determined by AAS in all samples. The values were very similar and differed by 0.97 to 4.1%.

## CONCLUSION

The present study shows that total iron levels present in the organs can be determined using square wave voltammetry with the adsorption of the complex iron-catechol onto the mercury film microelectrode. Due to the enhanced mass transfer at microelectrodes, the deposition time of metal ions can be accomplished without stirring the solutions and makes this technique very fast compared with a HMDE.

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#### REFERENCES

[1]. F. Kieffer, *In Metals and their Compounds in the Environment*, VCH, Weinheim, 1991.

[2]. K. Merritt, T. D. Crowe and S. A. Brown, *J. Biomed. Mater. Res.*, 23 (1989) 845.
[3]. S. A. Brown, K. Zhang, K. Merritt and J. H. Payer, *J. Biomed. Mater. Res.*, 27 (1993) 1007.

[4]. K. Brainina and E. Neyman, *Electroanalytical Stripping Methods*, J. D. Winefordner, John Wiley & Sons, NY (1993) Vol. 126.

[5]. S. B. Adeloju, A. M. Bond and M. H. Briggs, Anal. Chim. Acta, 164 (1994) 181.

[6]. B. J. Basu and S. R. Rajagopalan, Analyst, 117 (1992) 1623.

[7]. M. R. Cushman, B. G. Bennett and C. W. Anderson, *Anal. Chim. Acta*, **130** (1981) 323.

[8], K. R. Wehmeyer and R. M. Wightman, Anal. Chem., 57 (1985) 1989.

[9]. M. C. Pereira and J. P. Sousa, in press at Electroanalysis (1996).

[10], S. Morais, G. S. Carvalho and J. P. Sousa, in revision at Electroanalysis (1996).

[11]. C. M. G. van den Berg and Z. Q. Huang, J. Electroanal. Chem., 177 (1984) 269.

# RESEARCH OF DISTRIBUTION OF MEAN CURRENT IN NICKEL HYDROXIDE POROUS ELECTRODE WHILE POLARIZING WITH ASYMMETRICAL CURRENT

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At the previous work [1] we showed that the usage of alternative asymmetrical current let the possibility to get any distribution of mean current along the depth of a porous matrix, i.e. the distribution with maximum in the centre of the electrode. This fact is very important because it is the distribution of mean current that influences greatly on the coefficient of usage of the active mass and capacity taken and given by the electrode.

In this work the feature of alternative current named above was checked up on a physical model pore for nickel hydroxide porous electrode. A model pore is a glass tube with nickel wire even covered with nickel hydroxide filled with the solution (KOH 1.2 g/cm<sup>3</sup> + LiOH 20 g/l) and polarized on the one side (Fig. 1). In order to learn the distribution of average current along the depth of a physical model of a pore or the same along the length of a nickel wire it was slowly and even sunk into the solution of the same composition. Constant potential on the nickel wire -10 mV against mercury oxide electrode in the same solution in the point of entrance of the nickel wire into the solution was being kept (Fig. 2). At this time in the cell the current proportional to the charge of nickel hydroxide in the point of entering the wire into the solution is flowing, and the recorder connected to the cell draws the picture of distributing of average current along the length of nickel hydroxide wire. The calculation of current distribution along the depth of a pore was fulfilled with a numerical method on the base of macrohomogeneous model of a porous electrode.

 $\frac{d^2 j(x)}{dx^2} \bigg|_{x=1} < 0$  maximum of distribution of average current will be situated near the opposite side of the

electrode. In this formula  $j(x) = \frac{1}{T} \int_{0}^{T} i(x, t) dt$  is the average length current density. The calculation is fulfilled for asymmetrical alternative outer current in the form of rectangular impulses. The results of the calculations for two regimes are given in table 1. For the first regime maximum of the average current must be situated near the opposite side of the electrode with one-side entrance. For the second regime maximum approaches to the face side. Table 1.

The calculated regims of asymmetrical alternative outer current.

Regim	1, cm	$J_A$ , mA	$J_{K}$ , mA	<i>T<sub>A</sub></i> , s	<i>T<sub>K</sub></i> , s
1	1.0	4.34	6.61	0.2	0.1
2	2.0	4.36	6.68	0.2	0.1

In table 1  $J_A$ ,  $J_K$  -are amplitude meanings of anode and cathodic impulses of cur-

rent, and  $T_A$ ,  $T_K$ -are corresponding semiperiods.

Parameters of this device are the following: diameter of nickel wire is r = 1mm; inner diameter of a glass tube R = 1.6mm; specific resistance of solution is  $\rho = 0.025$  Ohm•m; specific surface of a volume unit is  $s = \frac{2r}{R^2 - r^2}$ . Length of a physical model of a pore was changed with putting the glass tube into the solution. The speed of moving nickel wire into the solution while reading the charge was 240 mm/hour. The speed of moving of the recoder was 50 s/cm.

Experimental curves for the calculated regimes are shown on figure 1, where it is





- 280 -

- Fig.1. Physical model pore for nickel hydroxide porous electrode. (1 - nickel wire even covered with nickel hydroxide;
  - 2 glass tube;
  - 3 opposite electrode;
  - 4 generator of impulses.)
- Fig.2. The device for learn the distribution of mean current along the depth of physical model. (1 - nickel wire even covered

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- with nickel hydroxide;
- 2 mercury oxide electrode;
- 3 opposite electrode;
- 4 the device of constant potential;

 $\frac{d\eta}{dx}\Big|_{x=1} = 0,$ 

5 - recorder.)

The main equation of this model in activation-ohm regime will be the following:

$$\frac{d^2\eta}{dx^2} = \rho si(\eta)$$

with border conditions

$$J = -\frac{1}{\rho} \frac{d\eta}{dx} \bigg|_{x=0} ,$$

where: *J* - density of alternative outer current;  $\eta$  - polarization;  $\rho$  - specific resistance of the solution; *s* - specific surface of a volume unit; *I* - thickness of an electrode;  $i(\eta)$  - nonsymmetrical polarization function which is equal  $A_1 sh(B_1\eta)$  for  $\eta > 0$  and  $A_2 sh(B_2\eta)$  for  $\eta < 0$ . This function has been found experimentally with the method discribed in the work [1]. Preliminary analytical investigations showed that with

seen that the given model let us calculate quite exactly real distribution of average current in nickel hydroxide porous electrode. But this model does not consider in any way the processes of redistributing in nickel hydroxide porous electrode, which is quite important. Namely, experimental curves written from the nickel wire at once after the process of charge and some time later differ from one another greatly, and it seems to us that it is connected only with the processes of redistribution. Newetherless this experimental check clearly shows that while polarizing with alternative current it is possible to get any distribution of average current in nickel hydroxide porous electrode and hence to increase greatly its exploitation characteristics.



- Fig.1. Experimental curves of distribution of average current along the depth of the physical model of a pore while one-sided polarizing it with alternative asymmetrical current. ( j(x) — average length current density;  $J_m$  — average outer current; l - the length of a pore)
- F.I. Kukos, Y.D. Kudriavtsev, N.E. Galushkin, *Electrochemistry* 25, N7(1989) 887. 1.

# PORTUGALIÆ ELECTROCHIMICA ACTA

Vol. 14, 1996

# ANNUAL INDEX

## **SUBJECTS**

Estimation of Bypass Current in a Bipolar Electrode Stack-Magnesium Bipolar Cell, H. Padmanabha Sarma, A. Antonyraj, G. N. Kannan and A. Selvakesavan	7
A New Approach to Current Efficiency Calculation in Magnesium Electrolysis, A. Antonyraj, T. Muthurocku, U. Shunmugam and C. O. Augustin	15
The Definition of Electrolyte, Victor M. M. Lobo	27
Activation of Complexes by Electron-Transfer Processes, M. Fátima C. Guedes da Silva	31
Diffusion Coefficients of 301 Electrolytes in Aqueous Solution from Onsager-Fuoss and Pikal Theories, V. M. M. Lobo, A. C. F. Ribeiro and S. G. C. S. Andrade	45
Opening Session of the VIII Meeting of the Portuguese Electrochemical Society, L. C. Carrilho Gonçalves	129
The Open-ended Capillary Cell - A Method to a Large Range of Concentrations of Electrolyte Aqueous Solutions, V. M. M. Lobo and Artur J. M. Valente	133
Cálculo de Coeficientes de Actividade a partir de uma Nova Equação Teórica, Ana Isabel S. F. Carvalho, José Inácio F. P. Martins	139
Mean Activity Coefficients of Potassium Chloride in Water-Ethanol Mixtures at 25 °C, A. Lopes, F. Farelo and M. I. A. Ferra	145
Structure-Potential Relationships for the Dinitrile Complexes trans- -[Fe(NCR) <sub>2</sub> (Et <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PEt <sub>2</sub> ) <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub> , Luísa M. D. R. S. Martins and Armando J. L. Pombeiro	151
Electrochemical Study of Some Vanadium Complexes, Cristina M. P. Ferreira, M. Fátima C. Guedes da Silva, Armando J. L. Pombeiro and Piotr Sobota	157
Electrosynthesis of Optical Active Dipeptides from Molybdenum Nitride Complexes, A. M. Fonseca, S. K. Ibrahim, C. J. Pickett and M. A. Queirós	163
Electrochemical Studies on Desulforedoxin and Desulfoferrodoxin, Two FeCys <sub>4</sub> Containing Proteins, Carla S. Ascenso, Maria João Lima, Frank Rusnak, Isabel Moura and José J. G. Moura	169
Comparative Study of the Redox Properties of Platinum, Palladium, Copper and Iron Camphor Derived Complexes, <i>M. Fernanda N. N. Carvalho, Armando J. L.</i> <i>Pombeiro and Rudolf Herrmann</i>	173

173