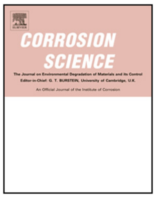
Corrosion Science 112 (2016) 255–263

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Electroactivity of Ni–Fe cathodes in alkaline water electrolysis and effect of corrosion

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ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 6 July 2016
Accepted 21 July 2016
Available online 22 July 2016

Keywords:
A. Alloy
A. Nickel
B. Polarization
B. XPS
C. Alkaline corrosion
C. Hydrogen overpotential

ABSTRACT

Alloys of Ni with 10–99 wt.% Fe were examined in 25 wt.% KOH at 80 °C. Electroactivity of the alloys toward HER increased with the increasing content of Fe up to about 90 wt.%, however also increased tendency to pitting corrosion during cathodic polarization. After anodic polarization or corrosion at OCP, cathodic curves of high-Fe materials exhibited a peak which was followed by significant current rise. The peak was ascribed to the reduction of oxide products to metals. It was suggested that the current rise was associated with the formation of active intermediates of freshly-electrodeposited metal-adsorbed hydroxides.

1. Introduction

Currently, production of hydrogen by water electrolysis provides only 4% of the world hydrogen requirements. This low contribution is due to high cost in comparison with the conversion of natural gas or coal. However, it is expected that the role of the electrolysis method will increase with the increasing availability of renewable energy sources and with the rising recognition of hydrogen as a clean fuel for transportation systems, and as a medium for storage of large amounts of energy [1,2]. Recent surveys on various technologies of water electrolysis are presented in [1,3–5].

Challenges for further development of alkaline water electrolysis include an improvement of catalysts made from cheap materials. At present, the most widely used are cathodes of nickel or its alloys with Mo and, to a lesser extent, with Fe, W, T, Co, V, Cr, Zn [6,7]. Out of these alloying metals, Fe can be the most advantageous owing to its low price and a good electrocatalytic activity for the hydrogen evolution reaction (HER) [5].

Ni–Fe materials are considered as potential active and low-cost electrocatalysts for water splitting which constitutes a vital step in a hydrogen economy [8]. These materials promote both HER and oxygen evolution reaction (OER). Recent work [9] shows that Ni–Fe/Nanocarbon hybrids exhibit good catalytic performances for both OER and HER under alkaline conditions.

Oxygen-containing Ni–Fe species (hydroxides, oxides or oxyhydroxides) are used mainly as anodes for water oxidation [10–15], but they are also catalytically active toward HER [16], although they may not be stable under conditions of cathodic polarization.

Electrocatalytic properties of Ni–Fe alloys toward HER are examined mainly on electrodes obtained by electrodeposition [16–19]. An enhanced electroactivity of electrodeposited Ni–Fe as compared to mild steel was ascribed to a slow recombination rate [16] or high porosity [18]. In paper [19] electrodeposits of Ni, Fe and Ni–Fe were obtained on copper substrate. It was shown that electrocatalytic activity of Ni–Fe coatings for HER in 1 M KOH at room temperature was higher than that of each of the components individually. The highest electroactivity was exhibited by a coating obtained from the plating bath with a molar concentration ratio of Ni^{2+}:Fe^{2+} of 4:6.

Iron exhibits a beneficial effect not only as a constituent in the bulk of electrodes, but also as a surface deposit. Nickel cathodes in industrial alkaline electrolysers undergo a deactivation, however, they reactivate when iron is electrodeposited from the bath. It was found that electrodeposition by reduction of ferric ions affects cathodic curves especially in hot solutions [20]. The deactivation of nickel cathodes was also prevented by iron deposited by magnetron sputtering [21].

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http://dx.doi.org/10.1016/j.corsci.2016.07.017
0010-938X/

Table 1
Materials and composition.

Designation	Main constituents (wt.%)
Ni	99.5 Ni, 0.09C, 0.09 Fe
90Ni–Fe	89.2 Ni, 10.6 Fe
60Ni–Fe	60.0 Ni, 39.8 Fe
10Ni–Fe	9.6 Ni, 90.2 Fe
1Ni–Fe	1.1 Ni, 98.7 Fe
Fe	99.9 Fe

The deactivation was ascribed to the formation of nickel hydride [22,23], whereas the beneficial effect of iron was explained by the increase in the true surface area [24,25], or by preventing the formation of nickel hydride [21]. It was also suggested that the activating effect of iron can be associated with the formation of reactive nascent iron during cathodic reduction of Fe(II) species [26,27].

Enhanced catalytic activity of electrodeposited Ni–Fe coatings can be associated with an increased intrinsic activity, increased surface area [18,24,25], hydrogen absorption [22,23], and also with incorporated admixtures from electrolytic bath. Separation of the intrinsic activity from 'real area factor' was considered in [28,29].

In the present work, cast Ni–Fe alloys of varying component contents were used. Their advantage over electrodeposited coatings includes easier manufacturing in large quantities for industrial electrolysers; also, owing to a uniform bulk compositions it is possible to determine intrinsic activity without contribution of porosity and admixtures occurring in electrodeposits. This work aimed at determining the effect of Ni–Fe composition on HER and on corrosion. It was intended to evaluate the role of intrinsic catalytic activity, of corrosion products and of absorbed hydrogen. Measurements were carried out in 25% KOH solution at 80 °C conditions in industrial electrolysers for hydrogen production [6,7]. The study involved electrochemical measurements, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

Measurements were performed on Ni, Fe and Ni–Fe alloys presented in Table 1. Samples of Ni and of Fe were in form of 10 × 6 × 0.1 mm foils which were vacuum annealed at 850 °C for 1 h and furnace cooled. Samples of Ni–Fe alloys were machined from commercial cold drawn rods; they were in form of 2-mm thick discs of 8-mm dia. Samples were ground with WC emery papers with final grit 1200, polished with 1-μm diamond spray and then washed ultrasonically in acetone. Electrical contact was ensured by attaching wires 0.5-mm in dia. of iron to Fe samples, and of nickel to Ni and Ni–Fe samples. The wires outside of the samples were insulated with polytetrafluoroethylene (PTFE) tubing. Sample holders were not used to minimise blocking of the surface by evolving hydrogen bubbles. Electrical resistance between samples and the attached wires was about 0.3 ohm, and the solution resistance between samples and reference electrode tip was about 0.5 ohm cm^2 (determined by impedance measurements).

Measurements were carried out in a PTFE cell (inner dia. 65 mm, height 100 mm) in a solution of 25 wt.% KOH at 80 °C. The cell was equipped with an external heater with a thermo-regulator, and with a vapour condenser. The solution was prepared from the reagent "Potassium Hydroxide semiconductor grade, 99.99% trace metals basis" ($\leq$150 ppm trace metals) made by Sigma-Aldrich, and demineralized water. In work [27] it was found that during a prolonged cathodic polarization of nickel in the solution of this reagent a deposition of iron or its oxides occurred, whereas cathodic pre-electrolysis considerably reduced this deposition. In the present work the solution was preelectrolysed using nickel electrodes at cathodic current density of 5 mA cm^{-2} for one week. Fresh solution was prepared for examination of each of the materials. The solution was deaerated by purging Ar (99.99%) before and during measurements.

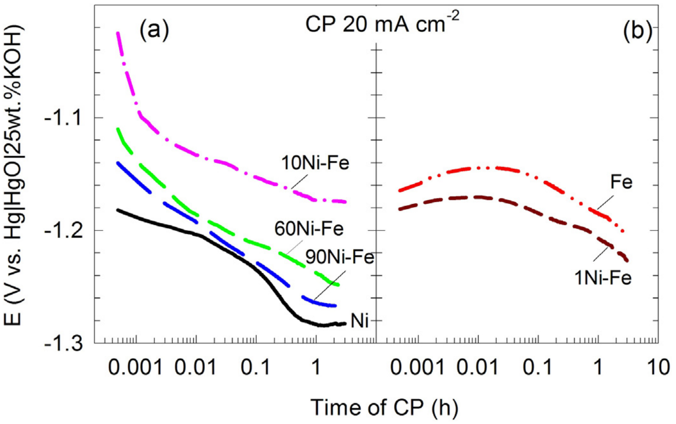

Fig. 1. Potentials as a function of time of galvanostatic cathodic polarization (CP) at 20 mA cm^{-2} for: (a) Ni, 90Ni–Fe, 60Ni–Fe and 10Ni–Fe, (b) Fe and 1Ni–Fe, in 25% KOH at 80 °C.

Value of pH of this solution at 25 °C was estimated with the use of activity coefficient which was calculated from the Debye-Hückel equation. The estimated value of pH at room temperature was 14.4 [26]. This corresponded to pH 13.3 at 80 °C [30].

The electrode potential was measured and presented in this paper against mercury oxide electrode Hg|HgO|25 wt.% KOH which was held at room temperature (0.00 V vs. Hg|HgO|25 wt.% KOH = 0.05 V vs. SHE). This electrode was given in abbreviation of Hg|HgO throughout this paper. Counter electrode was made of Ni wire which was placed inside an open tube in another vessel connected through the solution. This minimised entry of gaseous oxygen from the anode to cathode compartment. Voltammetric measurements were carried out at the potential sweep rate of 1 mV s^{-1}.

Typically three measurements were performed for each experimental parameter. Curves in figures show the most representative data. Results from several measurements are presented as arithmetic means with standard errors Δ (shown by bars) of the means:

$$\Delta = Sn^{-1/2} \qquad (1)$$

where S is the standard deviation and n is the number of measurements.

Surface analysis was performed with X-ray photoelectron spectroscopy (XPS). The measurements were carried out with Al Kα radiation at 10 kV and 10 mA. Depth profiles were obtained by Ar$^+$ sputtering at 3.0 kV and an ion gun current of 5 mA cm^{-2}. Binding energies in XPS spectra were assigned to species using the NIST XPS Database [31].

Spectra were recorded in the pulse counting mode, and atomic concentrations C_x were assessed using the relation:

$$C_x = (I_x/S_x)/\Sigma(I_i/S_i) \qquad (2)$$

where I_x is the peak height of element X, and S_x is a relative elemental sensitivity factor.

Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) examinations were made with Nova NanoSEM 450.

3. Results

3.1. Cathodic behaviour without interference of anodic oxidation

Potentials as a function of time of galvanostatic cathodic polarization at current density of 20 mA cm^{-2} are shown in Fig. 1(a) for