

Characterization and Electrochemical Behaviour of Nickel Hydroxide Films prepared from Characterization and Electrochemical Behaviour of Nickel Hydroxide Films prepared from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solutions.

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The  $\text{Ni}/\text{Ni}(\text{OH})_2$  electrode is the object of an intense research activity both because of its use in alkaline batteries<sup>1</sup> and in a variety of electro-oxidation reactions<sup>2,3</sup>. It was pointed out by many authors that an increase in the electrode porosity is a key step for enhancing the electrocatalytic activity of electrodes.

The methods of preparation of high area  $\text{Ni}(\text{OH})_2$  electrodes usually involve chemical or electrochemical precipitation. Electro-chemically,  $\text{Ni}(\text{OH})_2$  can be grown by cycling metal nickel in alkaline solutions<sup>3-5</sup> or by electrodeposition from  $\text{Ni}^{2+}$  containing solution. Typically,  $\text{Ni}(\text{OH})_2$  is grown at constant current from  $\text{Ni}(\text{NO}_3)_2$  containing solutions<sup>1,6,7</sup>. The preparation conditions strongly influence the morphology and the electrochemical behavior of the resulting deposits. Interestingly, these hydrous layers possess ion exchange properties and can be doped by several ions<sup>7,8</sup>, which also a marked influence on the electrochemical properties of the coated electrodes.

In the present work we examine the electrodeposition, at constant potential, of hydrous Ni layers on metal substrates such as Ni and Cu, from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solutions. Cyclic voltammetry curves in these solutions are given in Fig.1. It is seen that a pre-peak precedes metal Ni deposition at  $E < -0.7\text{V}$ ; its position and intensity depend on the Ni salt concentration. When electrodeposition is carried out at a potential corresponding to the peak maximum, or slightly negative of it, a black deposit forms on the electrode substrate. The SEM picture given in Fig.2 show a highly fractal surface, formed of compact islands separated by channels of small particles.

XPS and SIMS investigations reveal that the deposit contains metallic Ni, Ni oxide and hydroxide. The hydroxide component increases as the electrodeposition potential increase from  $-0.65$  to  $-0.75\text{V}$ . X-ray analysis shows only the presence of nickel although the deposit has a black color. The fact that a separate oxide-hydroxide phase is not seen is explained by its dispersed and amorphous character.

The oxidation of alcohols on Ni electrodes has been extensively investigated<sup>2,3</sup>, with particular attention being focused on the performance of high area electrodes. It seemed then interesting to assess the electrocatalytic activity of the "black nickel" electrodes of this work in the oxidation of some typical alcohols: methanol, ethanol and s-butanol have been examined. An example of the results obtained is given in Fig.3. Here we compare the electrooxidation of ethanol on "black Ni" with that on a Ni electrode that was cycled for 15 min between  $-0.4$  and  $0.9\text{V}$  vs. NHE, in order to grow a  $\text{Ni}(\text{OH})_2$  layer. The data in Fig.3 show a remarkable enhancement in the electrocatalytic activity especially at high currents. We established that this activity is maintained unaltered in a period of 6h polarization. Similar results have been obtained for the case of methanol and s-butanol. Reasons of this enhanced activity will be discussed.

## References

- 1) Mc Breen in R.E. White, J.O'M Bockris and B.E. Conway (eds) *Modern Aspects of Electrochemistry*, vol.21, Plenum Press, New York, 1989.
- 2) H.J. Schäfer in *Topics in Current Chemistry*, Springer Verlag, Berlin, 1987 and refs. Therein.
- 3) A.Kowal, S.N.Port and R.J. Nichols, *Catalysis Today*, **38**, 483 (1997)
- 4) A. Visentin, A.C. Chialvo, W.E. Triaca and A.J. Arvia, *J. Electroanal.Chem.*, **225**, 227 (1987) and refs. Therein

- 5) A. Visentin, W.E. Triaca and A.J. Arvia, *J.Appl.Electrochem.*, **26**, 493 (1996)
- 6) D.A. Corrigan, *J.Electrochem.Soc.*, **134**, 377 (1987)
- 7) P.M. Robertson, P.Berg, H. Reimann, K. Schleich and P. Seiler, *J.Electrochem.Soc.*, **130**, 591 (1973)
- 8) E.J. Casey, A.R. Dubois, P.E. Lake and W.J. Moroz, *J.Electrochem.Soc.*, **112**, 371 (1965)

Fig. 1 Cyclic voltammetry curves for Ni in solutions of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at different concentrations. Scan rate  $1\text{mV/s}$

Figure 2 – SEM micrograph of a Ni hydrous layer electrodeposited on Ni from  $100\text{ g/l NiCl}_2 \cdot 6\text{H}_2\text{O}$  at constant potential ( $0.95\text{V}$ , SCE)

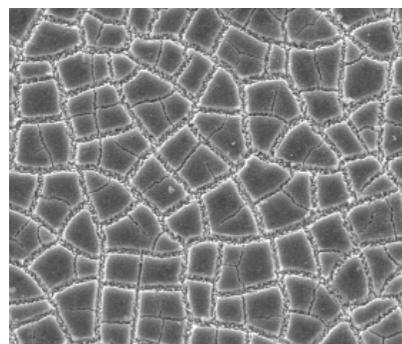
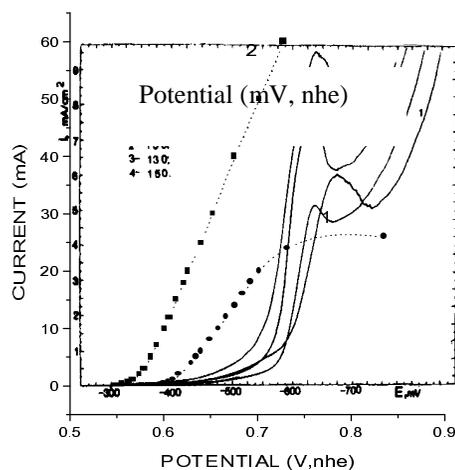


Fig.3 – Steady state polarization curves for the electrooxidation of  $1\text{M}$  Ethanol in  $1\text{M}$  NaOH on Ni (1) and black Ni (2) electrodes –  $T = 22^\circ\text{C}$  Electrodes geometric area:  $0.55\text{ cm}^2$

