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ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS OF NICKEL ELECTRODE ACTIVE MATERIAL

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ABSTRACT. Ternary electrodes Ni+Co+Cd, consisting of nickel hydroxide as cathode active material, and with Co and Cd hydroxides as additives were prepared by anodic polarization, in KOH electrolyte, of sintered nickel supports impregnated with mixed metal nitrate solutions. The electrochemical and structural characteristics of these electrodes were investigated by charge-discharge curves in galvanostatic regime, and by X-ray diffraction and scanning electron microscopy, respectively. The coulombic efficiencies determined from charge-discharge curves demonstrated the beneficial effects of LiOH addition to the electrolyte and of Co and Cd hydroxides presence in the active cathode material.

INTRODUCTION

The electrochemical and structural characteristics of nickel hydroxide have been the object of many studies, because its utilization as cathode active material in various alkaline batteries: nickel-cadmium, nickel-iron, nickel-zinc, nickel-hydrogen, and most recently, in nickel-metal hydride systems [1].

The processes that take place during charge-discharge of the nickel electrode are represented by equation:

$$NiOOH + H_2O + e^- \Leftrightarrow Ni(OH)_2 + HO^- \; ; \quad \varepsilon^0 = 0.490\ V/NHE \qquad (1)$$

The active material of the nickel electrode consists of Ni(II) hydroxide, in discharged state and Ni(III) oxihydroxide in charged state. Two distinct couples, β-$Ni(OH)_2$/β-$NiOOH$ and α-$Ni(OH)_2$/γ-$NiOOH$, can participate in the charge-discharge reactions of the nickel electrode [2-8]. The charge process of nickel electrode occurs usually in competition with oxygen evolution reaction (OER):

$$4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^- \qquad (2)$$

For an efficient charge of nickel cathode, the oxygen evolution must be minimized.

The addition of foreign metal ions (Co, Cd, Zn, Mg ions) to the nickel electrodes in alkaline batteries improves the utilization of the active material, increases the polarization of OER and depresses the capacity loss during long charge-discharge cycles [9 -16].

In recent years, high energy density nickel electrodes, were produced on sintered supports. The active material is precipitated in pores of these supports by chemical, electrochemical or thermal methods [17-21].

In this paper, the results of the electrochemical and structural investigations of the sintered nickel electrodes containing cobalt and cadmium hydroxides as additives in active material are presented.

EXPERIMENTAL

The sintered nickel supports (70 x 35 x 1 mm), having about 70% porosity, were prepared from nickel powder. Nickel powder was obtained by thermolysis of $Ni(NO_3)_2 \cdot 6H_2O$. Sintered supports were obtained by pressing a mixture of nickel powder (80 wt%) and $(NH_4)_2CO_3$ (20 wt%) on a current collector (a nickel plated iron screen), followed by a heat treatment at 800^0C.

For activation, the sintered supports, impregnated with nickel nitrate, were anodicaly polarized between two nickel cathodes in 42 wt% KOH solution, at a current density of aprox. 30 mA/cm^2. After polarization, the electrodes were washed with distilled water and dried at 80^0C [22].

A ternary electrode, Ni+Co+Cd, containing 5 wt% $Co(OH)_2$ and 5 wt% $Cd(OH)_2$ as additives in active material, was prepared by the same method. Thus, the sintered nickel support was immersed in a mixed metal nitrate solution: $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 6H_2O$ before anodic polarization.

The electrochemical behaviour of these electrodes has been investigated by charge-discharge curves in galvanostatic regime. The charge-discharge curves were performed in a half-cell consisting of the sintered nickel electrode as working electrode, a nickel plate as counter electrode and a SCE as reference electrode. All the potentials given in this paper are referred to SCE. The electrolytes are 6N KOH and 6N KOH containing 35 g/l LiOH as additive, respectively.

The crystal morphology of the electrodes was examined by scanning electron microscopy (SEM). The electron micrographs were obtained on a Tesla-Brno BS 340-1990 scanning electron microscope.

Phase compositions of electrodes in different states (uncycled, charged and discharged) were analyzed by X-ray diffraction (XRD) with a DRON-3 type diffractometer with a Cu-cathode, using k_α radiation (λ =1.57051Å).

RESULTS AND DISCUSSION

Electrochemical Characteristics

The charge-discharge curves of sintered nickel electrode containing cobalt and cadmium additives in active material, compared with the charge-discharge curves of nickel electrode without additives, in 6N KOH and in 6N KOH + 35 g/l LiOH electrolyte are shown in Fig. 1 and Fig. 2.

The coulombic efficiencies, determined from charge-discharge curves, demonstrate the beneficial effects of LiOH addition into electrolyte and of cadmium and cobalt hydroxides addition in active material (Table 1).

Table 1.

Coulombic efficiencies of nickel electrodes.

Electrode	Electrolyte	Q^{*}_{charge} (mAh)	$Q^{**}_{discharge}$ (mAh)	r_F (%)
Ni	6N KOH	550	350	63.63
	6N KOH+35 g/l LiOH	550	383	69.64
Ni+Co+Cd	6N KOH	550	425	77.27
	6N KOH+35 g/l LiOH	550	450	81.81

[*] corresponds to charging for 5.5 h at I = 100 mA;

[**] calculated from the plateau of the discharge curves at I = 100 mA.

The decrease of plateaus corresponding to OER from charge curves of Figs. 1 and 2, induced by Co and Cd addition, also demonstrates the increase of the charge efficiency and hence, the improvement of the discharge characteristics of Ni+Co+Cd electrode.

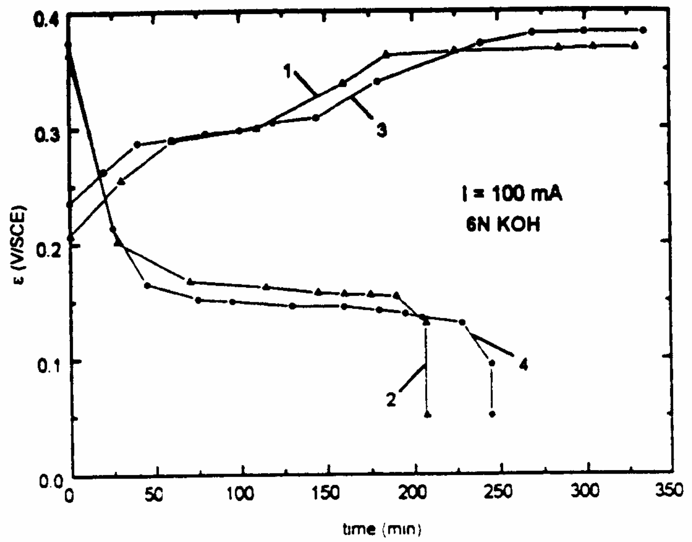

Fig. 1. Charge-discharge curves of Ni (1-2), Ni+Co+Cd (3-4), at I = 100 mA, in 6N KOH.

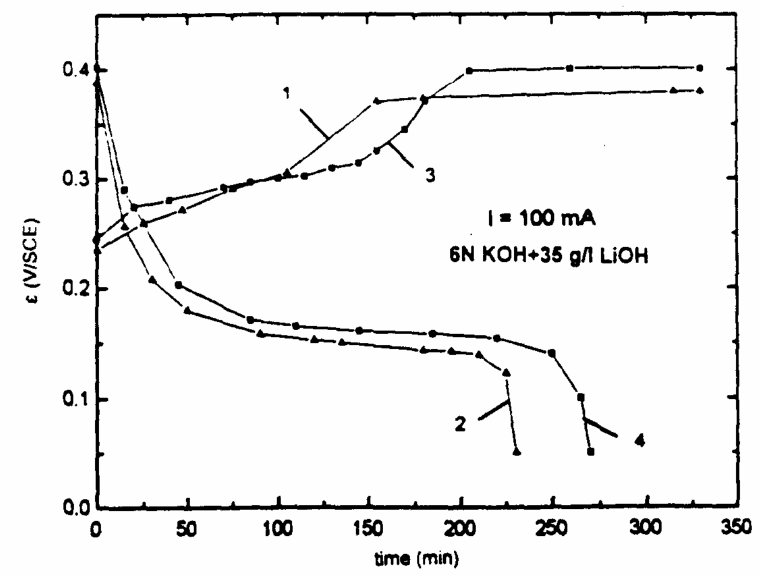

Fig. 2. Charge-discharge curves of Ni (1-2), Ni+Co+Cd (3-4), at I = 100 mA, in 6N KOH+35 g/l LiOH.

The reversible potentials ε_r of the electrodes, were evaluated from ε vs. lg t data, by intersecting the anodic and cathodic recovery lines (Fig. 3 and Fig. 4).

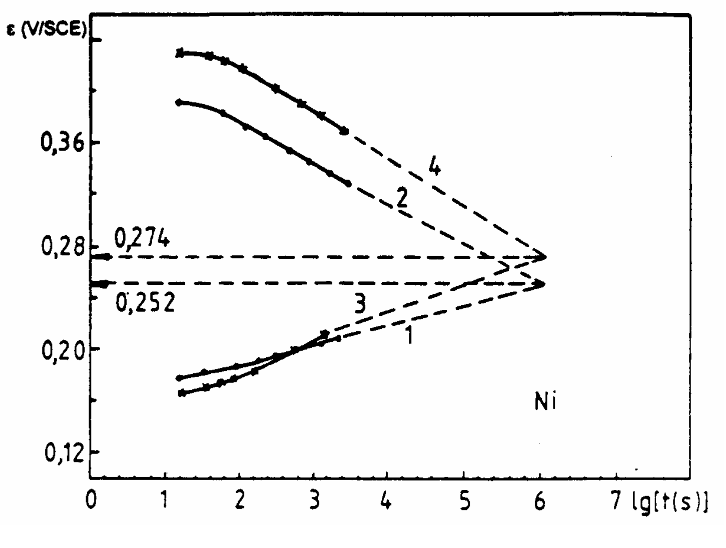

Fig. 3. Evaluation of reversible potentials of Ni electrode in 6N KOH (1-2) and in 6N KOH+35 g/l LiOH (3-4).

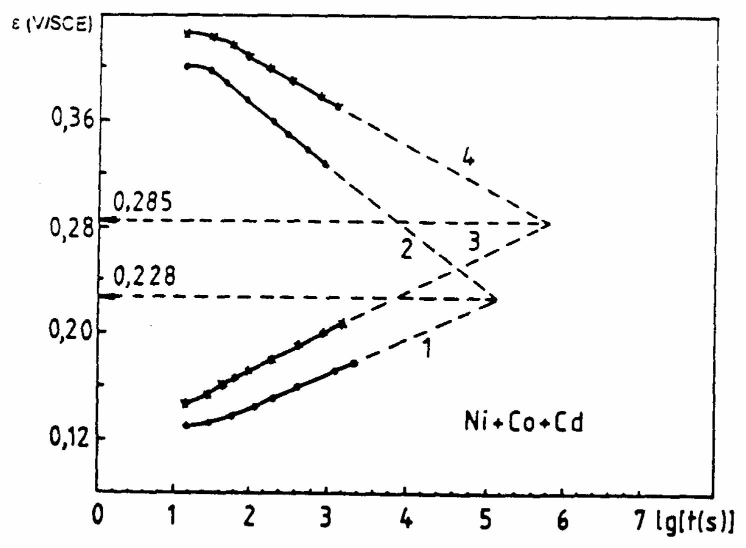

Fig. 4. Evaluation of reversible potentials of Ni+Co+Cd electrode in 6N KOH (1-2) and in 6N KOH+35 g/l LiOH (3-4).

The ascending recovery lines were obtained after a discharge of the electrodes with I = 100 mA, to 0.05 V.

The descending recovery lines were obtained after a charge of the electrodes with I = 100 mA for 5.5 h. The obtained values of ε_r are shown in Table 2.

Table 2.

Reversible potentials of nickel electrodes.

Electrode	Electrolyte	ε_r (V/SCE)
Ni	6N KOH	0.252
	6N KOH+35 g/l LiOH	0.274
Ni+Co+Cd	6N KOH	0.228
	6N KOH+35 g/l LiOH	0.285

In 6N KOH electrolyte, because the shift of ε_r to more cathodic value by addition of Co and Cd, the charge takes place at less positive potentials and it is more complete, minimizing the OER.

In the presence of LiOH in electrolyte, the charge efficiency was improved, because increasing the overpotential of oxygen evolution on electrodes [22].

Structural Characteristics

Our previous structural investigations of the nickel electrode without additives, by XRD and SEM, demonstrated the presence of α and β-Ni(OH)$_2$ in the discharged electrode, and of γ and β-NiOOH in the charged electrode [23].

The X-ray diffraction pattern in the 2θ = 4 - 63^0 range, obtained on the powder scraped from the surface of uncycled Ni+Co+Cd electrode, shows the well expressed (111) and (200) lines, corresponding to nickel and some lines of small intensity corresponding to Ni(OH)$_2$ (theofrasit), a nonstoechiometric Co and Cd compound, and to KNO$_3$, remained from the preparation step (Fig. 5, curve a).

The electron micrograph of the uncycled electrode reveals a microcrystalline-amorphous structure with porous texture (Fig. 6).

In the charged electrode, the XRD reveals an appreciable amount of γ-NiOOH and smaller amounts of CoCO$_3$ and CdCO$_3$ (Fig. 5, curve b). γ-NiOOH form of active material confers to electrode a more reduced self-discharge than β-NiOOH [24].

The SEM of the charged electrode shows a microcrystalline structure with porous texture, and two kinds of crystals: hexagonal crystals with lamellar habitus, of 1-4 μm, attributed to γ-NiOOH and smaller isometric crystals of 0.5 -1 μm attributed to CoCO$_3$ and CdCO$_3$ (Fig. 7).

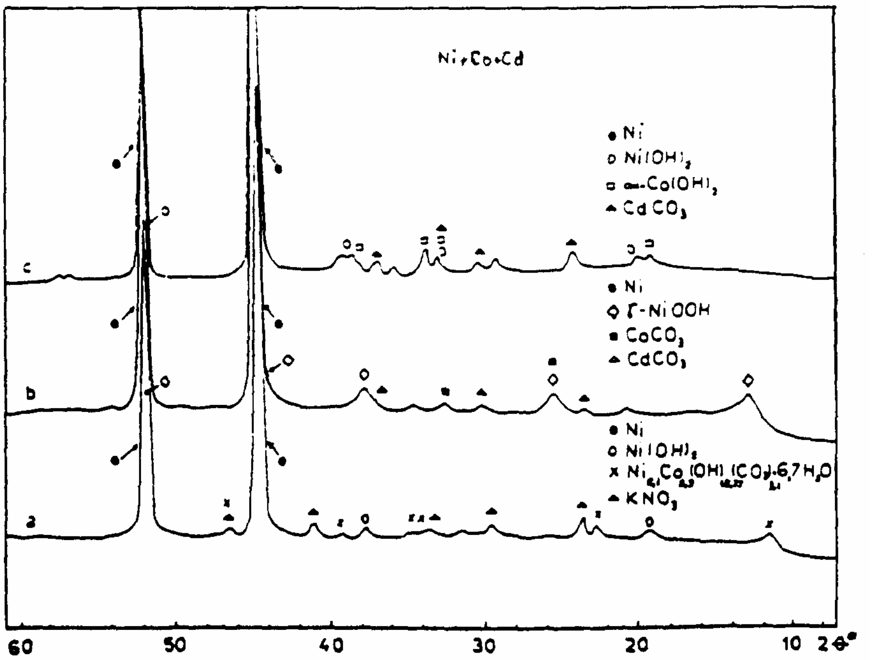

Fig. 5. X-ray diffractograms of Ni+Co+Cd electrode:
a) uncycled, b) charged, c) discharged.

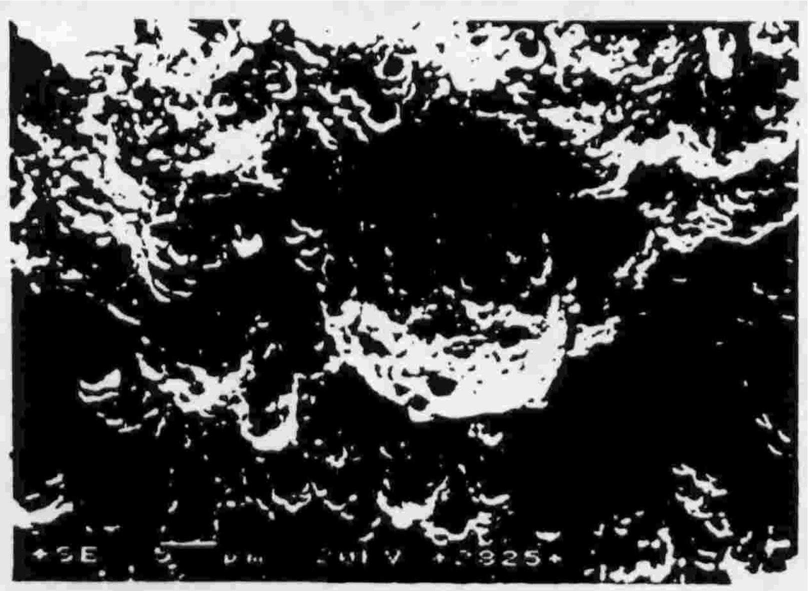

Fig. 6. SEM photograph of uncycled Ni+Co+Cd electrode.

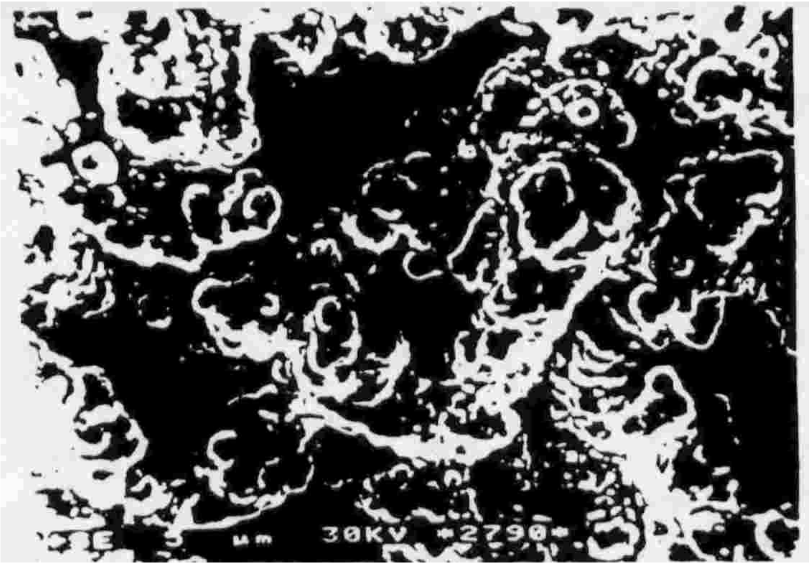

Fig. 7. SEM photograph of charged Ni+Co+Cd electrode.

In the discharged electrode, the active material is α-$Ni(OH)_2$ [22]. Cd compound remains as rhombohedral $CdCO_3$, while Co compound appears as trigonal crystals of α-$Co(OH)_2$ (Fig. 5, curve c and Fig. 8).

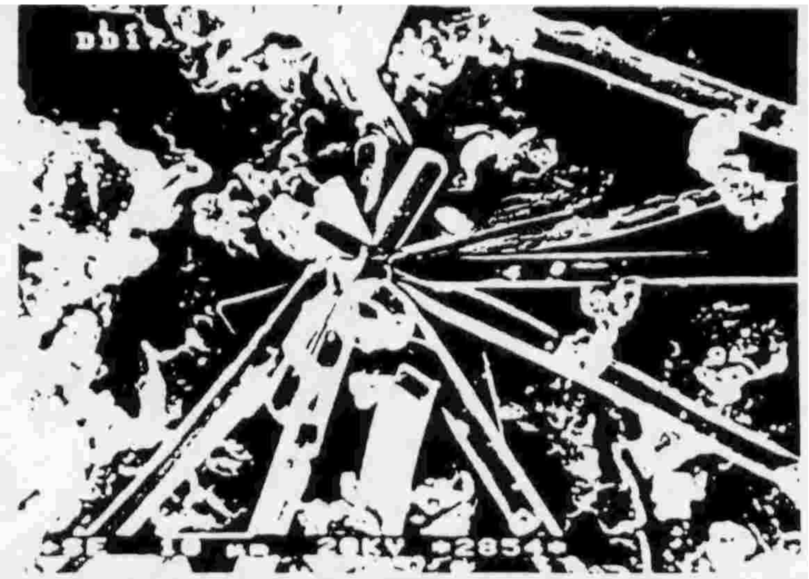

Fig. 8. SEM photograph of discharged Ni+Co+Cd electrode.

CONCLUSIONS

a) A ternary electrode, Ni+Co+Cd, containing nickel hydroxide active material, with 5 wt.% $Co(OH)_2$ and 5 wt.% $Cd(OH)_2$ as additives was prepared by electrochemical activation of sintered nickel support.

b) The coulombic efficiencies determined from charge-discharge curves, demonstrated the beneficial effects of LiOH addition into electrolyte and of Co and Cd hydroxides addition in active material;

c) The uncycled active material, impregnated in sintered support by anodical polarization, was in discharged form, $Ni(OH)_2$;

d) The charged form of active material was γ-NiOOH and the corresponding discharged form was α-$Ni(OH)_2$;

e) The electrochemical and structural characteristics of Ni+Co+Cd electrodes point to the possibility of their successful utilization as cathodes in alkaline batteries.

REFERENCES

1. L. Oniciu, E.M. Rus, *Surse electrochimice de putere,* Ed. Dacia, Cluj-Napoca, 1987.
2. J. Desilvestro, O. Haas, *J. Electrochem Soc.,* 1990, **137**, 5c.
3. R. Barnard, C.F. Randell, F.Y. Tye, *J. Appl. Electrochem.,* 1980, **10**, 109.
4. H. Bode, K. Dehmelt, J. Witte, *Electrochim. Acta,* 1966, **11**, 1079.
5. D.A. Corrigan, S.L. Knight, *J. Electrochem. Soc.,* 1989, **136**, 613.
6. G.W.D. Briggs, P.R. Snodin, *Electrochim. Acta,* 1982, **27**, 565.
7. P. Oliva, J. Leonardi, J.F. Laurent, C. Delmas, J.J. Braconnier, M. Figlarz, F. Fievet, A. de Guibert, *J. Power Sources,* 1982, **8**, 229.
8. B.C. Cornilsen, X. Shan, P.L. Loyselle, *J. Power Sources,* 1990, **29**, 453.
9. L. Oniciu, Eleonora Maria Rus, P. Ilea, Violeta Voina, Delia Constantin, *Rev. Chim.,* 1985, **36**, 340.
10. D.A. Corrigan, R.M. Bendert, *J. Electrochem. Soc.,* 1989, **136**, 723.
11. P.V. Kamath, M.F. Ahmed, *J. Appl. Electrochem.,* 1993, **23**, 225.
12. L.Demourgues-Guerlou, C. Delmas, *J. Electrochem. Soc.,* 1994, **141**, 713.
13. L. Oniciu, Delia Constantin, Eleonora Maria Rus, Violeta Voina, Cristina Corăbian, *Studia Univ. "Babes-Bolyai", Ser. Chem.,* 1994, **39**, 218.
14. C.A. Gervasi, J.R. Vilche, P.E. Alvarez, *Electrochim. Acta,* 1996, **41**, 455.
15. S.K. Tiwari, P. Chartier, R.N. Singh, *J. Electrochem. Soc.,* 1995, **142**, 148.
16. B.B. Ezhov, O.G. Malandin, *J. Electrochem. Soc.,* 1991, **138**, 885.
17. M. Paszkiewicz, *J. Appl. Electrochem.,* 1981, **11**, 135.
18. B. Lafage, M. Comtat, R. Routie, *J. Appl. Electrochem.,* 1988, **18**, 363.
19. M. Oshitani, Y. Sasaki, K. Takashima, *J. Power Sources,* 1984, **12**, 219.
20. M. Wales, *Electrochim. Acta,* 1979, **24**, 629.
21. K. Ho, J. Jorne, *J. Electrochem. Soc.,* 1990, **137**, 149.
22. Delia Maria Constantin, Ph.D. Thesis, "Babeş-Bolyai" Univ., Cluj-Napoca, Romania, 1996.
23. Eleonora Maria Rus, Delia Maria Constantin, L. Oniciu, L. Ghergari, *Croatica Chem. Acta*, 1999, **72**, 25.
24. B.B. Ezhov, O.G. Malandin, *J. Electrochem. Soc.,* 1991, **138**, 885.