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A simple and novel method for preparing $Ni(OH)_2$ Part I: Structural studies and voltammetric response

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$Ni/Ni(OH)_2$ electrodes were prepared by *in situ* precipitation of nickel hydroxide into porous nickel substrates. The thermal decomposition of urea in solutions containing Ni^{2+} was used for the synthesis of the active material. The compound prepared by this method was a poorly crystallized β(II)-type phase. The electrochemical behaviour of $Ni/Ni(OH)_2$ electrodes thus prepared was studied by cyclic voltamperommetry and the efficiency of the *in situ* precipitation was followed by the measurement of the cathodic charge obtained from the j–E response. The amount of incorporated material depends on the urea concentration and the electrochemical response of the electrodes was improved by increasing the number of impregnation cycles.

1. Introduction

Many methods have been developed to improve the impregnation process of the active material of positive nickel hydroxide electrodes for Ni–Cd, Ni–Fe or Ni–H_2 batteries. Chemical and electrochemical impregnation methods have been used since the beginning of the century [1–6].

In the pocket and sintered type electrodes, the nickel plates were frequently used as substrates in the manufacturing of Ni–Cd batteries [1]. Attempts have also been made to develop lighter substrates with higher porosity which allows incorporation of larger amounts of active material to obtain high capacity electrodes. Therefore porous substrates prepared from fibres and nickel powder have been recently produced [7–9].

Chemical impregnation has been used in the authors' laboratory for many years to prepare nickel hydroxide thin films on inert substrates [10–12]. Since it is difficult to incorporate the solid nickel hydroxide particles into the minute holes of porous substrates by chemical precipitation, a new *in situ* precipitation method based on the homogeneous chemical precipitation by thermal hydrolysis of urea [13] is reported in this paper. Urea hydrolyses according to the equation

$$CO(NH_2)_2 + H_2O \Longrightarrow CO_2 + 2NH_3 \qquad (1)$$

The hydrolysis is slow at room temperature but fairly rapid at 100° C. Thus the pH can be well controlled by controlling the temperature and time of heating. The net increase in pH due to the mixture of CO_2 and NH_3 lead to the precipitation of hydrolizable metallic cations. The precipitated products can be oxides, hydroxides, basic sulphates and/or carbonates of the metallic cation, depending on the conditions of synthesis such as pH, temperature, the nature of anions, salt concentration, etc. [14–15].

The purpose of this paper is to examine if this precipitation method, based on the thermal hydrolysis of urea, allows the generation of $Ni(OH)_2$ into the pores of the substrates so as to improve the impregnation process. The incorporation of this material was followed by cyclic voltammetry since it is possible to estimate indirectly the amount of material deposited as well as to obtain the electrochemical efficiency of the electrodes. The physicochemical characterization of the precipitated material was performed using thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential thermal gravimetric analysis (DTG), scanning electron microscopy (SEM), infrared spectroscopy (IR) and X-ray diffraction (XRD).

2. Experimental details

2.1. *Preparation of Ni(II) powder compounds* (ex situ *synthesis*)

In order to characterize the precipitated material, *ex situ* synthesis was made as follows: glass tubes containing a solution of $NiSO_4$ and urea were heated for 2 h at 90° C. After the heating, the resulting dispersions were centrifuged at 5 000 r.p.m. for 5 min, the supernatant solution was discarded and the particles were resuspended in deionized water. This process was repeated three times to rinse the solid material. Then, the purified particles were oven-dried at 120° C. In all of these syntheses the initial $NiSO_4$ concentration was kept constant (0.1 M) and the initial urea concentration was varied between 0 and 200 g dm^{-3} in order to find the optimum concentration for the precipitation.

2.2. *Preparation of nickel electrodes by precipitation of Ni(II) compounds into the substrates* (in situ *synthesis*)

A piece of Fibrex* (90% porosity) of 0.5 cm × 0.5 cm × 0.3 cm was first embedded in a urea/$NiSO_4$ solution for 30 min to fill the pores completely. Then, the embedded porous substrate was thermally treated as described before. The concentration of $NiSO_4$ was also kept constant (0.1 M) and the urea concentration was varied between 0 and 200 g dm^{-3}.

To determine the amount of precipitated material obtained by hydrolysis, the Ni^{2+} residual concentration after the thermal treatment was spectrophotometrically measured at 390 nm in a Shimadzu recording UV-260 spectrophotometer. The difference in the amount of Ni^{2+} before and after precipitation was expressed as grams of precipitated $Ni(OH)_2$.

2.3. *Characterization of Ni(II) powder compounds*

The XRD patterns of the powder material were obtained with a Philips PW 1140 diffractometer using Cu$K\alpha$ radiation at a sweep rate of 2 degrees min^{-1}.

For TGA, DTA, and DTG, 20 mg of the solid material were heated under nitrogen in a NETZSCH 5TA 328 instrument from 25 to 600° C at a rate of 10° C min^{-1} using alumina as the reference material.

I.r. spectra were obtained with a Nicolet 55X FTIR spectrophotometer. To make the measurements, the samples were thoroughly mixed with KBr (spectroscopic grade) and pressed into pellets.

SEM photographs were taken using a 507-B Philips microscope.

2.4. *Electrochemical measurements*

The electrodes are classified into three types (A) a Fibrex piece without any treatment which was used as a blank; (B) a Fibrex piece impregnated in a $NiSO_4$ solution; and (C) a Fibrex piece impregnated in a $NiSO_4$/urea solution. Electrodes B and C were thermally treated in the same way. The electrochemical study was performed by cyclic voltammetry using 5 M KOH as electrolyte. A Hg/HgO/1 M KOH and a large area platinum foil were used as reference and auxiliary electrodes, respectively. A short piece of nickel wire was used as a hook to produce electric contact with the working electrode. The experimental setup for the electrochemical measurements was the same as already described in previous publications [10–12, 16]. The electrodes were aged in the KOH electrolyte solution for 30 min before the electrochemical experiments started; then, they were cycled at 100 mV s^{-1} for 15 min in the 0–0.8 V potential range in order to obtain a stable profile. After this, a voltammperogram was recorded at a sweep rate of 10 mV s^{-1} from which the value of the cathodic charge (Q_c) was obtained. The current units in the voltammperograms were normalized to the weight of the substrate, since it was difficult to estimate the real surface area of the highly porous substrate.

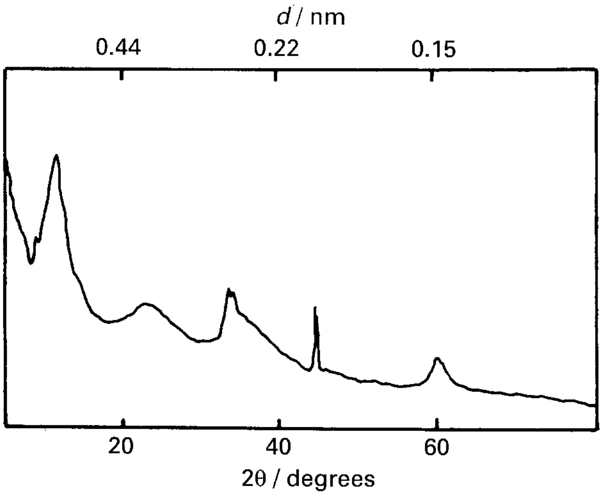

Fig. 1. X-ray diffraction spectra of a nickel (II) hydroxide powder sample obtained by urea decomposition.

The measurement of the amount of incorporated material was made according to the following procedure: after the electrochemical experiments, the nickel hydroxide generated on the substrate was dissolved in 1 ml of 1 M HNO_3 for 2 min under ultrasonic stirring. After that, the substrate was removed and 9 ml of 5 M HCl were added to the remaining solution. The determination of Ni^{2+} concentration was made by atomic absorption using a Jarrell Ash Mod. 82-529 spectrophotometer. The procedure was also applied to a substrate without thermal treatment.

3. Results and discussion

3.1. *Characterization of the precipitated material*

The precipitated material obtained *ex situ* by hydrolysis of urea consisted of spherical particles of about 2.5 μm average diameter as seen by SEM, although it is not certain whether the observed particles correspond to single particles or agglomerates of smaller ones.

The XRD pattern of this sample is shown in Fig. 1. In recent reports [17, 18], Delmas *et al.* reported X-ray spectra of a $\alpha + \beta_{bc}$-$Ni(OH)_2$ mixture, where β_{bc} is a poorly crystallized β(II)-type phase which showed similar XRD pattern to that of Fig. 1. According to Delmas *et al.*, this sample has a structure between α-turbostratic and β(II) well crystallized nickel hydroxide.

The i.r. spectrum (Fig. 2) of the precipitated material is also similar to that reported by Delmas *et al.* [17] for β_{bc}-$Ni(OH)_2$. A narrow band at 3650 cm^{-1} corresponding to the stretching vibration ν(OH) of non-hydrogen-bonded OH groups, a broad band centred at 3450 cm^{-1} and 1650 cm^{-1}, respectively, due to the stretching and bending modes of water molecules, a strong band at 520 cm^{-2}, due to the hydroxide groups' lattice vibration, δ(OH). The different bands observed in the 1600–700 cm^{-1} range

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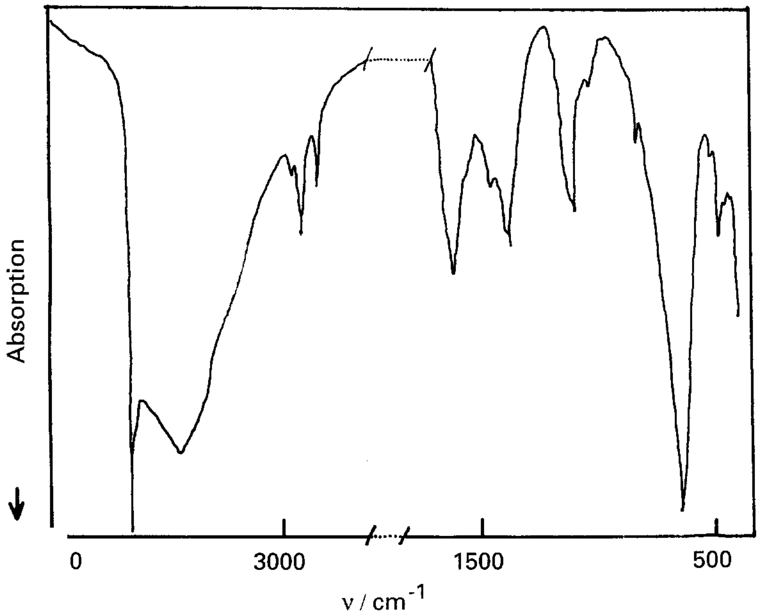

Fig. 2. Infrared spectra of a nickel (II) hydroxide powder sample obtained by urea decomposition (*ex situ* synthesis).

have been attributed to the presence of several ions such as carbonate and/or sulphate [19]. On the other hand, in the present case, the bands at 2850 and 2920 cm^{-1} may be assigned to residual urea and/or carbonate ions.

The TGA, DTG, and DTA of the precipitated sample are shown in Fig. 3. The TGA curve is similar to that previously reported [17] for α-nickel hydroxide. The weight loss below 240° C and the endothermic DTA curve can be attributed to the endothermic evolution of adsorbed water and part of intercalar water. Elimination of the remnant intercalar water and dehydroxilation of the hydroxide sheets proceed in a single step for temperatures higher than 240° C. The weight loss between 240 and 600° C was 23.2% whereas the theoretical weight loss corresponding to the reaction

$$\mathrm{Ni(OH)_2(s)} \Longrightarrow \mathrm{NiO(s)} + \mathrm{H_2O(g)} \qquad (2)$$

is 19.1%. These results indicate that some of the intercalar water is eliminated together with the water from dehydroxilation of hydroxide sheets, as reported in several papers [20–22].

The results in Figs 1, 2 and 3 corroborate the precipitation of Ni(II) hydroxide with a structure in between the disordered α-turbostratic phase and a relatively well crystallized β(II)-$\mathrm{Ni(OH)_2}$. This solid will be referred here as $\mathrm{Ni(OH)_2}$. The i.r. data indicate that the precipitated sample contained some sulphate and carbonate impurities; however, the principal product of reaction must be $\mathrm{Ni(OH)_2}$ as shown by XRD and thermogravimetric analysis.

3.2. *Effect of urea concentration on the precipitation yielding*

Figure 4 shows the variation of the $\mathrm{Ni^{2+}}$ concentration in the supernatant solution after the thermal treatment as a function of the urea concentration. This figure also shows the amount of precipitated $\mathrm{Ni(OH)_2}$ calculated from the decrease in the $\mathrm{Ni^{2+}}$ concentration, which increases linearly with the concentration of urea.

To corroborate the *in situ* precipitation into the porous Fibrex substrates, SEM observations were performed. Figure 5(a) shows micrographs of the Fibrex porous plate treated with $\mathrm{NiSO_4}$ and urea as described earlier (type C electrode). For comparison, the micrographs of the Fibrex porous plates without

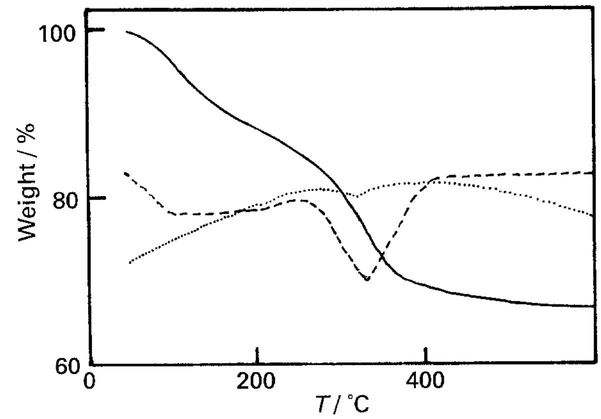

Fig. 3. TGA, DTA and DTG of a nickel (II) hydroxide powder sample obtained by urea decomposition. Key: (—) TGA; (- - -) DTG; (. . . . .) DTA.

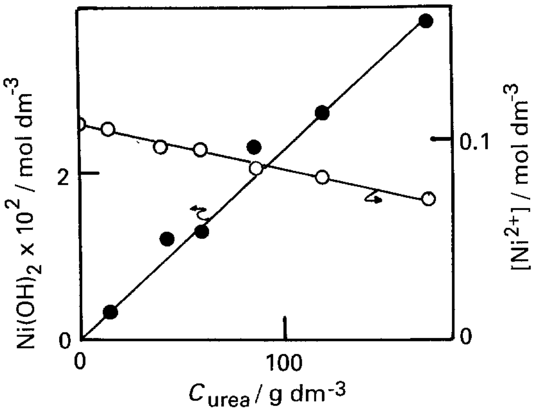

Fig. 4. Dependence of $\mathrm{Ni^{2+}}$ concentration in the supernatant solution after the thermal treatment as a function of the urea concentration. Initial concentration of $\mathrm{NiSO_4}$: 0.1 M. $\mathrm{Ni^{2+}}$ concentration was measured after 2 h at 90° C. The number of moles of $\mathrm{Ni(OH)_2}$ precipitated per litre of solution calculated from the diminution of $\mathrm{Ni^{2+}}$ in solution is also shown.

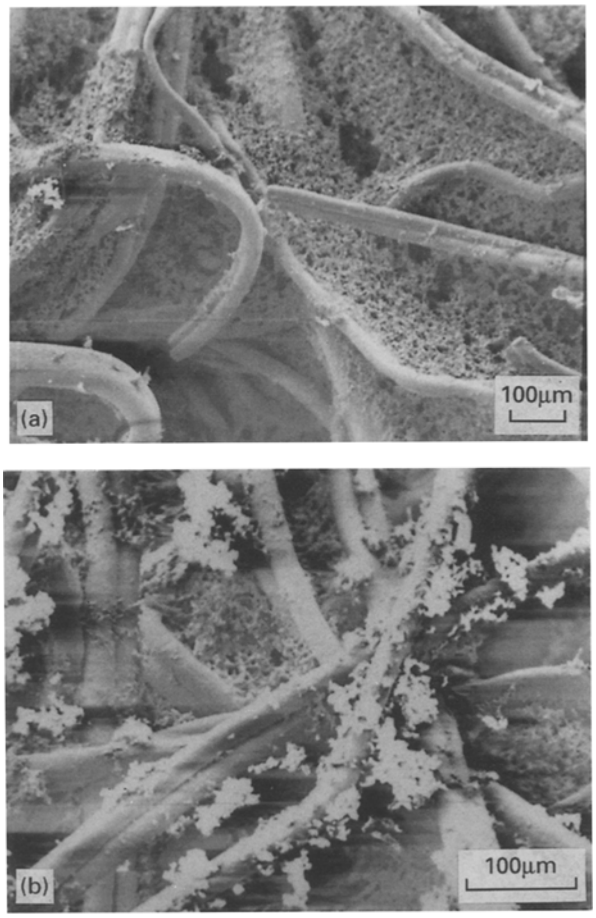

Fig. 5. SEM photographs of nickel substrates: (a) Before the precipitation of nickel hydroxide. (b) After the precipitation of nickel hydroxide by urea decomposition. Time of thermal treatment: 2 h. C_{urea}: 100 g dm^{-3}. Bar: 100 μm.

treatment (type A electrode) are shown in Fig. 5(b). Precipitation inside the substrate is effective with this method; the size and shape of the deposited particles are the same as those observed in powder samples of $Ni(OH)_2$ synthesized *ex situ*.

3.3. *Electrochemical behaviour*

The electrochemical behaviour of porous electrodes in 5 M KOH solution is shown in Fig. 6 for electrode types A, B and C. It is evident that the charge involved in type B is larger than that for type A. This can be explained taking into account that when the porous substrate is immersed in the 5 M KOH, the Ni^{2+} ions in the pores precipitate to form $Ni(OH)_2$.

The charge increase is even more pronounced when voltammograms are performed with type C. This shows that the amount of $Ni(OH)_2$ deposited inside the substrates is higher and corroborates the efficiency of the incorporation of $Ni(OH)_2$ as shown by SEM.

A typical value for the voltammetric cathodic charge for an electrode prepared with one impregnation cycle is 0.3 C, on the other hand, the quantity of nickel hydroxide precipitated is 4.77×10^{-6} moles; consequently a voltammetric discharge efficiency, η (defined by the relation $\eta = q/nF$) [11]), of 0.65 is obtained (0.65 moles of electrons interchanged by moles of nickel hydroxide precipitated).

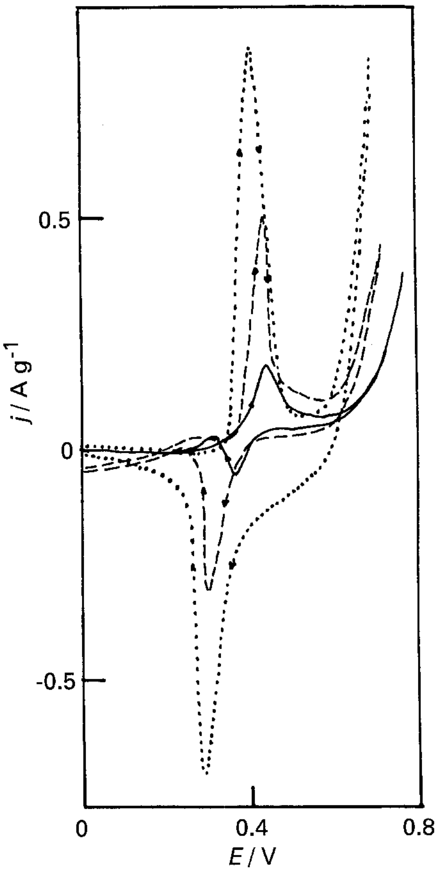

Fig. 6. j–E profiles of nickel electrodes at 0.01 V s^{-1}. (—) Type A electrode; (- - - -) type B electrode; (. . . .) type C electrode.

The effect of varying the urea concentration on the voltammetric cathodic charges of the electrodes is shown in Fig. 7. The voltammetric cathodic charge is here also normalized to the substrate mass and represented as a function of the concentration of urea. For 0.1 M $NiSO_4$ solutions, a saturation value is obtained when the concentration of urea is higher than 50 g dm^{-3}. This value does not correspond to the precipitation of all Ni^{2+} as evidenced from Fig. 4, since the concentration of free nickel for urea concentrations of 100 g dm^{-3} decreases only 10%.

The amount of impregnated active material and the voltammetric cathodic charge can be increased by repeating the impregnation process several times. In order to allow the further incorporation of more solu-

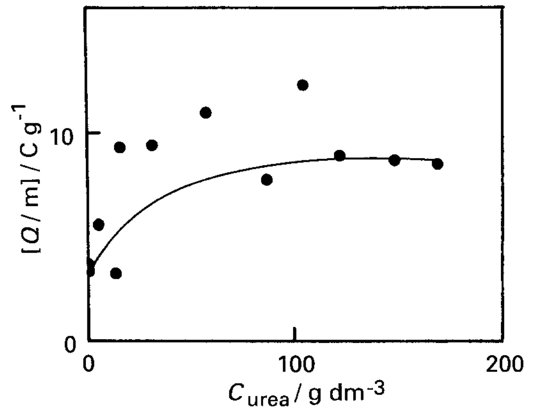

Fig. 7. Dependence of the Q/m ratio (cathodic charge normalized to the substrate mass) with the urea concentration. C_{NiSO_4}: 0.1 M. Time of thermal treatment: 1 h.

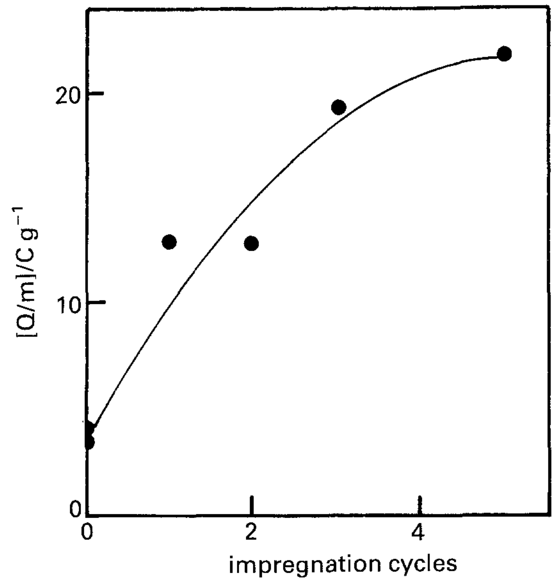

Fig. 8. Dependence of the Q/m ratio with the number of impregnation cycles. C_{NiSO_4}: 0.1 M. C_{urea}: 100 g dm^{-3}.

tion inside the pores, before a new impregnation process was performed, the electrodes were dried at 100° C for 30 min. In these experiments, the concentration of urea was kept constant at 100 g dm^{-3}. The charge value as a function of the number of impregnation cycles is shown in Fig. 8. The value reported for zero cycles of impregnation is that measured with the substrate treated only with a $NiSO_4$ solution. The magnitude of the charge significantly rises with the number of impregnation cycles, thus improving the efficiency in the deposition of $Ni(OH)_2$ into the substrates. From the data shown in Figs 4 and 7, the saturation value observed in Fig. 4 from urea concentrations higher than 50 g dm^{-3} is difficult to explain. An increase in the urea concentration does not produce an enhancement in the cathodic charge. On the other hand, repeating the impregnation process does enhance this charge. This apparent incongruence indicates that the precipitation process, and the incorporation of $Ni(OH)_2$ into the substrates, is a complex mechanism which is not completely understood. The precipitation mechanism is currently under study.

5. Conclusions

The preparation of nickel hydroxide electrodes based on the decomposition of urea is an efficient method for the precipitation of $Ni(OH)_2$ inside porous substrates.

Characterization by XRD, TGA, DTA and IR spectroscopy of the *ex situ* prepared materials shows the presence of β_{bc}-hydroxide with intercalar water molecules.

SEM and electrochemical measurements revealed that the $Ni(OH)_2$ impregnation is effective inside the substrate and that the amount of precipitated active material can be increased by repeating the decomposition process several times. This increase in the amount of active material and, therefore, of the charge density involved in the redox process, may allow the use of this method in the preparation of positive electrodes for alkaline batteries.

The efficiency of the active material obtained for one cycle of impregnation is a relatively good value for these electrodes, although it is calculated from voltammetric experiments. However, preliminary results obtained with galvanostatic experiments, now in progress, also indicate a good performance of these electrodes with cycling.

The results show that the electrodes have, in general, a good electrochemical response. It is necessary to carry out further studies to improve the efficiency of the active material incorporation process and to elucidate the mechanism of this process.

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