Synthesis of nickel microwires with nanostructured surface for electrodes of chemical current sources

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Abstract. Electrodes with a nanostructured surface based on nickel micro- and nanowires have wide application in magnetic materials and are tested in rechargeable batteries. For the synthesis of nickel wires a chemical method is used. A Ni electrode based on a Ni microwires with roughened surface was prepared and its electrochemical properties were investigated in electrode reaction for NiOOH.

1. Introduction

An increase in the charge/discharge rate of rechargeable batteries of more than one order of magnitude is required to meet the future demands of hybrid electric vehicles and efficient energy storage [1]. Limits exist because of the intrinsically slow diffusivity of the reactive ion in the solid state, which inevitably limits the rate of charge/discharge [1]. With carbon or carbon-buffered alloys as the anode a protecting and passivating solid-electrolyte interface (SEI) layer forms on the anode, this limits the safe charging rate of lithium-ion batteries [2]. There is also increasing interest in the possibility to use metal-based nanostructures instead of microstructures, with the goal of reducing the electrode volume, securing better safety, as well as achieving increased capacity [2].

NiOOH as cathode material for Ni-based batteries has a high theoretical capacity – 286 mAh/g, if the following electrode reaction takes place:

$$\text{NiOOH} + H_2O + e^- = \text{Ni(OH)}_2 + OH^-$$ (1)

A serious drawback of NiOOH is its low electrical conductivity [3]. The way of optimization of NiOOH electrode has directed to reach high rate capability of charge/discharge processes.

The highest capacity and good cycling behavior for NiOOH cathodes were observed for nickel sintered and nickel foam electrodes. The highest current density typically used for Ni sintered current collectors are about 2-3 mA/cm². Because NiOOH has a low electrical conductivity a high rate capability is only provided by using conductive additives like nickel [4]. But to the best of our knowledge nickel micro- and nanowires with roughened surface were not investigated yet as base material.

In technical applications nickel sintered plaque is used as current collector, because of its high specific surface area and the many routes towards the design of structured electrode. Nickel shows lower resistance compared to carbon – 69.3 nΩ·m⁻¹ vs. 7,800 nΩ·m⁻¹ for graphite. Nickel as current...
collector for positive electrodes of rechargeable batteries has good electrical conductivity in terms of weight and price [5]. So, nickel micro- and nanowires are well suited scaffolds for the NiOOH electrode. In addition, nickel wires are also interesting from the technological point of view because the synthesis of nickel wires via chemical deposition offers low cost and large-scale production [6-13].

Here we describe the preparation of a Ni electrode for nickel batteries based on nickel micro- and nanowires. The aim of the investigation was to demonstrate the high current density for NiOOH cathodes by using nickel scaffolds. We focus on the preparation of nano-architected electrodes based on nickel wires that are not expensive and can be applied in batteries.

2. Experimental

Ni wires were prepared by chemical deposition using the technique described in [12, 13] with the surfactant cetyl trimethylammonium bromide (CTAB) and polyethylene glycol (PEG, M=10000). 0.660 g NiCl₂·6H₂O (Acros organics, 2.8 mmol), 0.8 g PEG (Alfa Aesar, 0.08 mmol), 0.3 g CTAB (Acros organics, 1.1 mmol) and 45 ml distilled water were mixed into a 100 ml round-bottom flask at room temperature under stirring with magnetic stirrer. A grass-green color was observed in the solution. Then 5 ml of 80 wt % hydrazine hydrate solution was added dropwise into the solution under stirring with magnetic stirrer, and the color changed from grass-green to navy blue. The round-bottom flask with reaction mixture was closed tightly by tap and was placed into water thermostat at temperature 70 °C for 3 h. After the reaction was completed, the resulting black solid product floated to the top of the flask, indicating the formation of metallic nickel. The product was washed with distilled water and absolute isopropyl alcohol several times. For the control of synthesis magnetic field with magnitude between 0.05 and 0.86 T was used.

The structure and morphology of these products were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). XRD measurements were carried out on an XRD-7000 diffractometer from SHIMADZU. SEM images were taken with a Auriga Crossbeam (FIB-SEM) workstation microscope from Zeiss. The specific surface area of the wires was determined by Brunauer-Emmet-Teller (BET) method on an Autosorb-iQ MP surface area analyzer from Quantachrome. For AFM investigation Bruker Innova atomic force microscope was used.

The Ni/NiOOH electrodes with and without wires were tested in three electrode electrochemical cells. The prepared electrodes were used as working electrodes and Pt electrode was used as counter electrode. The reference electrode was Ag/AgCl. Prepared electrodes were tested in 0.1 M NaOH electrolyte solution. The specific feature of Ni/NiOOH wire electrode is dendrite structure with roughened surface compared to the sintered and foam electrode.

Cyclic voltammetry measurements of the electrodes were performed on a PGSTAT 302 N potentiostat/galvanostat from Metrohm Autolab.

3. Results of synthesis and characterization of nano-architected electrode based on a nickel wires with roughened surface

In figure 1 microstructures of the Ni/NiOOH sintered and wires electrodes surface are shown. In figure 2 Ni individual wires are shown. Influence by magnetic field during synthesizing of the wires causes a roughened surface with nanocones. The nanocones are about 200 nm – 750 nm in height, and wires do not stick together. The morphology of the prepared microwires agrees well with experimental data related to the structure of the Ni wires surface after hydrothermal synthesis [7, 8]. It can be seen from AFM images that the Ni nanocones distribute on the Ni electrodes surface.
Figure 1. AFM images of microstructure of the surface of: a) Ni sintered electrode; b) Ni wires electrode with roughened surface.

Figure 2. SEM images of individual nickel wires synthesized: a) without the magnetic field; b) under the influence of magnetic field 0.06 T.

AFM data were used for the analysis of roughness of the nickel electrodes (figure 3). The advantage of AFM investigation is 3D characterization of the electrodes surface. For the numerical analysis of roughness fractal dimension was used. From the analysis of AFM images it can be concluded that with increasing of roughness of the surface fractal dimension has increased. Fractal dimension for the sintered electrode is 2.27, fractal dimension for the nickel wires electrode with roughened surface is 2.55.

For the determination of chemical purity and crystal structure of the electrodes XRD measurements were carried out. On the spectra (figure 4) three main peaks were found and indexed by crystallographic planes of Ni: 57.6° - (111), 67.4° - (200), 102.2° - (220). There are no any impurities like oxides and hydroxides, that means high purity and crystal structure of nickel electrodes. Size of crystallites from Sherer equation was found about 40 nm, which corresponds to the data in [13].
Figure 3. Dependence of perimeter on the area of the islands on the nickel electrodes surface in logarithmic coordinates: a) nickel sintered electrode; b) Ni wires electrode with roughened surface.

Figure 4. XRD measurements of synthesized nickel wires (λ=0.193728 nm).

Figure 5. Voltammetry in the solution 0.1 M NaOH at 20 mV/s. 1) Sintered nickel electrode (SNI); 2) SNI with microwires without nanocones; 3) SNI with microwires with nanocones; 4) SNI with submicrowires (D=330 nm) with nanocones.
For the investigation of Ni/NiOOH electrode current density we analyzed cyclic voltammetry data for the wires electrode (figure 5). We observed a linear dependence of peak current vs. the square root of the voltage scan rate. The electrode shows stable performance at scan rates from 5 to 60 mV/s. The specific surface area of nickel submicrowires with nanocones from BET measurements is 5.5 m²/g. It is more than one order higher than for nickel sintered electrode, that express in high current density of nanostructured electrodes. The high current density capabilities of the Ni/NiOOH electrode are related to roughened nickel wires surface that acts as effective current collector.

Investigation of the influence of magnetic field on current density of the electrodes demonstrates the increasing of current density with increasing of magnetic field (figure 6). It was found that increasing of magnetic field result in increase of the electrodes surface area [14]. This proves that we see indeed the effect of the surface area on the current density of the electrodes. To compare the current density of synthesized nanostructured electrode with Ni/NiOOH sintered electrode we presented experimental data in the table 1.

![Figure 6. Voltammetry in the solution 0.1 M NaOH at 20 mV/s. 1) nickel foam electrode; 2) nickel foam electrode modified nanocones; 3) nickel foam electrode modified nanocones under the influence of magnetic field.](image)

| Table 1. Comparison of current density for foam Ni/NiOOH electrode and foam Ni/NiOOH electrode with roughened surface. |
|---------------------------------------------------------------|
| **Parameter**                                               | Foam Ni/NiOOH electrode | Foam Ni/NiOOH electrode with roughened surface |
|---------------------------------------------------------------|
| Current density per mass, mA/g                                | 34±3                     | 66±7                                      |
| Capacity density per surface area, mA/cm²                     | 3.3±0.3                  | 6.3±0.5                                   |

4. Conclusion
The new approach of using nickel nanostructures as base material for NiOOH electrodes as cathode for Ni-based batteries is presented. The electrodes with Ni microwires with roughened surface were prepared by chemical deposition. The electrochemical properties of the Ni/NiOOH wires electrode are investigated and the results reveal a high current density performance. This is explained by effective charge transport because of using nickel wires core as current collector. So, we presented an interesting way of preparing NiOOH electrodes that give fundamental understanding of the
mechanism how NiOOH cathodes work. The methods of the synthesis of Ni wires and the preparation of the electrode presented here are cheap, so it can be useful for preparation of NiOOH electrodes with high energy density.

Acknowledgments
This work is supported by RFBR, project № 12-02-97050-r_Volga region_a.

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