

20

ENVIRONMENTAL CATALYSIS

for a better World and Life

Proceedings of the 1st World Congress
Environmental Catalysis - For a better World and Life
Pisa (Italy), May 1-5, 1995

Editors

G. Centi and S. Perathoner

Dip. di Chimica Industriale e dei Materiali, Univ. Bologna, Italy.

C. Cristiani and P. Forzatti

Dip. di Ingegneria Chimica e Chimica Industriale, Politecnico Milano, Italy.

EFCE Publications - Series 112

SOCIETA' CHIMICA ITALIANA, Roma (Italy).

Nickel Anodes In-Situ Activation with Cobalt in Alkaline Electrolyzers

Leonardo GIORGI, Alfonso POZIO

ENEA, ERG-TEA-ECHI, CRE Casaccia, Via Anguillarese 301, 00060 S.Maria di Galeria (ITALY)

fax: +39-6-3048.6358

In-situ activation of nickel anodes with cobalt ions in KOH electrolyte during water electrolysis, results in a marked increase of electrocatalytic activity (decrease of both cell voltage and anodic overpotential), with an increase of hydrogen production rate, reduction of energy demand and environment pollution.

Introduction

The water electrolysis is the most efficient method to produce high purity hydrogen, to be use as fuel in engine or fuel cells, without pollution effect. The electrolyzer can be powered by continuous or intermittent sytem (nuclear or hydroelectric off-peak, photovoltaic field, etc.). The main problem of this technology is the energy demand due to the high cell voltage. In an electrolyzer, cell voltage and energy efficiency mainly depends by the anodic overvoltage [1]. For this reason anode activation is needed in order to reduce the Oxygen Evolution Reaction (OER) overvoltage. In-situ electrochemical activation [2] during electrolyzer operation looks inexpensive and particularly suited for electrolyzers working under intermittent conditions.

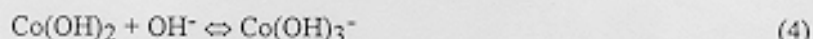
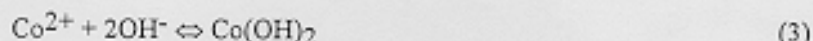
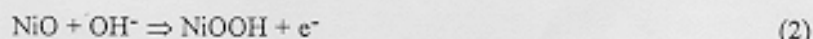
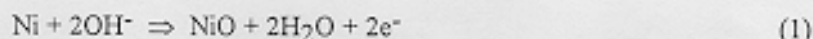
In this work, the in-situ activation of nickel anodes in at 25°C during electrolysis, has been investigated in the presence and absence of dissolved cobalt (II) nitrate salt in the KOH electrolyte.

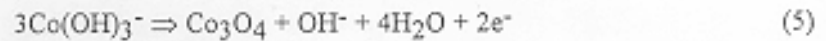
Experimental

Cyclic voltammetry was used to study nickel (purity 99.9999 %) anode behaviour, in KOH 0.25 M at 25 °C, and its in-situ electrochemical activation with cobalt ions. The electrocatalytic effect of cobalt was evaluated considering the changes of some parameters (cell voltage, anode overpotential, apparent oxygen evolution potential, charge density). Such parameters were obtained throught cyclic voltammetry measurements [3] carried out during electrolysis at a low (2 kA/m²) and a high (8 kA/m²) current density.

Results and discussion

From cyclic voltammetry data, after a short time of electrolyzer operation, a fast change in nickel electrode surface results. This phenomena can be attributed to the nickel (fig.1) or nickel-cobalt (fig.2) oxide film growth by oxidation of nickel electrode and cobalt hydroxide complex present in alkaline solution [1]:





The results show that very small cobalt ions amount (~2 ppm) in electrolyte strongly influences anode electrode kinetics and oxidative phenomena (fig. 2).

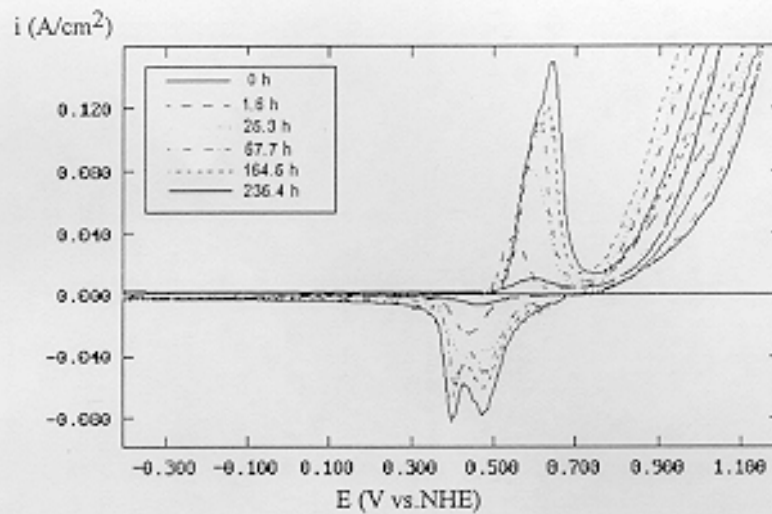


Fig. 1 Cyclic voltammetry on nickel anode, at different electrolysis time. (KOH 2.5 M, T=25 °C, $i=2 \text{ kA/m}^2$)

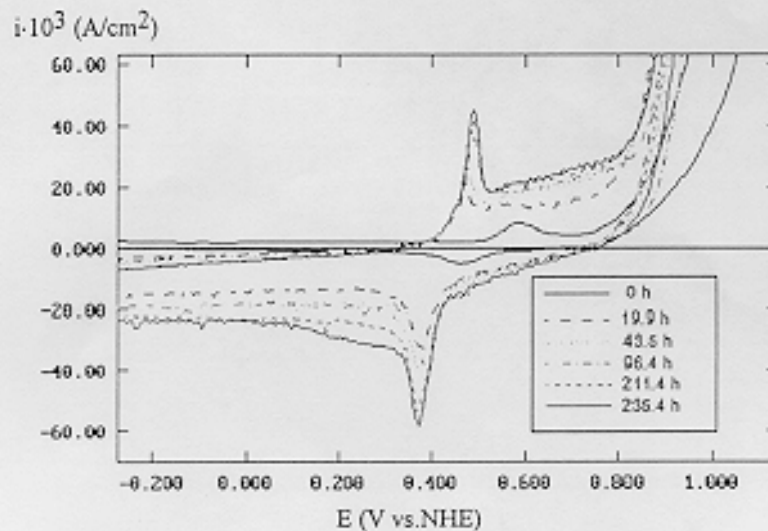


Fig. 1 Cyclic voltammetry on nickel anode, at different electrolysis time, in presence of Co²⁺. (KOH 2.5 M, T=25 °C, $i=2 \text{ kA/m}^2$)

Cobalt ions, both at high and at low current density, reduce cell voltage (fig.3) and anodic overpotential. Another positive effect is the generation of a stable porous oxide with a high active surface, particularly at high current density. The gain of catalytic activity, obtained in presence of cobalt ions, is higher at low current density (-0.13 V at 8 kA/m² and -0.25 V at 2 kA/m²).

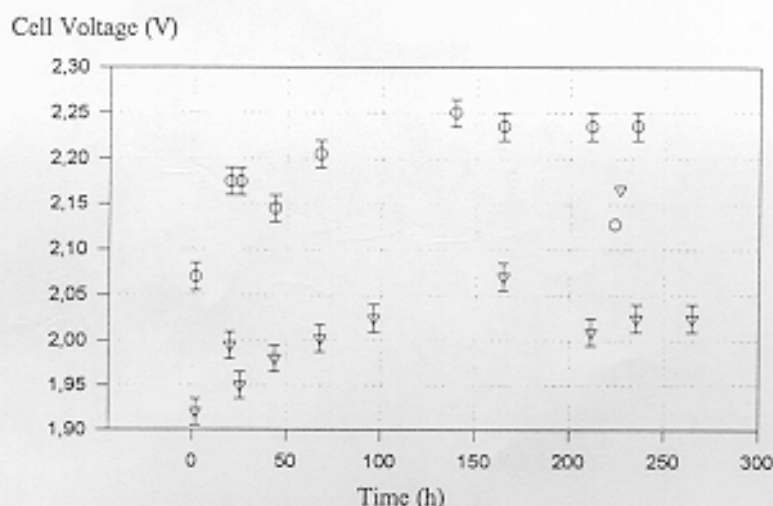


Fig. 3 Cell voltage during electrolysis in KOH 2.5 M at $i=2 \text{ kA/m}^2$. (○=without Co^{2+} , ▽=with Co^{2+})

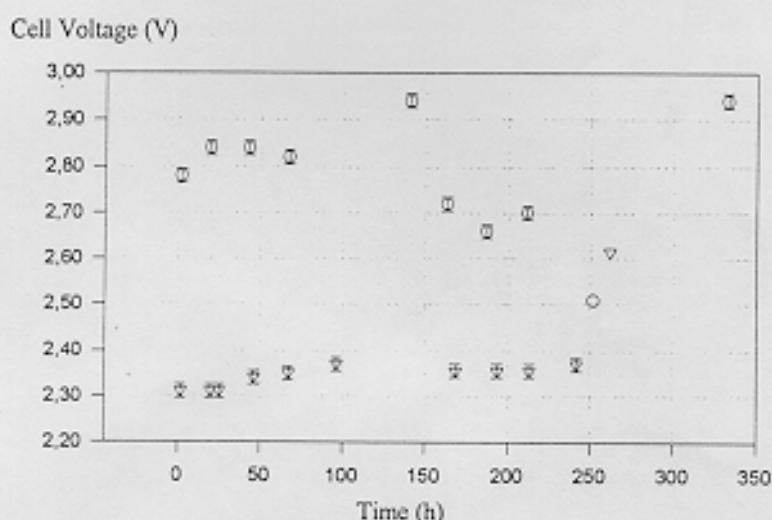


Fig. 4 Cell voltage during electrolysis in KOH 2.5 M at $i=8 \text{ kA/m}^2$. (○=without Co^{2+} , ▽=with Co^{2+})

Cobalt seems to prevent phase transition of the nickel oxide surface [5], as detected by splitting of voltammetric peaks [6,7] in absence of the cobalt during electrolysis (fig.1). Such changes of the crystalline structure could strongly influence the hydration and dehydration phenomena which take part in the OER catalysis mechanism.

The nature and morphology of the anodic coating, was influenced by presence of cobalt as indicated by optical microscopy analysis. Cobalt oxide reduces the deterioration of electrodes surface during electrolysis. An exponential relationship between anodic peaks charge density and electrolysis time (fig. 5 and 6) was found:

$$q = a + b \cdot t^n \quad (6)$$

with $n=0,28 \pm 0,03$. Being charge density proportional to the active sites numbers, the relationship can be regarded as the oxide catalytic growth rate during electrolysis. This growth results large without cobalt at low current density and with cobalt at high current density.

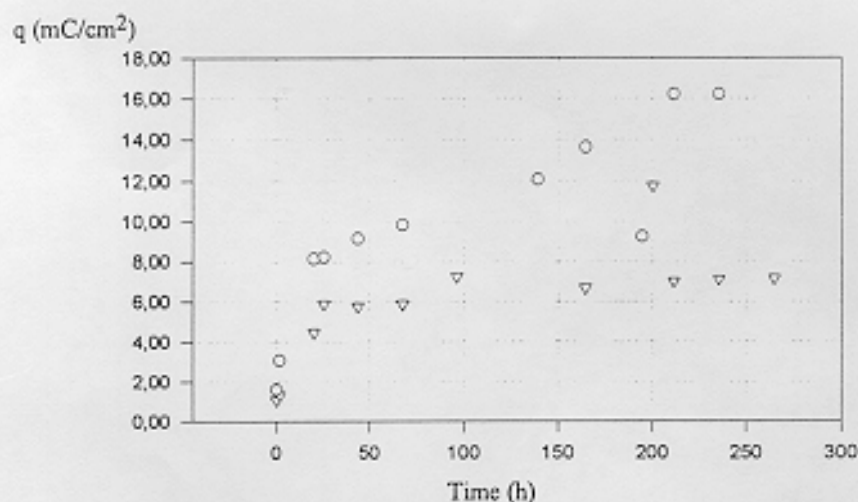


Fig. 5 Charge density of the anodic peak at $i=2 \text{ kA/m}^2$. (O=without Co^{2+} , ∇ =with Co^{2+})

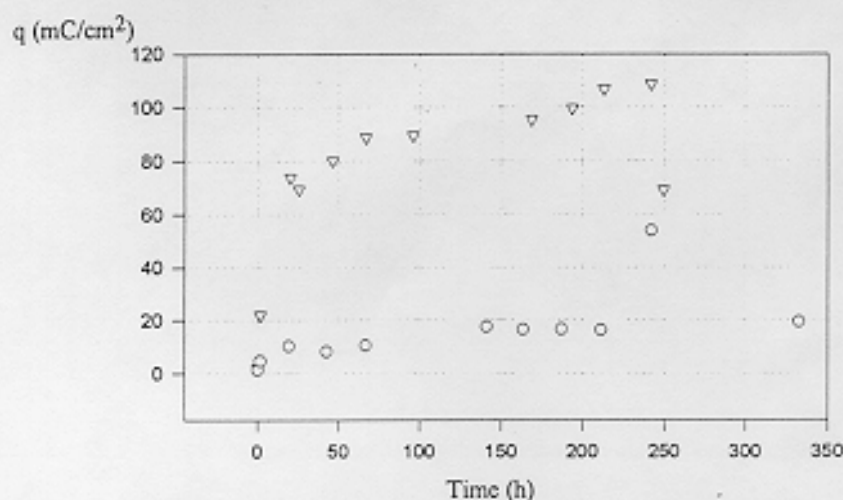


Fig. 6 Charge density of the anodic peak at $i=8 \text{ kA/m}^2$. (O=without Co^{2+} , ∇ =with Co^{2+})

We can conclude that the in-situ activation of nickel anode in alkaline electrolyzers with cobalt ions is a very cheap method to reduce the energy consumption in the production of hydrogen by electrocatalytic process, also if it is necessary more investigation on the electrolysis at high operative temperature (up to $160 \text{ }^\circ\text{C}$) and under intermittent operations.

References

1. L. Giorgi, ENEA Report, RTI/ERG/TEA/ECHI/94/01, 1994
2. H. Wendt, H. Hofmann, V. Pizak, Material Chem. and Phys., 22 (1989) 27
3. H. J. Miao, D. L. Piron, J. Appl. Electrochem., 21 (1991) 55
4. S. Trasatti, Electrochim. Acta, 36 (1991), 225
5. K. Lian, S.J. Thorpe, D. W. Kirk, Electrochim. Acta, 37 (1992), 2029
6. L. Giorgi, A. Pozio, ENEA Report, RTI/ERG-TEA-ECHI/94/02, 1994.
7. Giorgi, A. Pozio, GEI 1994, Giornate dell'Elettrochimica Italiana, 11-14 Ottobre 1994, Padova