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DEFINITION OF FACTORS INFLUENCING ON NI(OH)$_2$ ELECTROCHEMICAL CHARACTERISTICS FOR SUPERCAPACITORS

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Вивчено структурні, поверхневі та електрохімічні властивості зразків гідроксиду нікелю, отриманих методами декомпозиції, гомогенного осадження, електрохімічного синтезу, та промислового зразка. Показано, що найбільший вплив на питому ємність в суперконденсаторному режимі мають тип кристалічної решітки, кристалічність та здатність до розпаду агрегатів під час заряду-розряду; питома поверхня впливає слабо. Максимально отримана ємність сягає 650 Ф/г

Ключові слова: гідроксид нікелю, питома ємність, суперконденсатор, кристалічність, розпад агрегатів частинок

Изучены структурные, поверхностные и электрохимические свойства образцов гидроксида никеля, полученных методами декомпозиции, гомогенного осаждения, электрохимического синтеза, и промышленного образца. Показано, что наибольшее влияние на удельную емкость в суперконденсаторном режиме оказывают тип кристаллической решетки, кристалличность и способность к распаду агрегатов частиц в процессе заряда-разряда; слабо влияет удельная поверхность. Максимально достигнутая емкость составляет 650 Ф/г

Ключевые слова: гидроксид никеля, удельная емкость, суперконденсатор, кристалличность, распад агрегатов частиц

1. Introduction

Supercapacitors are modern electrochemical power cells and are being rapidly developed. Supercapacitors are widely used as power sources for electrical motors, starter batteries for internal combustion engines, uninterruptable power supply units for computers and other devices. Among various types of supercapacitors, hybrid supercapacitors are proven to possess the best characteristics. They are constituted by two electrodes: one utilizes charge-discharge of electric double layer and the second, also called Faradic electrode, utilizes rapid electrochemical reactions for charge storage. Supercapacitors are characterized by rapid charge-discharge rate. As a result, the electrochemical process occurs on a surface and thin surface layer of the Faradic active electrode material. This leads to special requirements for Faradic electrode active materials [1, 2], such as specific surface area, crystal structure and electrochemical activity. The active electrode material is required to have morphology constituted by nano- and submicron-sized particles and high specific surface area. Electrodes that utilize $Ni(OH)_2$ as active material are widely used for hybrid supercapacitors [3–7]. Synthesis of nickel hydroxide with specified properties is a relevant topic.

2. Literature review and problem statement

Synthesis method and its conditions define the micro- and macrostructure of particles, which, in turn, define the electrochemical properties of nickel hydroxide. Synthesis conditions influence crystal inhomoge~~i~~neity [8], microstructure [9], crystallinity [10, 11]. Works [8–10] only review influence on reversible capacity, and article [11] only describes influence on voltamperometric characteristics. Synthesis method primarily defines the phase composition of obtained nickel hydroxide [12]. Nickel hydroxide is known to exist in the form of two allotropic modifications: β-phase (chemical formula $Ni(OH)_2$, isostructural with mineral brucite) and α-phase (chemical formula $3Ni(OH)_2{\cdot}2H_2O$, hydrotalcite-like structure). Work [13] describes a series of intermediate phases of nickel hydroxide. α-$Ni(OH)_2$ can be prepared using various methods, such as homogeneous precipitation [14], from mixed solvent solution [15], under vacuum [17], and microwave synthesis [17]. This phase is more electrochemically active, but less stable than β-$Ni(OH)_2$. In order to stabilize the α-phase, various additives are introduced during synthesis, such as cations of other metals [18]. Another effective method is a formation of layered double hydroxides (LDH), in which part of nickel cations is substituted by tri- or tetravalent cations, with additional anions compensating for excessive positive charge: Al^{3+} and CO_3^{2-} [19, 20], Al^{3+} and NO_3^- [21–23], Al^{3+} and V^{3+} [24].

One of the ways to prepare a highly active electrode material for Faradic electrode of the supercapacitor is a synthesis of $Ni(OH)_2$ with high specific surface area. A generalized reaction of nickel hydroxide synthesis:

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2. \qquad (1)$$

During formation, the rate of nucleation is significantly higher than the rate of crystal growth. The formation mechanism of nickel hydroxide (and other precipitates of the same type) consists of two stages: the first stage (very rapid) – formation of the primal amorphous particle; the second stage (slow) – crystallization (ageing) of the primal particle [25]. This leads to formation of hydrophilic precipitate containing of significant amounts of trapped mother liquor. During filtering and subsequent drying precipitate particles are pressed and cacked, which leads to significant decrease of specific surface area. Synthesis of ultradisperced (nanosized and submicron particles) $Ni(OH)_2$ powders can be achieved in the presence of surfactants, that by adsorbing onto primal particle diminish its growth [26]. Alternatively, hydrothermal treatment of precipitate in mother liquor at 110–140 °C can be employed [27].

Influence of various factors on electrochemical properties of nickel hydroxide, as an active material for accumulators, is well studied only for individual parameters, for instance: precipitation conditions [8], structural defects [9], microstructure [10], crystallinity [11]. However, for $Ni(OH)_2$, as an active material for supercapacitors, the situation is fundamentally different. Almost all conducted researches follow the scheme "synthesis of predefined $Ni(OH)_2$" – "study of electrochemical and other properties". In addition, the synthesis method is chosen based on previously published works [4, 6], or on general theoretic statements, such as the requirement of particle nanosize [3, 5]. Generalization of the influence of synthesis method and its conditions on electrochemical properties of nickel hydroxide for supercapacitor applications is almost never done. In addition, the analysis and determination of factors defining high specific capacity of $Ni(OH)_2$, and evaluation of their significance have not been conducted yet. Without this knowledge, the choice of synthesis method and its conditions is done by trial and error. While in modern chemistry, synthesis method directed at substances with predefined properties, which are governed by application conditions, is the most effective.

3. Aim and objectives

The aim of the work was to define the parameters of nickel hydroxide, at which it demonstrates high specific capacity in supercapacitor cycling regime.

Objectives:

– conduct synthesis of nickel hydroxide using various methods, to prepare samples with different characteristics;

– study structural, surface and electrochemical properties of prepared samples;

– conduct a comparative analysis of samples' properties and determine parameteres of highly active nickel hydroxide for supercapacitor applications.

4. Sample preparation and characterization

To achieve the set out aim, it was necessary to prepare α- and β-phases of nickel hydroxide with different particle size and degree of crystallinity. Synthesis methods and their conditions are based on previously published works [29–32]. α-$Ni(OH)_2$ was prepared using homogeneous precipitation (urea hydrolysis) method. Highly crystalline β-$Ni(OH)_2$ was prepared using decomposition method. Layered hydroxide composed of both phases was prepared by electrochemical method. All reagents employed in synthesis were of analytical purity.

4. 1. Preparation of nickel hydroxide samples

Homogeneous precipitation [28]. A solution containing 60.9 g/l of $Ni(NO_3)_2{\cdot}6H_2O$ and 229.3 g/l of urea, was kept in a water bath at 80 °C for 3 h. Prolonged heating leads to hydrolysis of urea causing homogeneous basification of the solution, resulting in the formation of nickel hydroxide in the whole volume of solution. After the synthesis procedure, the reaction mixture was poured into a large volume of distilled water to quench the reaction. The prepared sample was labeled as 0C.

Decomposition method [29]. A solution of tetraammine nickel hydroxide was prepared by adding an excess amount of 25 % ammonia solution to nickel sulphate (12 g/l Ni^{2+}). During solution preparation, the following reactions occur:

$$NiSO_4+2NH_4OH=Ni(OH)_2\downarrow+(NH_4)_2SO_4, \qquad (2)$$

$$Ni(OH)_2+4\,NH_4OH=[Ni(NH_3)_4](OH)_2+4H_2O. \qquad (3)$$

The prepared solution was filtered, and transferred into a narrow-necked flask, and was sealed with cellulose membrane for 6 months. During this time the complex underwent decomposition caused by very slow evaporation of ammonia from solution:

$$[Ni(NH_3)_4](OH)_2\rightarrow 4\,NH_3\uparrow+Ni(OH)_2\downarrow. \qquad (4)$$

The obtained sample was labeled as *Decomp*.

Electrochemical synthesis. Electrochemical synthesis was conducted using slit diaphragm electrolyzer (SDE) (Fig. 1, *a*). A solution of nickel sulphate ($C_{Ni(2+)}$=12.7 g/l) was pumped through the cathodic space using a peristaltic pump, a solution of NaOH (40 g/l) was pumped through the anodic space. The feed rate of both solutions was 0.2 l/h (Fig. 1, *b*).

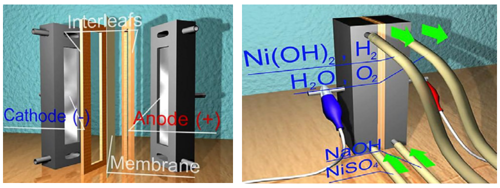
The synthesis was conducted at various current densities during 6–8 hours. Under applied current hydrogen evolves at the cathode leading to the formation of hydroxyl ion, that reacts with nickel cation forming precipitate of nickel hydroxide which is removed from electrolyzer with the catholyte flow. After leaving electrolyzer, the precipitate was immediately separated from the catholyte by vacuum filtering.

at the cathode:

$$2H_2O+2\bar{e}\rightarrow 2OH^{-}+H_2\uparrow; \tag{5}$$

in the catholyte:

$$2OH^{-}+Ni^{2+}\rightarrow Ni(OH)_2 \text{ (cathodic chamber).} \tag{6}$$



a *b*

Fig. 1. Slit diaphragm electrolyzer: *a* — components, *b* — assembled

By using SDE, 5 samples were prepared under slightly different conditions. Sample *S0.2-8* was prepared at current density 8 A/dm^2. Sample *S0.2-15.7* was prepared at 15.7 A/dm^2 [30]. Sample *S0.2-12M* was prepared at 12 A/dm^2, the cation-exchange membrane was used instead of diaphragm [32]. Sample *S0.2-12US* was prepared at 12 A/dm^2, and after leaving SDE the hydroxide suspension was ultrasonically treated. Ultrasound was generated by a magnetostriction emitter – a generator with a frequency of 21.5 kHz. A ferrite rod 14 cm long fixed on a coil was employed as magnetostriction material [31]. Sample *S0.2-12CO3* was prepared at current density 12 A/dm^2; 20 % (mol) Na_2CO_3 was added to the anolyte.

Industrial sample. As an example of crystalline β-$Ni(OH)_2$, an industrial sample, supplied by “Bochemia” (Czech Republic), was employed. The sample was labeled as *Bochemia*.

After the synthesis, all prepared samples were filtered, dried at 90 °C, ground in a mortar, sifted through a nickel grate, washed with distilled water and dried again.

4. 2. Sample characterization

Crystal structure of the samples was characterized using X-ray diffraction (XRD), using DRON-3 diffractometer (Russian Federation) (Co-Kα radiation, range 10–90° 2θ, scan rate 0.1 °/s).

Low-temperature nitrogen adsorbtion-desorbtion was conducted using the Surface Area Analyzer Quantochrome Corp., NOVA 2200 E. Specific surface area was calculated using BET method [33, 34].

Electrochemical properties of nickel hydroxide samples were evaluated by means of galvanostatic charge-discharge cycling, using Elins P-8 Potentiostat (Russian Federation) and a three-electrode cell. Working electrode was prepared by pasting a mixture of samples of nickel hydroxide (82.5 % wt.), graphite (16 % wt.) and PTFE (1.5 % wt.) on a nickel foam electrode. Electrolyte – 6M KOH. Counter-electrode – nickel mesh, reference electrode – Ag/AgCl (KCl saturated). Charge-discharge cycling was conducted in a supercapacitor regime at current densities of 5, 10, 20, 40, 80 and 120 mA/cm^2 (10 cycles at each current density). Specific capacities C_{spec} (F/g) were calculated from discharge curves.

5. Characterization results of nickel hydroxide samples prepared by various methods

Fig. 2 shows XRD patterns of various samples. Decomp samples is a highly crystalline β-$Ni(OH)_2$. This is explained by the fact, that during ammine complex decomposition, the rate of nucleation is comparable to the rate of crystallization, leading to the formation of precipitates with large crystal size.

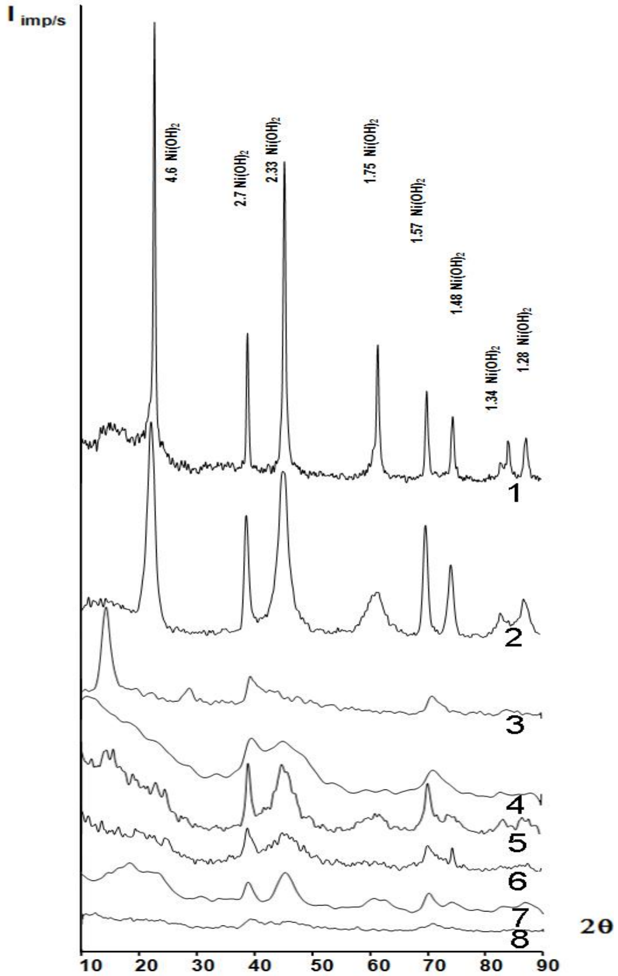


Fig. 2. XRD patterns of nickel hydroxide samples: 1 — Decomp, 2 —Bochemia, 3 — 0 C, 4 — S-0.2-12US, 5 — S-0.2-15.7, 6 — S-0.2-8, 7 — S-0.2-12M, 8 — S-0.2-12CO3

The industrial sample Bochemia is also a highly crystalline β-$Ni(OH)_2$. Sample 0C, prepared by homogeneous precipitation, is a highly crystalline α-$Ni(OH)_2$, which is characteristic of hydroxides prepared by this method [14]. Electrochemically prepared samples using SDE (Fig. 1, 4–8), have a layered structure and are composed of both β-$Ni(OH)_2$ and α-$Ni(OH)_2$ [28]. SDE provides unique synthesis conditions: when nickel hydroxide particle passes through cathode slit of electrolyzer its crystal growth rate is accelerated by Joule heating. As a result, the degree of crystallinity is proportional to current density: sample S-0.2-15.7 has an average crystallinity, and crystallinity of sample S-0.2-8 is low. The use of membrane instead of diaphragm almost did not affect the crystallinity: crystallinity of samples S-0.2-8 and S-0.2-12M is almost the same. Carbonate-activated samples S-0.2-12CO3 is X-ray amorphous. The sample was prepared by feeding base-carbonate solution into the anodic chamber. Carbonate ion diffuses through the diaphragm and is incorporated into the structure of nickel hydroxide. This is accompanied by a decrease of crystallinity. Samples S-0.2-12US was prepared by treating $Ni(OH)_2$ suspension with ultrasound, immediately after it left SDE.

Ultrasound treatment has lead to significant changes in crystal structure. The content of α-$Ni(OH)_2$ was increased considerably while the degree of crystallinity is reduced significantly.

Results of BET analysis are listed in Table 1. It should be noted, that high specific surface area and smaller pore radius are characteristic for samples prepared by chemical synthesis methods that also have a high degree of crystallinity. Electrochemically prepared samples have low specific surface area and large pore radius. A trend can be observed – the lower the crystallinity the lower the specific surface area. Samples S,02-12US, prepared with ultrasound treatment, stands out by all parameters listed in Table 1. This sample demonstrated the lowest specific surface area (6 m^2/g), the largest specific pore volume (0.35 sm^3/g) and the largest average pore radius (1181 Å). It is probably because of cavitation caused by ultrasound treatment, that leads to the formation of micro shockwaves that, on the one hand, smooth out the particle surface, while on the other – cause microtearing inside of it.

Table 1

Specific surface area, porve volume and average pore size of $Ni(OH)_2$ samples

Samples	$S_{sp.}$ BET m^2/g	Specific pore volume, cm^3/g	Average pore radius, Å
Decomp	100	0.12	20
Bochemia	96	0.13	26
0 C	150	0.12	45
S-0.2-15,7	48	0.14	120
S,02-12 US	6	0.35	1181
S,02-8	32	0.18	113
S-0.2-12M	42	0.17	115
S-0.2-12CO3	26	0.21	109

Fig. 3 shows specific capacities of the studied samples under different current densities during galvanostaitc charge-discharge cycling in the supercapacitor regime.

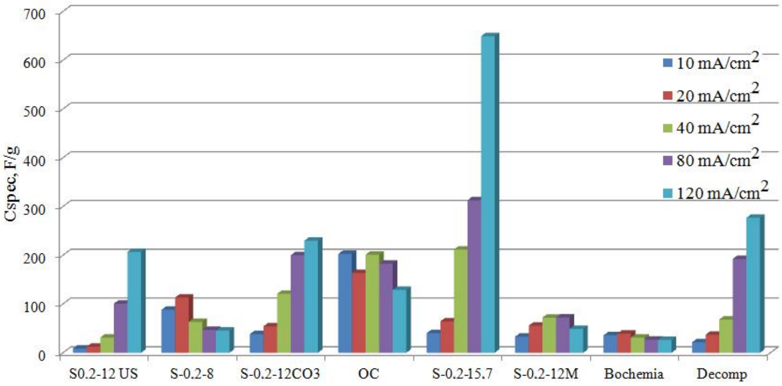


Fig. 3. Specific capacities of the studied nickel hydroxide samples under different current densities during galvanostatic charge-discharge cycling, F/g

Samples Bochemia and S-0.2-12M demonstrate the lowest specific capacities. Relatively high capacities (190–210 F/g) are demonstrated by samples S-0.2-12SU, S-0.2-12CO3, 0C, which differ significantly by phase composition, crystallinity and specific surface area. Even higher capacity (277 F/g) is demonstrated by Decomp sample. The highest capacity (650 F/g) is demonstrated by sample S-0.2-15.7, that was prepared by electrolysis in a slit diaphragm electrolyzer. Such specific capacity value is comparable to, and even exceeds the parameters of the world's best samples [6, 7].

6. Discussion of nickel hydroxide samples characterization results

Specifics of supercapacitor operation [2] clearly indicate that in order to achieve high specific capacity, the active material is required to have a high specific surface area. However, in case of Faradic electrode, the increased depth of electrochemical process also increases specific capacity. The rate of the charge-discharge process of $Ni(OH)_2$ is governed by H^+ mobility, which is determined by the degree of crystallinity and crystal structure. The following discussion is based on analysis of these three parameters.

Type of nickel hydroxide crystal structure. Based on occurring reaction, α-$Ni(OH)_2$ ($3Ni(OH)_2 \cdot 2H_2O$) should possess higher specific capacity, because of the presence of water in its crystal structure. The obtained data proves this assumption: specific capacities of sample 0C (α-$Ni(OH)_2$) and sample Bochemia (β-$Ni(OH)_2$.) of similar crystallinity are 201 F/g and 31 F/g correspondingly. This means that α-$Ni(OH)_2$ possesses higher specific capacity. However, prepared samples that have a layered structure that contain both β-$Ni(OH)_2$ and α-$Ni(OH)_2$, possess even higher value of specific capacity – 630 F/g (sample S-0.2-15.7).

Crystallinity. The effect of crystallinity has only been studied for β-$Ni(OH)_2$. Works [9, 14] indicate that lowering crystallinity of β-$Ni(OH)_2$ leads to the formation of β_{bc}-$Ni(OH)_2$ (bc – badly crystalline), that possesses higher capacity. However, this data was acquired only for accumulator regime. The data acquired in the present work is conflicting (Fig. 1, 2). Sample Decomp with a very high degree of crystallinity demonstrated a high specific capacity (up to 231 F/g), while highly crystalline sample Bochemia demonstrated the lowest specific capacity 32 F/g. It is possible, that for electrochemically prepared samples, there is some optimal degree of crystallinity that determines high specific capacity. Such degree of crystallinity is characteristic of sample S-0.2-15.7, that has demonstrated very high specific capacity under high current density. Lower crystallinity also leads to a decrease of specific capacity. However, the data listed above was obtained under high charge-discharge current density (80–120 mA/cm^2). Under low current densities (10–20 mA/cm^2), which is characteristic of both supercapacitors and high rate accumulators, the dependency described in literature [9, 10, 14, 45] can be observed – the highest specific capacity is demonstrated by sample S-0.2-8, with a very low degree of crystallinity, while samples with a higher degree of crystallinity demonstrate lower capacities.

Specific surface area. Based on the supercapacitor operation principle, the specific surface area is one of the main parameters of active material [1, 2]. However, the data obtained doesn't correspond to this principle completely. Comparison of specific surface area data (Table 1) and specific capacity data (Fig. 2) revealed the following facts. Samples S,02-12 US with specific surface area of 6 m^2/g have demonstrated the specific capacity of 207 F/g, samples Bochemia – 96 m^2/g and 39 F/g, samples 0C – 150 F/g and 202 F/g. This data allows for a conclusion, that for nickel hydroxide, as an active material for supercapacitor's Faradic electrode, the specific surface area does not play a key role. The increase of specific surface area can increase the specific capacity only upon optimization of other parameters.

Other parameters. As a result of conducted studies, a few additional parameters that can improve specific capacity of nickel hydroxide samples were determined.

Activation. Activation of nickel hydroxide, by CO_3^{2-} in particular, leads to increase of specific capacity. This is proved by specific capacities of sample S-0.2-12CO3 (intentionally activated with carbonate) and S-0.2-12M (prepared under conditions that prevent carbonate from entering into cathodic space): 230 F/g and 72 F/g correspondingly (Fig. 2). This indicates an increase of specific capacity by more than 3 times.

Ability of hydroxide sample to undergo agglomerate breakdown during cycling. During galvanostatic charge-discharge cycling, a new occurrence has been observed: for some samples (Decomp, S-0.2-12CO3, S-0.2-15,7, S-0.2-12US) the increase of current density leads to increase of specific capacity (Fig. 2). However, theoretically under higher current density, the reaction depth is less and specific capacity should decrease. It is assumed, that the observed behavior is tied to the breakdown of hydroxide particles agglomerates, leading to larger active surface. Samples S-0.2-12CO3, S-0.2-15,7, S-0.2-12US after preparation were vacuum filtered and dried, caused particles to press and cake leading to the formation of unstable agglomerates. Sample Decomp consists of large crystals weakly bonded to each other.

The results of this research could be used for directed synthesis of highly active nickel hydroxide with predefined properties, leading to improved properties of supercapacitors.

7. Conclusions

1. Structural, surface and electrochemical properties~~,~~ of nickel hydroxide sample prepared by homogeneous precipitation, decomposition, electrochemical synthesis using a slit diaphragm electrolyzer under various current densities, with diaphragm or membrane, carbonate activation, immediate ultrasound post-treatment and an industrial sample, prepared by chemical route have been studied. It has been found, that specific capacity is affeceted by the type of crystal structure, crystallinity, specific surface area, structure activation, and ability to undergo agglomerate breakdown during charge-discharge cycling. It has been demonstrated that only two parameters definitely improve specific capacity: the presence of activating additive and the ability of particle agglomerates to undergo breakdown during charge-discharge cycling. Influence of other parameters is ambiguous and should be evaluated in complex with other parameters.

2. It has been demonstrated, that specific capacity of nickel hydroxide is the most affected by the parameters that increase the depth of discharge process and the ability to undergo agglomerate breakdown. The influence of parameters decreases in the order "ability to undergo particle agglomerate breakdown" – "(α or (α+β) type of crystal structure" – "low and average cristallinity" – "activation". The influence of specific surface area on increase of specific capacity is not significant. The highest specific capacity of 650 F/g is characteristic characteristic of the sample that has a layered type of crystal structure (α+β), average cristallinity and is composed of agglomerates that can undergo breakdown into smaller particles during charge-discharge cycling.

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