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APPLIED ELECTROCHEMISTRY  
AND CORROSION PROTECTION OF METALS

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# Intensification of Impregnation of Metal–Ceramic Supports in Fabrication of Nickel Oxide Electrodes by the Nitrate Technique

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**Abstract**—The possibility of making shorter the time of fabrication of a nickel oxide electrode by impregnation of a metal–ceramic support in a nickel nitrate solution with addition of sodium nitrite was studied.

The duration of multicycle procedures in fabrication of nickel oxide electrodes (NOE) on metal–ceramic (MC) supports is mainly determined by the time of impregnation of MC supports in a solution that contains nickel salts, most frequently  $\text{Ni}(\text{NO}_3)_2$  ( $\text{pH} < 7$ ) [1]. Up to 97–98% of the total impregnation time (up to 15 h) is necessary for obtaining the active substance via oxidation of nickel from the support, which occurs by the electrochemical mechanism [1, 2]. The fraction of the active substance obtained via oxidation of nickel from an MC support in a  $\text{Ni}(\text{NO}_3)_2$  solution is about 30% [3]. To make shorter the time in which MC NOEs are fabricated and to diminish the power consumption and labor intensity of the process, it is necessary to accelerate the oxidation of nickel in the course of impregnation.

The influence exerted by  $\text{NaNO}_2$  on impregnation of MC supports was studied by Zhdanov *et al.* [4]. However, in contrast to our study, Zhdanov *et al.* [4] used a chloride solution, which has a lower oxidation capacity and does not undergo disproportional self-regeneration.

The aim of this study was to examine the influence exerted by addition of  $\text{NaNO}_2$  to  $\text{Ni}(\text{NO}_3)_2$  solution on the rate of etching of nickel contained in MC supports and on the electrical characteristics of MC NOEs obtained.

## EXPERIMENTAL

The electrodes studied were fabricated on  $30 \times 10 \times 1.6$ -mm MC nickel supports with a bulk porosity of 70–75%. The MC supports were filled with nickel(II) hydroxide by the following scheme: impregnation

with an  $\text{Ni}(\text{NO}_3)_2$  solution ( $c_{\text{Ni(II)}} = 300\text{--}330 \text{ g l}^{-1}$ ) containing  $\text{NaNO}_2$  ( $5\text{--}10 \text{ g l}^{-1}$ ),  $\text{pH} 1\text{--}5$ , temperature  $60\text{--}80^\circ\text{C}$ ,  $\tau = 1 \text{ h}$ ; crystallization in air (30 min); treatment in an alkali solution ( $c_{\text{KOH}} = 300\text{--}330 \text{ g l}^{-1}$ ,  $T = 60\text{--}80^\circ\text{C}$ ,  $\tau = 1 \text{ h}$ ); washing to remove the alkali; and drying ( $T = 110^\circ\text{C}$ ). Changes in the mass of the MC supports were determined as the difference of masses before impregnation and after a full cycle of the procedures performed. The mass of nickel dissolved from the MC support was determined by complexometric titration [5]. The characteristics of the nickel etching process were found using the model described in [5]. The chemical composition of the active substance in NOE was determined by the procedure described in [6].

The composition of the corrosion products formed was identified by X-ray diffraction analysis on a DRON-2 diffractometer at an acceleration voltage of 32 kV, current of 0.8 mA, slit dimensions of  $1 \times 8 \times 1 \text{ mm}$ , and filter wavelength of  $0.58 \text{ \AA}$ . Qualitative analysis of the X-ray diffraction patterns was made using the procedure described in [7].

The rate-determining stage of reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  was identified using a potentiodynamic method in which polarization curves were measured with a linear potential sweep at a rate of  $2\text{--}20 \text{ mV s}^{-1}$ .

The capacity characteristics of the electrodes fabricated were determined by discharge in cells with auxiliary electrodes made of cut-through nickel foil with separators fabricated from perforated rigid PVC. As an electrolyte served a KOH solution ( $1.19\text{--}1.20 \text{ g cm}^{-3}$ ). In the course of charging, 150% of the theoretical capacity of the electrodes was imparted to them at a current density of  $4.4 \text{ mA cm}^{-2}$  [8]. The

discharge was performed at the same current density until the working potential changed abruptly.

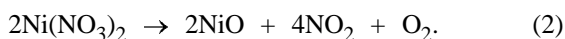
Analysis of the corrosion diagram obtained for the system under study (Fig. 1) shows that nickel is etched in a  $\text{Ni}(\text{NO}_3)_2$  solution with a  $\text{NaNO}_2$  additive by the electrochemical mechanism with a cathodic control. The rate of nickel dissolution in solutions with addition of sodium nitrite increases by a factor of approximately 5 as compared to that of nickel etching in a  $\text{Ni}(\text{NO}_3)_2$  solution (Fig. 1).

The introduction of a  $\text{NaNO}_2$  additive into a  $\text{Ni}(\text{NO}_3)_2$  solution changed its oxidation power: the equilibrium potential of the redox system in solution was 1.1 V, and the shift of the potential, 0.13 V (Fig. 2). At first sight, this dependence seems to be anomalous: the product formed in cathodic reduction of nitrates,  $\text{NO}_2^-$  ions, has a higher oxidation power than the starting reagent,  $\text{NO}_3^-$ . Such an anomaly can be accounted for only by formation of an electrochemically active substance with a higher oxidation power.

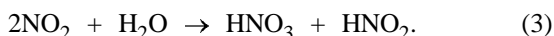
According to [9], the following slow reaction of autocatalysis, which precedes the discharge, occurs in concentrated nitrate solutions:



Nitrites are always present in nitrate solutions because of the partial decomposition of the  $\text{Ni}(\text{NO}_3)_2$  solution at elevated temperatures (100–300°C) [6]:



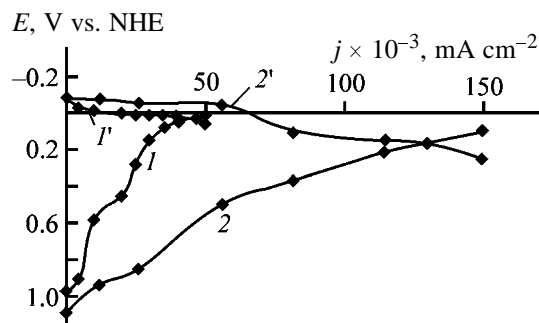
Nitrogen oxide  $\text{NO}_2$  reacts with water [10]:



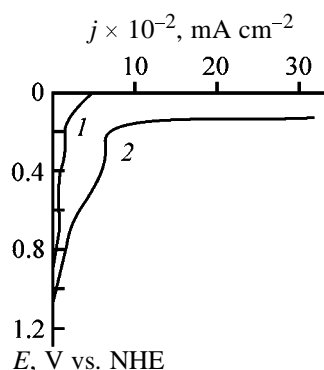
The presence of  $\text{NO}_2^-$  ions in a  $\text{Ni}(\text{NO}_3)_2$  solution must facilitate formation of the active component  $\text{N}_2\text{O}_4$  by shifting the equilibrium of reaction (1) to the right. The content of nitrite in the  $\text{Ni}(\text{NO}_3)_2$  solution will be maintained constant, in the case of its low values, by disproportionation of  $\text{HNO}_2$  in hot acid solutions [10]:



Nitrogen(II) oxide being formed by reaction (4) can be oxidized in the presence of oxygen to  $\text{NO}_2$  [10], which dimerizes to  $\text{N}_2\text{O}_4$  [9, 11]. This dimer is a strong oxidizing agent ( $E^0 = 1.2$  V [12]), which can convert basic salts of nickel(II), contained within



**Fig. 1.** Corrosion diagram obtained on nickel in a  $\text{Ni}(\text{NO}_3)_2$  solution without an additive and with a  $\text{NaNO}_2$  additive.  $T = 80^\circ\text{C}$ ,  $c_{\text{Ni(II)}} = 320 \text{ g l}^{-1}$ , pH 3; the same for Fig. 2. ( $E$ ) Potential and ( $j$ ) current density; the same for Fig. 2.  $\text{NaNO}_2$  content ( $\text{g l}^{-1}$ ): (1) 0 and (2) 10; the same for Fig. 2. Curves: (1, 2) cathodic, obtained on Pt; (1', 2') anodic, obtained on Ni.



**Fig. 2.** Cathodic potentiodynamic polarization curves obtained on Pt. Potential sweep rate  $2 \text{ mV s}^{-1}$ .

pores of the MC supports, into  $\text{NiOOH}$  ( $E^0 = 0.6$ – $1$  V [8]).

The voltammetric curve obtained on Pt in a  $\text{Ni}(\text{NO}_3)_2$  solution at a potential sweep rate of  $2 \text{ mV s}^{-1}$  shows at potentials of 0.35–0.1 V a region of the limiting current density, which is associated with reduction of  $\text{NO}_3^-$  ions to  $\text{NO}_2^-$  (Fig. 2). Upon addition of  $\text{NaNO}_2$  to a  $\text{Ni}(\text{NO}_3)_2$  solution, the limiting current density increases by a factor of approximately 5 (Fig. 2). This suggests the occurrence of joint reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  ions ( $E_{\text{NO}_3^-/\text{NO}_2^-}^0 = 0.83$  V,  $E_{\text{NO}_2^-/\text{NH}_4^+}^0 = 0.86$  V [12]) and increase in the total concentration of the depolarizing agent in solution.

At potential sweep rates of 5–10  $\text{mV s}^{-1}$ , the voltammograms show a peak of the cathodic current. A  $\text{Ni}(\text{NO}_3)_2$  solution without additives and with a  $\text{NaNO}_2$  additive is characterized by a linear dependence of the current density on the square root of the

**Table 1.** Effect of the solution composition on the intensity of lines in the X-ray diffraction pattern

Solution	Film composition	<i>I</i>
Ni(NO <sub>3</sub> ) <sub>2</sub>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·Ni(OH) <sub>2</sub>	100, 58, 50
Ni(NO <sub>3</sub> ) <sub>2</sub> + NaNO <sub>2</sub>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·Ni(OH) <sub>2</sub> ·β-NiOOH	84, 32

potential sweep rate,  $j_p = f(V^{1/2})$ . This dependence is extrapolated into the origin of coordinates, which is due to a slowed-down diffusion of the depolarizing agent to the electrode surface [13]. As the potential sweep rate is made faster, films of basic compounds of nickel, which appear when the pH of the near-electrode zone increases, have not enough time to be formed. The process passes into the quasi-reversible region: the dependence  $j_p = f(V^{1/2})$  deviates from a linear behavior, which suggests occurrence of a slowed-down chemical reaction preceding the discharge.

The diffusion coefficient was calculated by the Randles–Shevchik equation [13]

$$j_p = 0.446 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} D^{1/2} V^{1/2} c_{\text{ox}}^0, \quad (5)$$

where  $j_p$  is the peak current density (A cm<sup>-2</sup>);  $c_{\text{ox}}$ , oxidant concentration (M);  $D$ , diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>);  $V$ , potential sweep rate (V s<sup>-1</sup>);  $n$ , number of electrons exchanged in an elementary event;  $T$ , process temperature (K);  $F$ , Faraday number (C mol<sup>-1</sup>); and  $R$ , universal gas constant (J K<sup>-1</sup> mol<sup>-1</sup>).

For a Ni(NO<sub>3</sub>)<sub>2</sub> solution with addition of NaNO<sub>2</sub>, the diffusion coefficient of the oxidizing agent was  $9.4 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, which exceeds by a factor of 6 its value in the Ni(NO<sub>3</sub>)<sub>2</sub> solution ( $1.5 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>). This indicates that the diffusion hindrance to the process is partly lifted in the case of joint reduction of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions. The rate of the cathodic process in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with addition of NaNO<sub>2</sub> starts to be determined, to a greater extent than that in the Ni(NO<sub>3</sub>)<sub>2</sub> solution, by the rate of the chemical reaction (1), in which nitrate ions react with nitrite ions.

The presence of a NaNO<sub>2</sub> additive in the Ni(NO<sub>3</sub>)<sub>2</sub> solution makes higher the rate of the cathodic stage and the overall intensity of the process. In addition, impregnation of MC supports in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive leads to formation of higher nickel oxides of general formula NiO<sub>1.5–1.6</sub> within the pores of the electrode. The high electrochemical activ-

ity of the resulting compound is confirmed by the fact that electrodes subjected to a single act of impregnation in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive have a specific discharge capacity of 2.25 mA h cm<sup>-3</sup> without any preliminary charging. The deep oxidation of nickel in the impregnation of MC supports was favored by the presence in solution of a strong oxidizing agent, formed in disproportionation of NO<sub>2</sub><sup>-</sup> ions.

An X-ray diffraction analysis demonstrated (Table 1) that a smaller amount of the solid phase is formed in the presence of NO<sub>2</sub><sup>-</sup> ions, compared to a Ni(NO<sub>3</sub>)<sub>2</sub> solution without additives, as indicated by the lower intensity *I* of diffraction lines. In this case, higher nickel oxides with a structure of β-NiOOH are contained in the film formed on cathodic areas of nickel in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive.

The optimal conditions of impregnation of MC support in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive were determined taking into account that the equilibrium of reaction (4) must shift to the right as temperature is elevated and pH of the solution decreases [10]. It is inadvisable to raise the impregnation temperature to above 80°C for process reasons. The rate of nickel etching in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive does increase as the acidity of the solution is made higher. In this case, the oxidation state of nickel increases to NiO<sub>1.8</sub> at pH 1. This can be attributed to a shift of the equilibrium of reaction (4) to the right, which leads to an increase in the content of the oxidizing component N<sub>2</sub>O<sub>4</sub> in solution.

The rate of nickel etching in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive grows during the first hour of the process and then decreases somewhat, which is due to the formation of difficultly soluble films of basic nickel compounds on the surface.

The greatest weight gain of the MC support and a fairly high nickel etching rate (0.1 g g<sup>-1</sup> h<sup>-1</sup>) were obtained at the following impregnation conditions:  $c_{\text{Ni(II)}} = 300\text{--}330$  g l<sup>-1</sup>,  $c_{\text{NaNO}_2} = 5\text{--}10$  g l<sup>-1</sup>, pH 3,  $T = 60\text{--}80^\circ\text{C}$ ,  $\tau = 1$  h.

The results obtained in impregnation of MC supports and the electrical characteristics of the MC NOEs fabricated under the optimal impregnation conditions are listed in Table 2.

The rate of Ni dissolution in a Ni(NO<sub>3</sub>)<sub>2</sub> solution with a NaNO<sub>2</sub> additive is by a factor of approximately 4 higher than that in the Ni(NO<sub>3</sub>)<sub>2</sub> solution (Table 2). In the second cycle of impregnation, when higher nickel oxides are present in pores of the MC supports, the maximum rate of nickel oxidation is observed

**Table 2.** Parameters of the process and MC NOE after impregnation in a  $\text{Ni}(\text{NO}_3)_2$  solution\*

Parameter	Concentration of $\text{NO}_2^-$ ions, $\text{g l}^{-1}$	
	0	10
Relative weight loss of the MC support, $\Delta m$ , $\text{g g}^{-1}$ :		
1st cycle	0.04	0.1
2nd cycle	0.03	0.12
$\Sigma$ in 5 cycles	0.11	0.43
Weight change of MC supports upon impregnation, $\Delta m$ , $\text{g cm}^{-3}$		
$\Sigma$ in 5 cycles	0.74	0.97
$Q$ , $\text{A h cm}^{-3}$	0.23	0.31
$K_{\text{util}}$ , %	100	100

\*  $Q$ , specific discharge capacity;  $K_{\text{util}}$ , coefficient of utilization of the active substance.

because of the operation of a Ni-NiO<sub>x</sub> cell. The subsequent decrease in the oxidation rate in a  $\text{Ni}(\text{NO}_3)_2$  solution with a  $\text{NaNO}_2$  additive is due to partial exhaustion of the oxidizing agent,  $\text{N}_2\text{O}_4$ . The mass of the active substance, necessary for obtaining a specific discharge capacity of  $0.3 \text{ A h cm}^{-3}$  [2] of MC supports impregnated by the technique developed, is accumulated in 5 cycles of impregnation for 1 h (Table 2). At the same time, only 76% of the required mass is obtained in metal-ceramic supports impregnated under the same conditions in a  $\text{Ni}(\text{NO}_3)_2$  solution without an additive. Up to 61% of the active substance is formed through etching of nickel contained in an MC support in the case of impregnation in a  $\text{Ni}(\text{NO}_3)_2$  solution with a  $\text{NaNO}_2$  additive, and only 35%, in impregnation of MC supports in a  $\text{Ni}(\text{NO}_3)_2$  solution (Table 2). The stronger oxidation of the nickel support in nitrate-nitrite solutions does not impair the mechanical strength of the electrodes obtained, because only 15% of the total amount of nickel is oxidized (up to 20% is acceptable [8]).

The electrochemical activity of  $\text{Ni}(\text{OH})_2$  obtained from a  $\text{Ni}(\text{NO}_3)_2$  solution with a  $\text{NaNO}_2$  additive was tested in forming of MC NOE. The utilization coefficient of the active substance in electrodes of this kind is the same as that for electrodes impregnated in a  $\text{Ni}(\text{NO}_3)_2$  solution (Table 2).

When a  $\text{NaNO}_2$  additive was introduced into a  $\text{Ni}(\text{NO}_3)_2$  solution, the total time of impregnation of MC supports decreased to 5 h, whereas in the case of the "nitrate" technique, the necessary amount of the active substance in an MC support is only accumulated after 18 h of impregnation in a  $\text{Ni}(\text{NO}_3)_2$  solution [3]. As demonstrated by experiments on dissolution of nickel from an MC support, the influence exerted by the  $\text{NaNO}_2$  additive is preserved during

5 to 6 cycles. Further, the rate of Ni oxidation in a  $\text{Ni}(\text{NO}_3)_2$  solution with a  $\text{NaNO}_2$  additive becomes the same as that in the  $\text{Ni}(\text{NO}_3)_2$  solution.

## CONCLUSIONS

(1) The time of impregnation of metal-ceramic supports of nickel oxide electrodes becomes 30–38% shorter, compared to an ordinary nitrate impregnation, upon introduction of 5–10  $\text{g l}^{-1}$   $\text{NaNO}_2$  into a  $\text{Ni}(\text{NO}_3)_2$  solution. A process for nitrate-nitrite impregnation is suggested.

(2) The effect of the nitrite additive is attributed to disproportionation of nitrites to give an electrochemically active dimer of nitrogen(IV) oxide.

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## REFERENCES

1. Dasoyan, M.A. and Novoderezhkin, V.V., *Proizvodstvo elektricheskikh akkumulyatorov* (Manufacture of Electric Batteries), Moscow: Vysshaya Shkola, 1970.
2. Pozin, Yu.M. and Shtertser, N.I., *Zh. Prikl. Khim.*, 1970, vol. 43, no. 7, pp. 1482–1486.
3. Levinzon, L.M., Pozin, Yu.M., and Shtertser, N.I., *Tekhnologiya proizvodstva khimicheskikh istochnikov toka: Sbornik nauchnykh trudov* (Technology for Manufacture of Chemical Power Cells: Coll. of Works), Leningrad: Energoizdat, 1985.
4. Zhdanov, V.V., Poltavchenko, V.S., Tikhonov, K.I., and Pozin, Yu.M., *Zh. Prikl. Khim.*, 1982, vol. 55, no. 3, pp. 694–696.

5. Kuzina, T.E. and Bachaev, A.A., *Zh. Prikl. Khim.*, 2002, vol. 75, no. 11, pp. 1839–1842.
6. Sorokina, N.V., in *Sbornik rabot po KhIT* (Coll. of Works on Chemical Power Cells), Nikol'skii, V.A., Ed., Leningrad: Energiya, 1974, issue 9.
7. Gorelik, S.S., Skakov, Yu.A., and Rastorguev, L.N., *Rentgenograficheskii i elektronno-opticheskii analiz* (X-ray Diffraction and Electron-Optical Analyses), Moscow, 1994.
8. Pervushin, Yu.N., A Study in Technology of Fabrication of an MC NOE for Alkaline Battery, *Cand. Sci. Dissertation*, Novocherkassk, 1968.
9. Safonova, T.Ya. and Petrii, O.A., *Elektrokhimiya*, 1995, vol. 31, no. 12, pp. 1373–1377.
10. Cotton, F.A. and Wilkinson, G., *Advanced Inorganic Chemistry*, New York: Interscience, 1966.
11. Vetter, K.J., *Elektrochemische Kinetik*, Berlin: Springer, 1961.
12. Gur'yan, L.I., *Okislitel'no-vosstanovitel'nye reaktsii i potentsialy v analiticheskoi khimii* (Redox Reactions and Potentials in Analytical Chemistry), Moscow: Khimiya, 1989.
13. Galus, Zb., *Teoretyczne podstawy elektroanalizy chemicznej*, Warsaw: Naukowe, 1971.