

Розроблено метод отримання ультрависококристалічного β -Ni(OH)₂ методом повільної декомпозиції гідроксиду тетраамінікелю. Проведено порівняльне вивчення електрохімічних властивостей ультрависококристалічного та висококристалічного комерційного зразків. Показана низька електрохімічна ефективність (низький коефіцієнт використання) ультрависококристалічного β -Ni(OH)₂ в акумуляторному режимі. Виявлено, що ультрависококристалічний β -Ni(OH)₂ проявляє високі питомі характеристики в режимі суперконденсатора. Максимальні отримані ємності складають 120,4 мА·год/г і 276 Ф/г

Ключові слова: гідроксид нікелю, висока кристалічність, питома ємність, суперконденсатор, лужний акумулятор, метод декомпозиції

Разработан метод получения ультравысококристаллического β -Ni(OH)₂ способом медленной декомпозиции гидроксида тетрааминникеля. Проведено сравнительное изучение электрохимических свойств ультравысококристаллического и высококристаллического коммерческого образцов. Показана низкая электрохимическая эффективность (низкий коэффициент использования) ультравысококристаллического β -Ni(OH)₂ в аккумуляторном режиме. Выведено, что ультравысококристаллический β -Ni(OH)₂ проявляет высокие удельные характеристики в режиме суперконденсатора. Максимально достигнутые ёмкости составляют 120,4 мА·час/г и 276 Ф/г

Ключевые слова: гидроксид никеля, высокая кристалличность, удельная ёмкость, суперконденсатор, щелочной аккумулятор, метод декомпозиции

DEFINITION OF EFFECTIVENESS OF β -Ni(OH)₂ APPLICATION IN THE ALKALINE SECONDARY CELLS AND HYBRID SUPERCAPACITORS

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1. Introduction

Alkaline nickel-cadmium, nickel-zinc, nickel-iron, nickel-hydrogen and nickel-metal hydride batteries with nickel hydroxide electrode are widely used as traction, starter or stationary chemical power sources (CPS). One of the most relevant applications of alkaline batteries is the use in buffer systems of "green" power grids [1]. The capacity of alkaline accumulators is defined by the capacity of nickel oxide electrode and 70 % of its cost amounts to the cost of nickel hydroxide.

The other modern CPS are supercapacitors (SC). SC are widely used for starting and powering various electric motors, as automotive batteries, uninterruptable power supply units for computers and other devices. The hybrid (asymmetric) supercapacitors demonstrate the best characteristics. The hybrid SC are composed of two electrode types. One electrode type (non-Faradic) is based on charge-discharge of the double electric layer, and the other type (Faradic) – is based on fast electrochemical reactions. Supercapacitors operate at high charge-discharge rates, as there are special re-

quirements for the active material of Faradic electrode [2, 3]. Nickel oxide electrode with Ni(OH)₂ as an active material is widely used as a Faradic electrode for hybrid supercapacitors [4], often in the form of nano-sized particles [5–7] or composites with nanocarbon materials [8, 9].

The main requirements for accumulators and supercapacitors are long lifespan and stability over time. The main disadvantage of alkaline accumulators and hybrid supercapacitors is capacity loss during operation. The paper [10] demonstrates the degradation of specific capacity during cycling. The modern tendency for the nickel hydroxide synthesis is to prepare the powder with high chemical and electrochemical activity, the opposite side of which is low stability. Research directed toward synthesis and study of nickel hydroxide that is stable during cycling; almost had not been conducted; because of theoretical assumption of its low activity. Thus, the method development for the synthesis of highly stable nickel hydroxide and evaluation of its effectiveness for use in alkali accumulators and supercapacitors is of relevance.

2. Literature review and problem statement

Synthesis method and its conditions define micro- and macrostructure of nickel hydroxide particles, which largely define electrochemical properties. Synthesis conditions affect structural disorder [11], microstructure [12], crystallinity [13, 14]. Synthesis method also determines the modification of $\text{Ni}(\text{OH})_2$ [15]. There are two allotropes of nickel hydroxide: β -modification (formula $\text{Ni}(\text{OH})_2$, brucite structure) and α -modification (formula $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, hydrotalcite-like structure). At the same time, the paper [16] describes the existence of a number of intermediate structures in-between α - $\text{Ni}(\text{OH})_2$ and β - $\text{Ni}(\text{OH})_2$.

α - $\text{Ni}(\text{OH})_2$ possesses better electrochemical properties than β - $\text{Ni}(\text{OH})_2$, however, its stability is sufficiently lower: in concentrated alkali, and especially at high temperatures, the α -modification transforms into the β -modification [17], which results in loss of capacity. This also occurs during charge-discharge cycling. α - $\text{Ni}(\text{OH})_2$ and nickel-based Layered Double Hydroxides (LDH) can be prepared using various methods: titration or precipitation at high supersaturation [18], homogeneous precipitation [18, 19], electrochemical synthesis in slit-diaphragm electrolyzer [20], cathodic deposition onto substrate [21, 22].

In order to reduce particle size, template (matrix) compounds are used. The template can be used in any synthesis method, including homogeneous precipitation [19] and cathodic deposition [23, 24].

β - $\text{Ni}(\text{OH})_2$ possesses high cycling stability and is widely used as an active material in accumulators [25] and supercapacitors [10, 26]. Synthesis of β - $\text{Ni}(\text{OH})_2$ can be conducted chemically, [25, 28], electrochemically using slit-diaphragm electrolyzer [26] and on the substrate surface [27]. High-temperature synthesis is also used [29, 30].

Influence of various parameters of the crystal lattice, particularly, structural defects [11], microstructure [12], and crystallinity [13] on electrochemical properties of nickel hydroxide as an active material for accumulators, had been largely studied. However, β - $\text{Ni}(\text{OH})_2$ samples used in the studies had average or low crystallinity, and sometimes were almost X-ray amorphous. The results were interpolated onto high crystallinity, however, the correctness of such approach is doubtful. Possibly, the direct study had not been conducted owing to difficulties of preparing highly crystalline β - $\text{Ni}(\text{OH})_2$. For $\text{Ni}(\text{OH})_2$, as an active material of supercapacitors, the situation differed significantly. Almost all studies had been conducted according to the procedure “preparation of specific type of $\text{Ni}(\text{OH})_2$ ” – “study of electrochemical properties”. The highly crystalline hydroxide had been prepared using two-stage high-temperature synthesis [30]. Its properties for use in supercapacitors were studied in [10]. However, it should be noted that the sample prepared using two-stage high-temperature synthesis is not only the ultracrystalline β - $\text{Ni}(\text{OH})_2$, but also has fractal geometry and is composed of particles with nano-scale thickness [10]. This significantly complicates evaluation of highly crystalline β - $\text{Ni}(\text{OH})_2$ for use in hybrid supercapacitors.

Thus, it should be noted that from a theoretical and practical point of view, preparation of ultracrystalline β - $\text{Ni}(\text{OH})_2$ and direct study of its properties are promising.

3. The aim and objectives of the study

The aim of the work is to determine the possibility of using highly crystalline β - $\text{Ni}(\text{OH})_2$ for preparation of effective alkaline accumulators and hybrid supercapacitors.

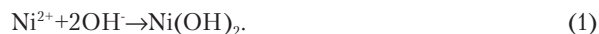
To achieve the aim, the following objectives were stated:

- to develop a method for the preparation of ultracrystalline β - $\text{Ni}(\text{OH})_2$ and to prepare hydroxide samples;
- to study structural, surface properties and electrochemical characteristics of prepared β - $\text{Ni}(\text{OH})_2$ samples as active materials of alkaline accumulators and supercapacitors;
- to conduct a comparative analysis of characteristics of synthesized nickel hydroxide samples and compare them to the reference samples in order to evaluate the effectiveness of highly crystalline β - $\text{Ni}(\text{OH})_2$ for application in alkaline accumulators and supercapacitors.

4. Materials and methods for synthesis and characterization of nickel hydroxide samples

Rationale behind method development for preparation of ultracrystalline nickel hydroxide. Method development for the preparation of nickel hydroxide should be based on an understanding of the compound formation mechanism.

General expression for the reaction of nickel hydroxide synthesis can be written as follows:



Additionally, Wasserman [31] says that for $\text{Ni}(\text{OH})_2$, the nucleation rate is higher than the rate of crystal growth. The formation mechanism consists of two stages: the first stage (very fast) – formation of the primal amorphous particle; the second stage (slow) – ageing (crystallization) of the primal particle. On the macro level, fast occurrence of the first stage leads to the formation of a sponge-like structure that includes a large volume of mother liquor, resulting in the formation of a hydrophilic precipitate.

With two stages of this mechanism occurring, it is rather problematic to prepare highly crystalline nickel hydroxide. Crystallinity of forming nickel hydroxide depends on ageing conditions: temperature and composition of mother liquor. In order to obtain very high crystallinity, it is necessary to reduce the rate of the first stage. Ideally, if the nucleation rate would be comparable or higher than the crystallization rate, the two-stage mechanism could change to single-stage, which results in the direct formation of highly crystalline nickel hydroxide precipitate.

Choice of reference samples. Commercially available nickel sample “Bochemie” (Czech Republic) was chosen as a reference. Sample label – Bochemie.

Characterization of nickel hydroxide samples.

Crystal structure of the samples was studied by means of X-ray Diffraction (XRD) analysis using DRON-3 diffractometer (Russia) (Co-K α radiation, scan range 10–90° 2 θ , scan rate 0.1 °/s).

Specific surface area was calculated using the BET method, by low-temperature nitrogen adsorption conducted on high-speed gas sorption analyzer Quantochrome Corp., NOVA 2200 E.

Electrochromic properties of highly crystalline nickel hydroxide samples were studied by means of charge-discharge cycling in the accumulator and supercapacitor regimes.

Charge-discharge cycling in the accumulator regime was conducted using specifically designed accumulator model (Fig. 1). Working electrode: substrate – nickel mesh on nickel foil; active mass – 81 % hydroxide, 16 % graphite, 3 % PTFE. Electrolyte – 6 M KOH. Counter-electrode – cadmium with significantly higher capacity. Reference electrode – Ag/AgCL (KCl sat.). Charging was conducted in the 10-hour regime with 10 % overcharge and discharge until the working electrode potential reached 0 mV. Discharge curves were recorded on a computer using digital multimeter UT-17. Specific capacity Q_{spec} (mA·h/g) was calculated from discharge curves.

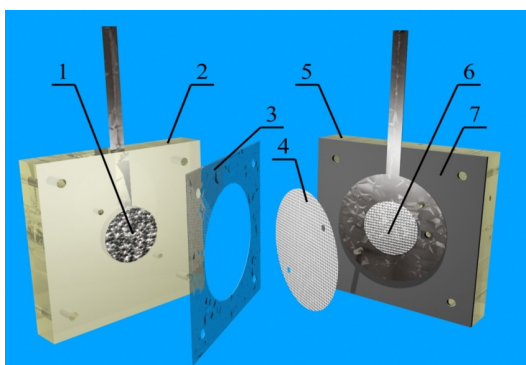


Fig. 1. Accumulator model for galvanostatic charge-discharge cycling: 1 – counter-electrode; 2, 5 – Plexiglas half-elements; 3 – spacer; 4 – separator; 6 – working electrode; 7 – rubber spacer

Charge-discharge cycles in the supercapacitor regime were recorded in a special cell YSE-2, using digital potentiostat Ellins P-8 (Russia). For experiments, the working electrode was prepared by pasting a mixture of nickel hydroxide sample (82.5 % wt.), graphite (16 % wt.) and PTFE (1.5 % wt.) [33] on the nickel foam matrix. Electrolyte – 6M KOH. Counter-electrode – nickel mesh, reference electrode – Ag/AgCL (KCl sat.). Charge-discharge cycling in the supercapacitor regime was conducted at current densities of 5, 10, 20, 40, 80 and 120 mA/cm² (10 cycles at each current density). Specific capacities C_{sp} (F/g) and Q_{spec}^{sc} (mA·h/g) were calculated from discharge curves.

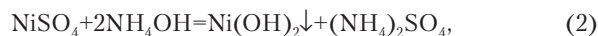
5. Results of synthesis method development and characterization of highly crystalline nickel hydroxide

Synthesis method of ultracrystalline β -Ni(OH)₂.

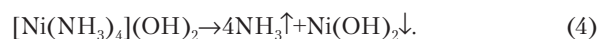
Previously, it was stated that for the preparation of highly crystalline β -Ni(OH)₂, it was necessary to decrease the nucleation rate as the first stage of nickel hydroxide formation. In order to achieve that, it was proposed to use decomposition method. It was proposed to employ slow decomposition of nickel complex. The nickel ammine complex was chosen, which slowly decomposes during evaporation of ammonia.

For the realization of the method, a solution of tetraammine nickel hydroxide was prepared by add-

ing an excess of 25 % ammonia solution to the nickel sulfate (12 g/l Ni²⁺) solution. During preparation, the following reactions occur:



The prepared solution was filtered, transferred into a narrow-necked flask, which was sealed with cellulose membrane. The synthesis was conducted for 6 months under very slow evaporation of ammonia and decomposition of the complex according to the reaction:



Visual observation revealed that within 6 months the solution color had been changing from violet to blue, which indicates complex decomposition. Additionally, a highly dispersed crystalline, rather than hydrophilic, precipitate was formed on the flask walls and bottom.

The prepared sample was labeled as Decomp.

Study of physicochemical properties of the samples.

Fig. 2 shows XRD patterns of the samples Decomp and Bochemie. The sample Decomp (Fig. 2, a) is ultracrystalline β -Ni(OH)₂, with the crystallite size in the direction of (001) plane of 825 Å. Commercial sample Bochemie is also β -Ni(OH)₂, but its crystallinity is significantly lower, with the crystallite size in the direction of (001) plane of 360 Å.

Table 1 shows the parameters of Ni(OH)₂ obtained with the BET method. It should be noted that both high crystallinity samples (Decomp, Bochemie) have similar parameters.

Table 1

Specific surface area, pore volume, and pore radius of Ni(OH)₂ samples

Sample	S_{sp} BET m ² /g	Specific pore volume, cm ³ /g	Average pore radius, Å
Decomp	100	0.12	20
Bochemie	96	0.13	26

Study of electrochemical properties of the samples.

Fig. 3 shows specific capacities and coulombic efficiency for the samples Decomp and Bochemie in the accumulator regime.

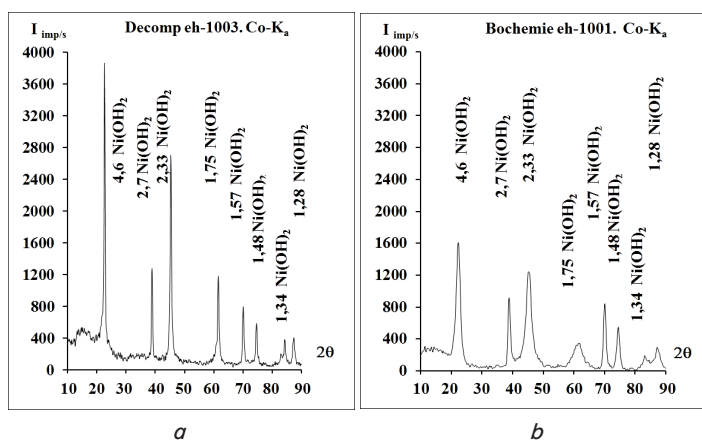


Fig. 2. XRD patterns of nickel hydroxide samples: a – Decomp, b – Bochemie

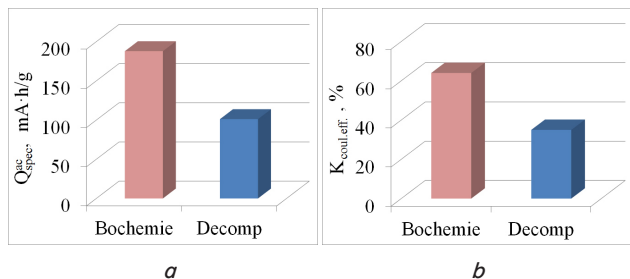


Fig. 3. Electrochemical parameters of $Ni(OH)_2$ samples in the accumulator regime: *a* – specific capacity, mA·h/g, *b* – coulombic efficiency, %

It should be indicated that the specific capacity and coulombic efficiency of ultracrystalline sample Decomp are significantly lower than those of the sample Bochemie. Very low coulombic efficiency of the sample Decomp (35 %) signifies low effectiveness for use of the ultracrystalline sample in alkaline accumulators.

Fig. 4 shows specific capacities of the samples Decomp and Bochemie at different charge-discharge current densities in the supercapacitor cycling regime.

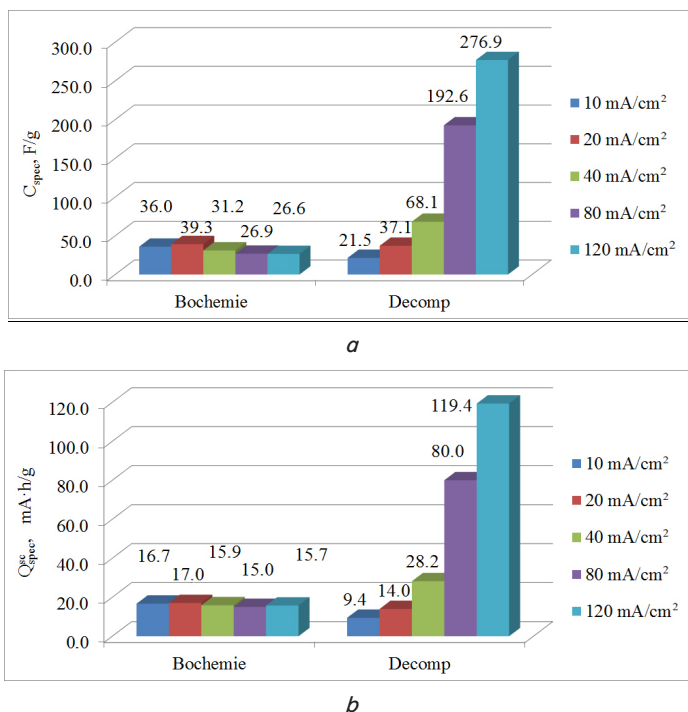


Fig. 4. Electrochemical parameters of $Ni(OH)_2$ samples at different current densities of charge-discharge cycling in the supercapacitor regime: *a* – specific capacity C_{sp} , F/g; *b* – specific capacity Q_{spec}^{ac} , mA·h/g

It should be mentioned that for use in supercapacitors, the situation with specific characteristics of the samples was the opposite. The sample Bochemie shows very low specific characteristics: 15–17 mA·h/g and 26.6–39.3 F/g. Additionally, its specific capacities almost didn't change with increasing cycling current density. The sample Decomp demonstrates a different behavior. At low current densities, the specific characteristics of ultracrystalline sample Decomp are lower than those of commercial sample Bochemie. However, with an increase of cycling current density, specific capacities increase significantly and at 120 mA/cm² reach 119.4 mA·h/g and

276.9 F/g. Such high specific capacities are comparable and even surpass those of the world's best samples.

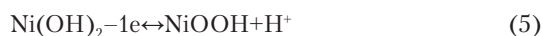
6. Discussion of results of the synthesis method development and characterization of nickel hydroxide samples

Method development for synthesis of ultracrystalline $\beta-Ni(OH)_2$. Visual control of nickel hydroxide precipitation using the proposed method of ammine complex decomposition showed the correctness of the proposed hypothesis. At very slow evaporation of ammonia, crystalline, rather than hydrophilic, precipitate was formed. Thus, it can be indicated that during slow decomposition of tetraammine nickel hydroxide, the formation of $Ni(OH)_2$ occurs in one stage, i. e. the rates of nucleation and crystallization are comparable.

Study of physicochemical properties of the samples. The results of studying the crystal structure have revealed that using the proposed decomposition method, a sample of $\beta-Ni(OH)_2$ with very high crystallinity has been prepared. So, this validates that the method for preparation of ultracrystalline $\beta-Ni(OH)_2$ has been developed. It should be mentioned that crystallinity of the sample Decomp significantly exceeds that of the commercial sample Bochemie, while specific surface area, volume and average radius are almost the same.

Study of electrochemical properties of the samples.

When discussing the results of studying the electrochemical characteristics of nickel hydroxide samples, it is necessary to take into account the specifics of electrochemical processes that occur in accumulators and supercapacitors. For accumulators, the significant characteristic is coulombic efficiency, because the charging process occurs rather slowly, and the nickel hydroxide particle should be deeply oxidized. So, the reaction of nickel hydroxide charge-discharge



is solid-state, its rate is determined by the rate of H^+ and electron transfer. And the transfer of H^+ inside the solid particle significantly depends on crystal structure.

Supercapacitors operate at high current densities, and the electrochemical process is localized on the particle surface or within a thin surface layer. In this case, it is necessary to employ nickel hydroxide with small particle size and high surface area. Herewith, if at higher charge-discharge rates the depth of the process increases, the specific capacity of the material would increase drastically. And again, the depth of the electrochemical process is determined by the rate of H^+ transfer within the solid phase, which depends on crystal structure.

Analysis of galvanostatic charge-discharge cycling results shows that electrochemical characteristics of ultracrystalline hydroxide sample Decomp as an accumulator active material are very low, especially in comparison to the commercial sample Bochemie, which is used for industrial production of accumulators. Coulombic efficiency of the samples Bochemie and Decomp are 64 % and 35 %, correspondingly. This can be explained by the fact that the H^+ diffusion rate in larger, more perfect crystals would be lower than in smaller and more defective. Thus, the effectiveness

of using ultracrystalline $\text{Ni}(\text{OH})_2$ in accumulators would be rather low and such material is not suited for the production of accumulators.

Analysis of the results of cycling in the supercapacitor regime shows that the industrial sample Bochemie has low specific capacity at low current densities ($10 \text{ mA}/\text{cm}^2$). With increasing the current density to $120 \text{ mA}/\text{cm}^2$, the capacity of the sample Bochemie somewhat decreases, which is characteristic of industrial nickel hydroxide. At the same time, ultracrystalline sample Decom demonstrates a different electrochemical behavior. At low current densities, the capacities of the ultracrystalline sample Decom are lower than those of the sample Bochemie. However, with increasing the current density, its capacity greatly increases from $9.4 \text{ mA}\cdot\text{h}/\text{g}$ to $119.4 \text{ mA}\cdot\text{h}/\text{g}$ and from $21.5 \text{ F}/\text{g}$ to $276.9 \text{ F}/\text{g}$. It is assumed that the discovered behavior is related to the breakdown of nickel hydroxide particle agglomerates; into smaller components leading to the increased surface area. Because of the specifics of the formation mechanism, hydroxide particles of the sample Decom are composed of crystals that are weakly bound to each other, which can break down to smaller ones at high current density. Thus, it can be stated that highly crystalline nickel hydroxide can be effectively used in supercapacitors if its particles could break down to smaller ones.

7. Conclusions

1. A method was developed for the preparation of ultracrystalline nickel hydroxide using the decomposition method: slow decomposition of tetraammine nickel hydrox-

ide complex. Visual observation has revealed a change of the hydroxide formation mechanism, which resulted in the formation of scale-like crystalline precipitate instead of hydrophilic one.

2. Structural and surface properties of the sample synthesized using the developed method and reference sample had been studied. By means of XRD analysis, it was confirmed that decomposition method results in ultracrystalline $\beta\text{-Ni}(\text{OH})_2$. It was demonstrated that values of specific surface area, pore volume and average pore radius of both samples are very close to each other.

3. A comparative analysis of electrochemical characteristics of the ultracrystalline sample, prepared using decomposition method, and reference sample – commercially available hydroxide “Bochemie” (Czech republic), had been conducted. Electrochemical characteristics were studied in the accumulator and supercapacitor regimes. In the accumulator cycling regime, ultracrystalline samples demonstrated very low effectiveness: coulombic efficiency of 35 %, in comparison to 64 % for the commercial sample. For the supercapacitor cycling regime, it was demonstrated that for the ultracrystalline sample prepared using decomposition method, an increase of current density from $10 \text{ mA}/\text{cm}^2$ to $120 \text{ mA}/\text{cm}^2$ leads to significant increase of capacity from $9.4 \text{ mA}\cdot\text{h}/\text{g}$ to $119.4 \text{ mA}\cdot\text{h}/\text{g}$ and from $21.5 \text{ F}/\text{g}$ to $276.9 \text{ F}/\text{g}$. Such behavior is explained by the breakdown of particle agglomerates, which results in an increase of specific surface area. At the same time, the commercial sample demonstrates very low specific capacities. Thus, it was shown that highly crystalline $\beta\text{-Ni}(\text{OH})_2$ has high effectiveness for use in supercapacitors, if particle aggregates can undergo breakdown during charge-discharge.

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