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ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS OF CADMIUM ELECTRODE ACTIVE MATERIAL

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ABSTRACT. Cadmium electrodes were prepared by cathodical polarization, in 25% KOH electrolyte, of sintered nickel supports impregnated with $Cd(NO_3)_2.4H_2O$.The electrochemical characteristics of sintered cadmium electrodes were investigated in a half-cell, by charge-discharge curves in galvanostatic regime, in 6N KOH electrolyte and 6N KOH with 35 g/l LiOH additive, respectively.

The structural characteristics of active material in uncycled, charged and discharged forms were investigated by X-ray diffraction and scanning electron microscopy.

INTRODUCTION

The cadmium electrode has been the object of many studies because of its utilization as anode in nickel-cadmium and silver-cadmium alkaline batteries [1-8].

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

$$Cd + 2OH^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Cd(OH)_2 + 2\bar{e} \qquad (1)$$

$$\varepsilon^0 = -0.809V/NHE$$

For the best conditions of charge-discharge processes, it is necessary an easy diffusion of electrolyte inside electrodes. From this point of view, the sintered type electrodes are extremely efficient. Sintered supports are prepared by pressing and sintering the nickel powder on a current collector. Activation is performed by precipitation of active material in the pores of supports by a chemical, electrochemical or thermal method. They have high specific capacities and energies and good mechanical properties.

Despite the long technological history of cadmium electrode, its electrochemistry is not yet fully understood. This is due to the participation of different modifications of discharged active material: α, β and γ $Cd(OH)_2$, CdO and CdO_2 in the potential-determining reactions [9-12]. The existence of these species is related to the preparing method of active material, charge-discharge cycling conditions, electrolyte concentration and composition [13].

In this paper the results of the electrochemical and structural investigations of the sintered cadmium electrode prepared by an original method are presented.

EXPERIMENTAL

Cadmium electrodes were prepared by electrochemical activation of the sintered nickel supports impregnated with $Cd(NO_3)_2 .4H_2O$ [14]. The sintered nickel plates were realized from nickel powder obtained by thermolysis of $Ni(NO_3)_2.6H_2O$ [15].

The sintered supports were immersed in a saturated solution of $Cd(NO_3)_2.4H_2O$ for 24 h, at room temperature, and then were dried at 80^0C. After impregnation with the cadmium nitrate, the supports were cathodically polarized between two cadmium plates (99.99 wt% Cd) in 25 wt% KOH electrolyte.

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

The different forms of active material (uncycled, charged and discharged) were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffractograms were obtained with a Dron 3 powder diffractometer, using CuK_α radiation. SEM photographs were taken using a BS 340/1990 Tesla-Brno microscope.

RESULTS AND DISCUSSION

Preparation of Sintered Cadmium Electrodes

The processes that occur in the electrochemical activation step, are:

- At the cathode, NO_3^- ions are reduced to NH_3:

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \quad (2)$$

The active material, $Cd(OH)_2$, is deposited inside the pores of the sintered support by a chemical precipitation reaction:

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2 \qquad (3)$$

- At the anode, the oxygen evolution reaction takes place:

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

Electrochemical Characteristics

The sintered cadmium electrodes (70x35x1 mm) were charged and discharged in galvanostatic regime. It is known that, in Ni-Cd battery, the addition of LiOH in KOH electrolyte enhances the discharge capacities and the coulombic efficiencies of nickel electrodes [16,17]. In order to study the influence of LiOH addition on Cd electrode behaviour, the performance curves were performed in 6N KOH electrolyte and in 6N KOH+35 g/l LiOH, at I = 300 mA (Fig. 1).

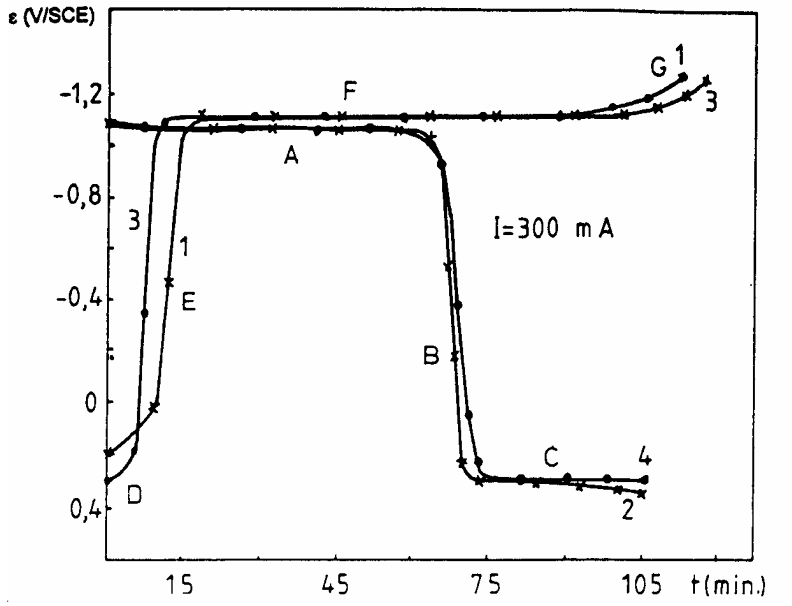

Fig. 1. Charge-discharge curves of sintered cadmium electrode, for I = 300 mA, in 6N KOH + 35 g/l LiOH electrolyte(1-2) and in 6N KOH electrolyte (3-4).

It is evident that the presence of LiOH in electrolyte does not influence the processes, that occur in active material, in negative potentials range.

Thus, the plateau A (curves 2 and 4) corresponding to oxidation of Cd to $Cd(OH)_2$ (discharge process) and respectively, the plateau F (curves 1 and 3) corresponding to reduction of $Cd(OH)_2$ to Cd (charge process) are at the same potentials for both electrolytes.

The LiOH addition influences only the processes that occur in positive potentials range, regarded to the transformations of NiOOH and $Ni(OH)_2$ from sintered nickel support (regions C and D).

The reversible potential (ε_r) values of cadmium electrode, evaluated from ε vs. lg t data by intersecting the anodic and cathodic recovery lines, in 6N KOH (Fig. 2) and in 6N KOH + 35 g/l LiOH (Fig. 3) were found being identical.

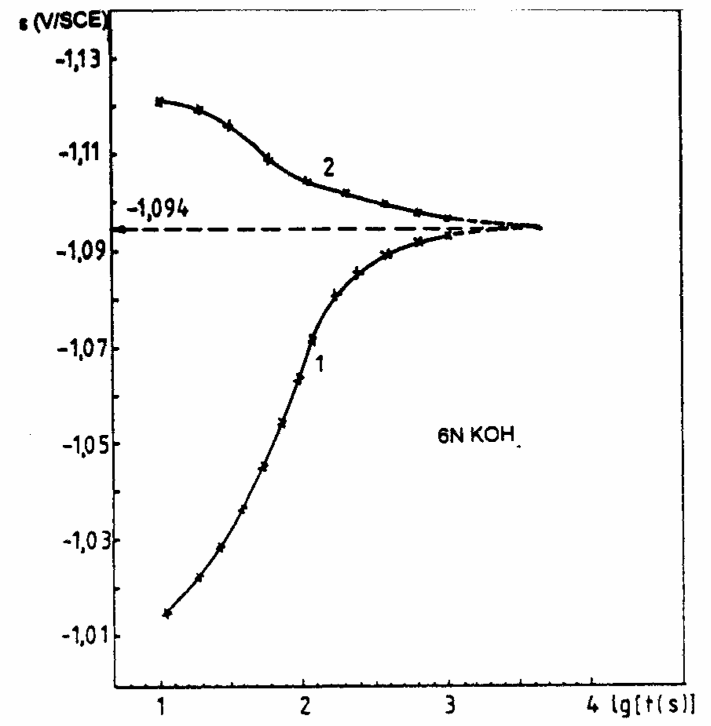

Fig. 2. Evaluation of reversible potential of sintered cadmium electrode in 6N KOH electrolyte.

This fact confirms that the presence of LiOH in electrolyte does not influence the electrochemical behaviour of cadmium electrode in alkaline batteries.

For 6N KOH electrolyte, the experimental value, ε_r = -1.094 V/SCE, is comparable with the theoretical value, $\varepsilon_{r,\,t}$ = -1.088 V/SCE, calculated for t = 20^0 C [18].

From galvanostatic charge-discharge curves (I = 100, 400, and 500 mA) were determined the discharge capacities and the coulombic efficiencies of the sintered cadmium electrodes in 6N KOH + 35 g/l LiOH electrolyte (Table 1).

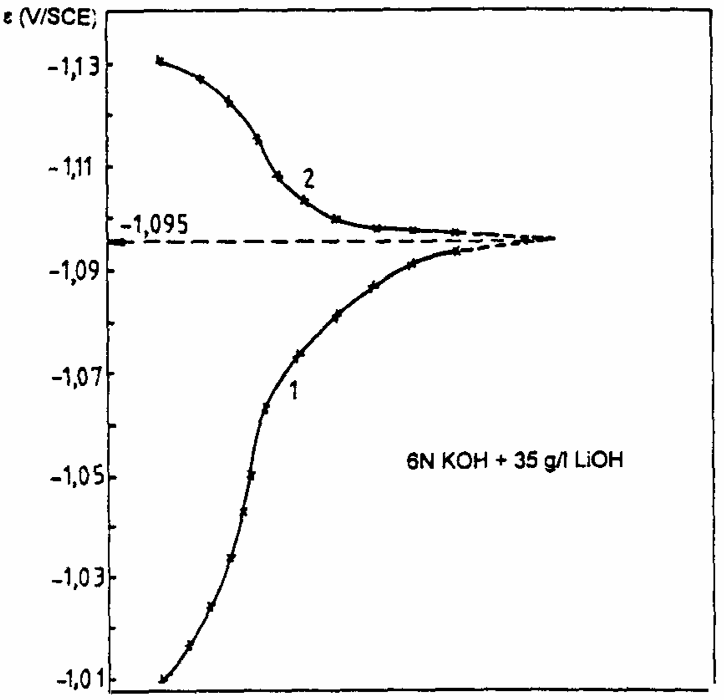

Fig. 3. Evaluation of reversible potential of sintered Cd electrode in 6N KOH + 35 g/l LiOH electrolyte.

Table 1.

Coulombic efficiencies of sintered cadmium electrodes.

I_{charge} (mA)	t_{charge} (h)	C_{charge} (mAh)	$I_{discharge}$ (mA)	$t_{discharge}$ (h)	$C_{discharge}$ (mAh)	Coulombic efficiency (%)
100	6	600	100	5	500	83.33
400	1.46	584	400	1.16	464	79.45
500	1.08	540	500	0.80	400	74.07

Structural Characteristics

For uncycled electrode, the electron micrograph reveals a microcrystalline structure with porous texture (Fig. 4).

The compounds deposited on sintered nickel support consist largely of $Cd(OH)_2$ and a small amount of $CdCO_3$. Unreacted or partly changed $Cd(NO)_3$ crystals remained, here and there.

Fig. 4. SEM photograph of uncycled sintered cadmium electrode.

The X-ray diffraction patterns in the $2\theta = 4 - 63^0$ range, obtained on the powder scraped from the electrode surface, show two characteristic lines, (111) and (200), for nickel of the sintered support, appreciable amounts of $Cd(OH)_2$ and some lines of small intensity corresponding to $CdCO_3$ (Fig. 5, curve a).

It should be pointed out that, by cathodical polarization, the active material was impregnated in sintered support in discharged form.

The charged active material consists largely of microcrystalline structure of metallic cadmium, containing a small amount of CdO octahedral crystals (Fig. 6).

The XRD patterns evidenced also a small number of lines corresponding to $Cd(OH)_2$ remained in discharged form (Fig. 5, curve b).

In the discharged active material $Cd(OH)_2$, there are undischarged Cd and a small amount of $CdCO_3$ (Fig. 5, curve c and Fig. 7).

The presence of unreduced $Cd(OH)_2$ in charged active material and of unoxidized Cd in discharged active material can be explained by the higher capacity of sintered cadmium electrode than of nickel plate electrode, used as counter electrode.

The presence of $CdCO_3$ in active material is a result of the action of CO_2 from air on KOH electrolyte solution and of the pronounced tendency of substitution of NO_3^- ions, remained from the preparation step, by CO_3^{2-} ions.

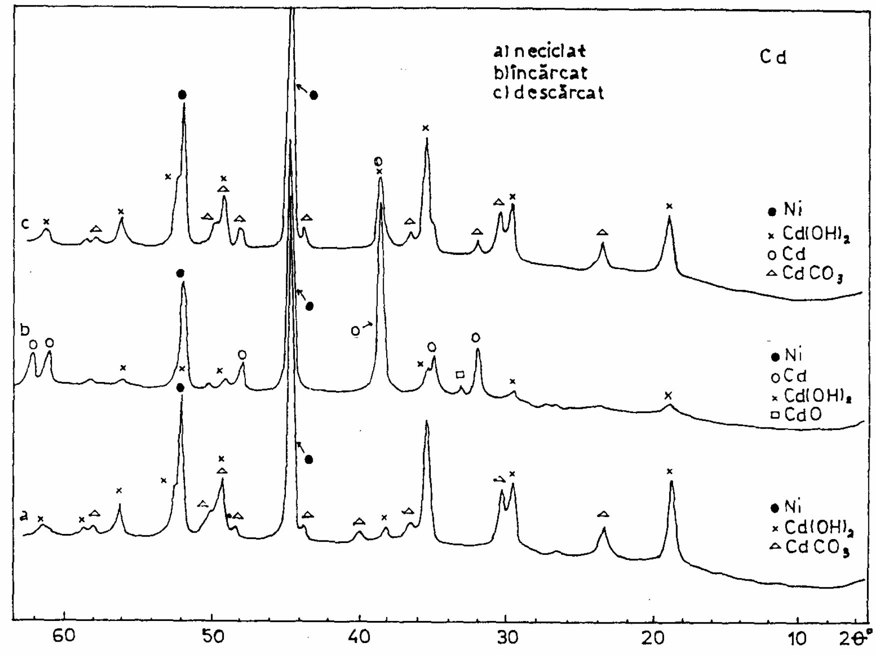

Fig. 5. X-ray diffractograms of sintered cadmium electrode:
a) uncycled, b) charged, and c) discharged.

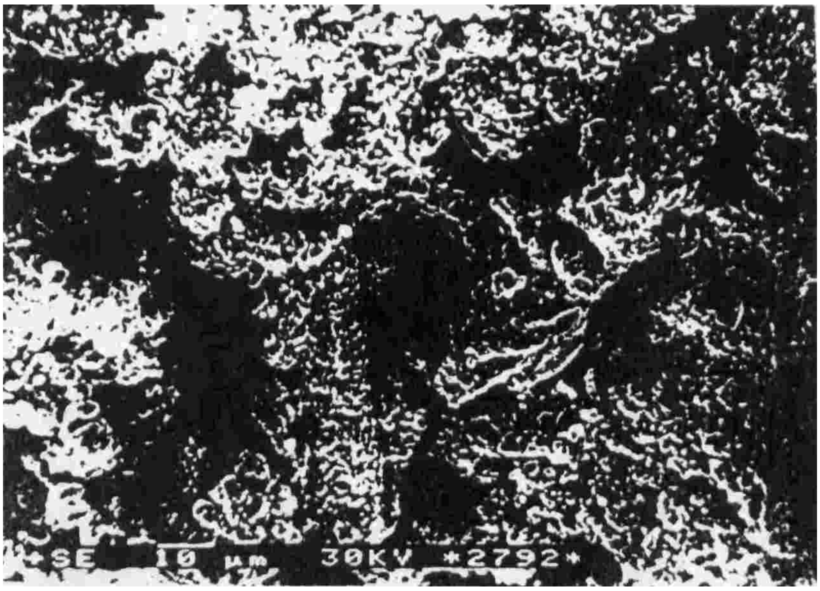

Fig. 6. SEM photograph of charged sintered cadmium electrode.

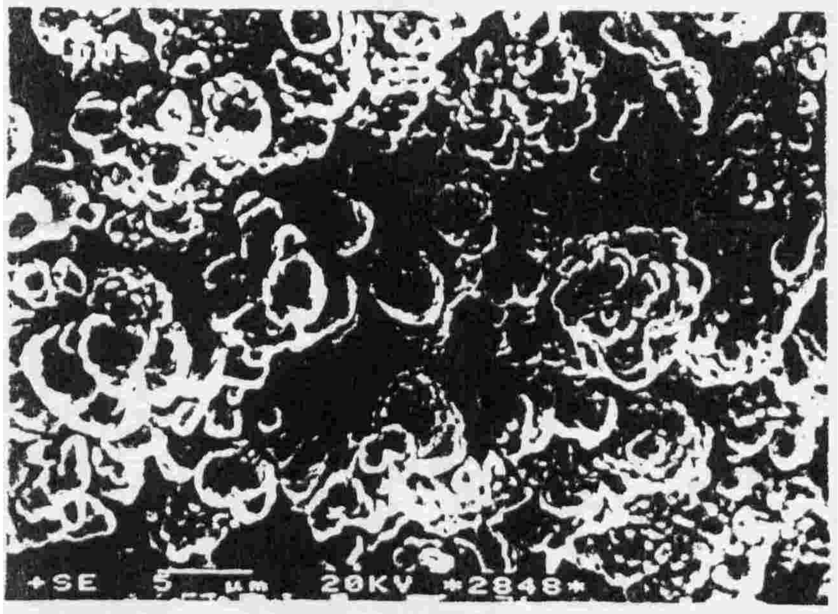

Fig. 7. SEM photograph of discharged sintered cadmium electrode.

CONCLUSIONS

From the investigation of structural and electrochemical characteristics of sintered cadmium electrodes, prepared by us, the following conclusions can be drawn:

a) The uncycled active material, impregnated in sintered support by cathodical polarization, is in discharged form, $Cd(OH)_2$;
b) The charged active material consists largely of microcristalline structure of Cd, containing small amounts of CdO crystals and $Cd(OH)_2$ remained in discharged form;
c) The discharged active material consists of $Cd(OH)_2$, containing a small amount of Cd remained in charged form;
d) The presence of $CdCO_3$ in active material is a result of the action of CO_2 from air on KOH electrolyte solution and of the pronounced tendency of substitution of NO_3^- ions, remained from the preparation step, by CO_3^{2-} ions;
e) The addition of 35 g/l LiOH in 6N KOH electrolyte didn't influence the electrochemical behaviour of cadmium electrode;
f) The characteristics and the performance of our sintered cadmium

electrodes, prepared by electrochemical activation of sintered nickel supports impregnated with cadmium nitrate, point to the possibility of their successful utilization as anodes in alkaline batteries.

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