batteries (e.g., Ni–Cd, Ni–Fe, Ni–MeH).

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