

Electrochemical obtaining of nickel hydroxide from nickel plating waste water for application in the alkali secondary cells

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The rinsing and waste water of the plating industry, containing the heavy metal cations, are the source of environmental pollution. Nickel cations have a strong biological hazard. At the same time, up to 30% of nickel compounds spent on nickel plating are irretrievably lost to the rinsing water. Purification of the rinsing and wastewater from heavy metal cations is expensive. It's economically effective to develop the methods of local treatment of plating rinsing water with the recovery of the heavy metals in the easy utilizing forms. The hydroxide is the most perspective form for nickel as it has high electrochemical activity and can be used for alkaline secondary cell production. The method of electrochemical synthesis of the nickel hydroxide in the slit diaphragm electrolyzer from the rinsing water of bright nickel plating has been proposed. The treatment of rinsing water of the bright nickel plating for surfactants recovery has been made. The samples of nickel hydroxide obtained from treated and untreated rinsing water, have been studied by XRD, voltammogram and charge-discharge cycling in the secondary cell regime. The comparative analysis shows that even the nickel hydroxide sample obtained from untreated rinsing water can be used as an active substance of the positive electrode of alkaline secondary cells. This sample's specific capacity is 142 mA·h/g with cost of 4 \$/kg (in comparison with 182 mA·h/g and 18–22 \$/kg for industrial sample). It was detected that the nickel hydroxide sample obtained from the rinsing water of bright nickel plating after purification from surfactant by bubble-film extraction, has the highest parameters. In this case specific capacity is 194 mA·h/g compared 182 mA·h/g for the industrial sample produced by Bochemie JSC (Czech Republic).

Keywords: nickel hydroxide, rinsing water, bright nickel plating, slit diaphragm electrolyzer, alkaline secondary cell.

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Электрохимическое получение гидроксида никеля из промывных вод никелирования для использования в щелочных аккумуляторах

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Предложен метод электрохимического синтеза гидроксида никеля из промывных вод блестящего никелирования в щелевом диафрагменном электролизёре. Проведена обработка промывных вод блестящего никелирования для удаления поверхностно-активных веществ (ПАВ). Образцы гидроксида никеля, полученные из обработанных и необработанных промывных вод, изучены методами рентгенофазового анализа, циклической вольтамперометрии и гальваностатического зарядно-разрядного циклирования в режиме аккумулятора. Сравнительный анализ электро-

химических характеристик показал, что даже образец гидроксида, полученный из необработанной промывной воды, может использоваться в качестве активного вещества положительного электрода щелочных аккумуляторов. Его удельная ёмкость составляет 142 мА·час/г при себестоимости 4 \$/кг (по сравнению с 182 мА·час/г и 18–22 \$/кг для промышленного образца). Выявлено, что наилучшими параметрами обладают образцы гидроксида никеля, полученные из промывных вод блестящего никелирования после очистки от ПАВ методом пузырьково-плёночной экстракции. Удельная ёмкость в этом случае составила 194 мА·ч/г по сравнению с 182 мА·ч/г промышленного образца производства фирмы «Vochemie» (Чехия).

Ключевые слова: гидроксид никеля, промывные воды, блестящее никелирование, щелевой диафрагменный электролизёр, щелочной аккумулятор.

The modern world is nearing an ecological, economic and energetic crisis. However, all three ones are interconnected and constitute a single problem. Contamination of environment is a major issue, which causes not only ecological (danger to human, flora, and fauna), but also an economic problem (investments into waste purification and re-processing, loss of valuable resources). On the other hand, a solution of the energetic problem requires significant financial investments and leads to contamination of the environment.

Compounds of heavy metals are not biodegradable and are hazardous to the environment [1]. Besides, nickel compounds are hazardous to human health [2].

Contamination with heavy metals is usually caused by technogenic factors. Particularly washing waters of galvanic plants, owing to their volume and toxicity is one of the major contaminants of the hydrosphere. Many methods for treating waste water from heavy metals have been developed [3, 4], particularly chemical precipitation [5]. Sorption methods are widely used [6–10]. Ion-exchange methods are used for post-treatment and concentration [5, 11]. Membrane technologies also found wide application [12–14]. Electrochemical methods are the most promising [15–17].

The main disadvantage of all the mentioned methods is that they are only aimed at water purification. Any purification methods require a financial investment, which is passed onto the cost of the product. In order to make methods for waste water treatment from heavy metal cations cheaper, or even profitable, the treatment should be split into two stages.

1) Treatment of local concentrated waters, which contain only one metal. The metal should be extracted in easy to utilize form, with a remaining concentration of metal cations being economically viable.

2) Combination of treated local water with general wastewater and additional treatment to Threshold Limit Value (TLV) levels. Such two-stage processing would be to make wastewater treatment economically viable.

Nickel can be extracted in one of two economically viable forms: metallic nickel and nickel

hydroxide. From technological and economical points of view, nickel hydroxide is a more viable form. Nickel hydroxide can be prepared in a various way under simple conditions than a metallic nickel. Nickel hydroxide can be utilized as the active material in alkaline batteries and hybrid super capacitors, which are used “eco-friendly” transport and alternative energy systems. This results in double ecological effect: removal from waste water (purification) and use in eco-devices. It should be noted that the cost of nickel hydroxide in amounts to 60–70% of battery cost. Thus extraction of $\text{Ni}(\text{OH})_2$ from wastewater can significantly decrease the cost of the battery.

The electrochemical activity of nickel hydroxide is mainly governed by its structure [18]. Two forms of nickel hydroxide are known: β -form (chemical formula $\text{Ni}(\text{OH})_2$, brucite structure) and α -form (chemical formula $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, hydrotalcite-like structure). However, paper [19] describes nickel hydroxide structures that are intermediate between α - $\text{Ni}(\text{OH})_2$ and β - $\text{Ni}(\text{OH})_2$.

α - $\text{Ni}(\text{OH})_2$ has better electrochemical characteristics than β - $\text{Ni}(\text{OH})_2$. However, its stability is low. α - $\text{Ni}(\text{OH})_2$ and nickel-based layered double hydroxides (LDH) can be synthesized chemically and electrochemically in slit-diaphragm electrolyzer [20]. β - $\text{Ni}(\text{OH})_2$ is significantly more stable during storage and cycling, and so it is widely used as an active material of alkaline accumulators [21]. β - $\text{Ni}(\text{OH})_2$ can be prepared chemically or electrochemical in the slit-diaphragm electrolyzer.

A mixed (α/β) structure $\text{Ni}(\text{OH})_2$ possesses advantages of both nickel hydroxide structures. Paper [22] describes the formation of highly active ($\alpha+\beta$) nickel hydroxide with a layered structure, that is not just a mixture of two forms. Hydroxide was synthesized in slit-diaphragm electrolyzer (SDE) from nickel sulfate solution. The sample showed high electrochemical activity, exceeding that of β - $\text{Ni}(\text{OH})_2$ and α - $\text{Ni}(\text{OH})_2$. High activity of ($\alpha+\beta$) nickel hydroxide makes synthesis in slit-diaphragm electrolyzer very attractive.

It should be noted, that highly active nickel hydroxide was synthesized in SDE from pure nickel solution. At the same time, washing waters of

glossy nickel plating also contain other electrolyte components. The biggest threat to the activity of nickel hydroxide are surfactants and iron cations.

The aim of the work is to evaluate the possibility of preparing highly active nickel hydroxide from washing water from glossy nickel plating plants for use in alkaline accumulators. Following objective were formulated to achieve the set aim:

1) conduct treatment of washing waters of glossy nickel plating;

2) prepare nickel hydroxide samples from treated and untreated washing waters by means of electrochemical synthesis in slit-diaphragm electrolyzer;

3) conduct comparative analysis of synthesized samples and evaluate the possibility of preparing highly active $\text{Ni}(\text{OH})_2$ from washing water and find the best solution of treating washing waters.

Research object and methods

Synthesis of nickel hydroxide samples. Synthesis method [20, 23] is based on electrolysis conducted in slit-diaphragm electrolyzer (SDE) (Fig. 1, see color insert). Washing water of glossy nickel plating with $C(\text{Ni}^{2+}) = 12.7 \text{ g/L}$, was fed into cathodic chamber via a peristaltic pump, and the anodic chamber was fed with NaOH at the same rate of 0.2 L/h . Cathode was Ti , anode – insoluble, Ni . Electrolysis was conducted at an optimal current density of 12 A/dm^2 .

Current flow through cathode of SDE resulted in hydrogen evolution (reaction 1) and formation of hydroxyl ions, which react in volume with nickel cations forming nickel hydroxide precipitate. The formed precipitated is then carried out from electrolyzer by the flow of catholyte. In side of cathode chamber, the nickel hydroxide particles undergo partial crystallization at elevated temperature, which results in unique structure and electrochemical properties [22]. To prevent excessive aging, the nickel hydroxide was immediately separated from catholyte through vacuum filtering upon leaving SDE.

Nickel hydroxide is a matrix structure, similar to those of polymer composites [24], with mother liquor acting like a filler. In order to remove ballast soluble compounds, the hydroxide was subjected to following treatment: drying at $90 \text{ }^\circ\text{C}$, grinding with mortar and pestle, sifting through 71μ mesh, soaking in distilled water for a day, filtering and drying [20].

Composition and treatment of washing waters of nickel plating. Real washing water of glossy nickel plating with the following composition, was used in the experiment (g/L): $\text{NiSO}_4 \cdot$

$7\text{H}_2\text{O} - 250-280$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - 70-80$, $\text{H}_3\text{BO}_3 - 40-50$, *Glitter-forming surfactant Nigal 1 - 0.6-0.8*, *Nigal 2 - 15-20*, *Nigal 3 - 0.1-0.25*.

To evaluate influence of admixtures (surfactants and iron cations) on electrochemical activity of $\text{Ni}(\text{OH})_2$, a series of samples was prepared from wastewaters subjected to different treatments: untreated (sample A); treatment with H_2O_2 , followed by boiling and filtration (sample B); bubble-film extraction, based on bubbling of air through washing water using especial extractor for removal of surfactants into acceptor vessel. Water was treated for 3 hours (sample C); bubble-film extraction with additional surfactant removal with active carbon. Additional treatment was conducted for 2 hours (sample D).

A commercial sample of $\text{Ni}(\text{OH})_2$ “Bochemie”, Czech (sample E) was used as a reference.

Sample analysis method. Crystal structure of the samples has been studied by means of X-ray diffraction (XRD) analysis, using DRON-3 diffractometer (Russia) ($\text{Co-K}\alpha$ radiation, 2θ range $10-90^\circ$, scan rate $0.1^\circ/\text{s}$).

Electrochemical characteristics of $\text{Ni}(\text{OH})_2$ were studied using following methods: cyclic voltammetry conducted in YSE-2 cell using PI-50-1 potentiostat. Working electrode: current collector – Ni mesh on Ni foil; active mass – 81% hydroxide, 16% graphite, 3% PTFE [51]. Electrolyte – 4.5 M KOH . Counter-electrode – nickel mesh. Reference electrode – Ag/AgCl (KCl sat.). Scan rate 1 mV/s ; Galvanostatic charge-discharge cycling was conducted in specially assembled Ni-Cd accumulator. Counter-electrode – Cd , current collector – nickel foam. Working electrode: current collector – Ni mesh on Ni foil; active mass same as for cyclic voltammetry. Accumulator model was charged in 18 h regime with 20% overcharge. The accumulator was discharged at 0.2C to $E = 0.1 \text{ V (NHE)}$.

Results and discussions

XRD patterns (Fig. 2) allow concluding that synthesized compounds are combinations of α and β phases of nickel hydroxide. All samples also show peak shift towards lower angles, which indicates the presence of α (13°) and β (21°).

This leads to the conclusion that there are α -like phases present in all prepared samples. Such structure is close to the structure that is described [22] as optimal for nickel hydroxide with high electrochemical characteristics. At the same time, XRD patterns of sample D indicate an increase in crystallinity of nickel hydroxide.

Cyclic voltammogram of sample A (Fig. 3, see color insert) shows no pronounced charge

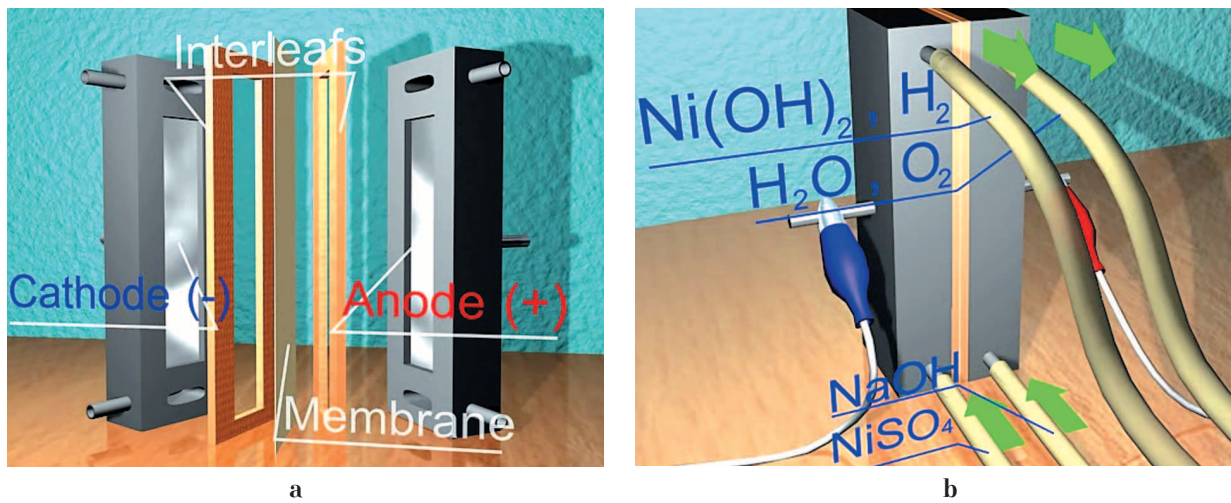


Fig. 1. Slit diaphragm electrolyzer (SDE) for Ni(OH)_2 obtaining
 a – disassembled SDE; b – assembled SDE with flows indication

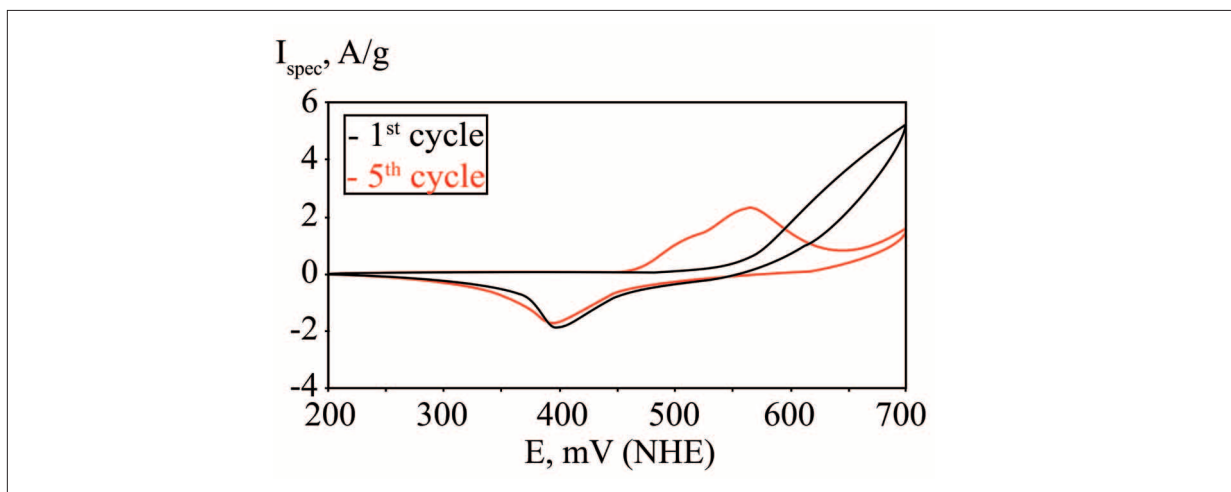


Fig. 3. The cycling voltammogram of the sample A

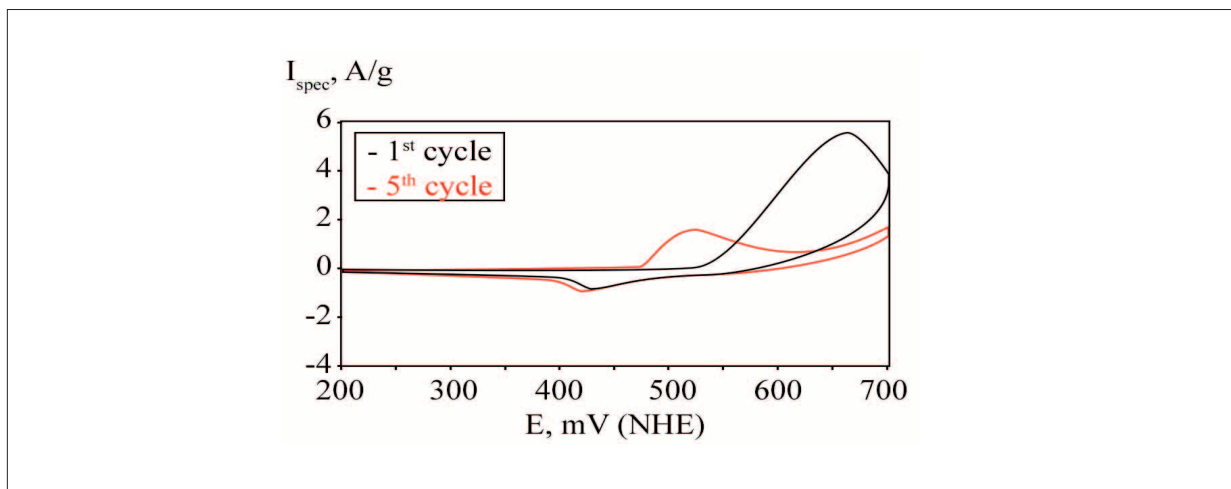


Fig. 4. The cycling voltammogram of sample C

peak, while the discharge peak is present. Further cycling showed a shift to cathodic peaks into lower potential values, indicating of working through of material. During cycling of sample C (Fig. 4, see color insert), almost no shifting was observed for cathodic and anodic peaks. The first cycle also showed pronounced charge peak. Based on the results of charge-discharge cycling, sample C has the highest electrochemical activity.

Analysis of K_u and Q_{spec} , shown in Figure 5, a, b revealed following:

- utilization coefficient of sample A, from untreated washing water, is 42%. This is lower than K_u of commercial sample E, however, it is sufficient for use as a partial substitute of commercial hydroxide for production of non-critical accumulators to reduce their cost;

- removal of surfactants from washing waters results in improved characteristics of synthesized nickel hydroxide samples. The best parameters (K_u and Q_{sp}) are demonstrated by sample C, which was prepared from water that was treated by bubble-film extraction.

A preliminary cost of nickel hydroxide sample prepared from washing waters of glossy nickel plating was calculated. The cost of $Ni(OH)_2$ prepared from untreated waters is estimated to be 4 \$/kg; the cost of the sample prepared from water treated with bubble-film extraction is 5 \$/kg. For comparison, the cost of a commercial sample is 19–22 \$/kg.

Conclusions

1) Treatment of washing water from glossy nickel plating has been conducted. Electrochemi-

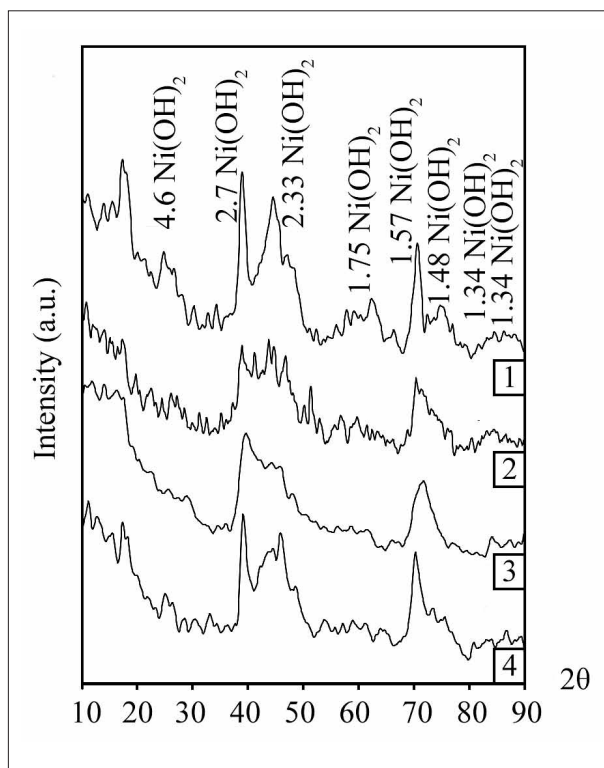


Fig. 2. XRD patterns of the $Ni(OH)_2$ sample: 1 – sample A; 2 – sample B; 3 – sample C; 4 – sample D

cal characteristics of nickel hydroxide samples prepared from treated and untreated washing water have been studied.

2) Characteristics of prepared samples have been compared with commercial nickel hydroxide. It was found that nickel hydroxide prepared from untreated washing water had a specific capacity of 121 mA·h/g (compared to 182 mA·h/g of commercial sample), while it's cost is about 18–22%

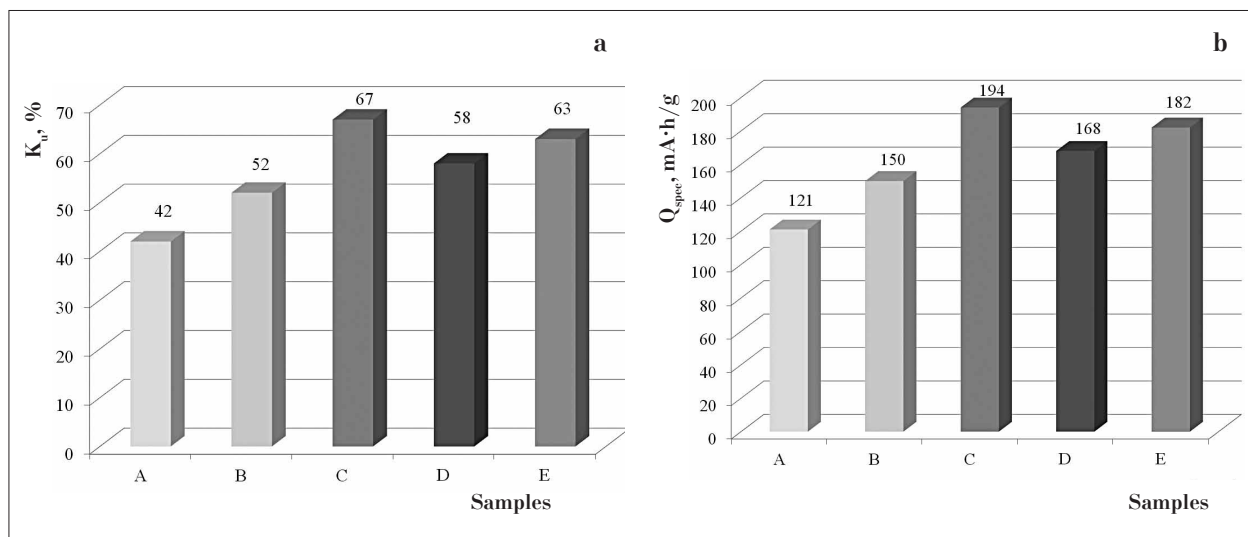


Fig. 5. Electrochemical properties of the samples a – mass utility (K_u), %; b – specific capacity (Q_{spec}), mA·h/g

of the commercial sample. It was concluded that this sample can be used as a partial substitute of commercial hydroxide in order to reduce the cost of accumulators. It was found that highest specific capacity (194 mA·h/g) was demonstrated by nickel hydroxide sample prepared from washing water of glossy nickel plating that was treated with bubble-film extraction.

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