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Hydrogen evolution on plasma carburised nickel and effect of iron deposition from the electrolyte in alkaline water electrolysis

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ABSTRACT

Presence of carbon in electrodeposited nanocrystalline Ni-Fe-C cathodes renders a high electroactivity for hydrogen evolution reaction (HER) in hot alkaline solutions. In the present work carbon was introduced into nickel cathodes by plasma treatment in $CH_4 + H_2$ gas mixture at 470 °C. Electrochemical measurements were carried out in the solution of 25 wt.% KOH (reagent p.a.) at 80 °C. In some measurements the solution was pre-electrolysed to remove heavy metals. Carburisation resulted in a significant enhancement of catalytic activity of nickel for HER during short cathodic polarisation. Later, differences between the materials almost disappeared, evidently due to deposition of iron and of other heavy metals from the solution. Cathodes with iron deposits underwent an activation following anodic polarisation. It was proposed that the activating effect of iron can be associated with the formation of highly reactive iron during cathodic reduction of oxide species (probably $Fe(OH)_4^{2-}$). The activating effect of prior anodic polarisation can be due to the formation of large amounts of oxide species which can undergo the reduction to reactive iron.

1. Introduction

Production of hydrogen by water electrolysis has a hundred-year tradition, but currently only 4% of world hydrogen requirements is produced by this method. Its small contribution is due to high cost in comparison with the conversion of natural gas or coal. It is expected that this method will be gaining in the importance with the increasing availability of renewable energy sources (solar and wind) and with the increasing recognition of the role of hydrogen as a clean fuel for transportation systems, and as a medium for storage of large amounts of energy [1]. Recent surveys on various technologies of water electrolysis (alkaline, PEM, high-temperature) are presented in [1–4]. Challenges for further development of alkaline water electrolysis include, among others, improved catalysts with low overvoltages [1].

The operating efficiency of nickel cathodes in KOH electrolytes decreases with time. It is manifested by the rise of cathode overpotential at constant cell current [5–7] which was ascribed to hydrogen absorption [5] and formation of nickel hydride [6,7]. The deposits of iron on nickel cathodes prevented the efficiency loss. This effect of iron was attributed to an increase in surface area by the deposited metal [8] and by preventing the formation of nickel hydride [9].

Cathodes for alkaline water electrolysis are made mainly of nickel or its alloys with Mo and, to a lesser extent, with Fe, W, Ti, Co, V, Cr, Zn [10,11]. High activity towards hydrogen evolution reaction (HER) is exhibited especially by electrodeposited metals and alloys. Activity increases for materials in the sequence: nickel < electrodeposited iron < electrodeposited Ni-Fe < electrodeposited Ni-Fe-C [12].

Electrodeposited nanocrystalline Ni-Fe-C alloys showed the highest activity among known electrodes for hydrogen evolution in a hot concentrated hydroxide solution [12]. Activity of electrodeposited Ni-Fe-C alloys in seawater electrolysis varies with the grain size [13] and carbon content [14].

In a search for other methods to produce carbon-containing cathodes for water electrolysis, low-temperature plasma carburising was examined in this work. This method was used for austenitic stainless steels to enhance hardness and resistance of surface layers to wear and corrosion [15]. Owing to high hardness, plasma carburised cathodes might be more resistant to damaging effect of evolving hydrogen gas, and to corrosion which occurs on hydrogenated nickel alloys [16].

Unlike stainless steel, nickel is not able to incorporate large amounts of carbon because of a very low solubility of carbon in nickel and instability of nickel carbides [17]. Nevertheless, thin

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films of nickel-carbon (with varying carbon content) were obtained by d.c. magnetron sputter deposition [18,19].

The aim of the present work was to determine the electrochemical behaviour of nickel cathodes with carbon introduced by surface plasma alloying. It was intended to obtain surface layers with strongly bound carbon and, therefore, of high hardness and increased resistance against corrosion and damage by evolving hydrogen gas bubbles. Also, it was attempted to separate the effect of the increased surface area (carbon deposited on the surface) from the catalytic effect (carbon dissolved in the metal substrate). The effect of deposition from bath of heavy metals, especially of iron, was examined and its explanation was proposed.

2. Experimental

Rod of commercially pure nickel Ni 201 (in wt.%: min. Ni 99, max. C 0.02, Fe 0.40, Mn 0.35, Si 0.35, Cu 0.25) was machined into samples in form of discs 14 mm in dia. and 2.0 mm thick. The samples were ground with a SiC wheel and finally with wet SiC grinding papers down to the 1200 grade.

Carbon was introduced into surface layers in a commercial plasma treatment unit. The process of carburising was carried out under conditions established in [20]. First, heating of the samples was achieved by ion bombardment in a hydrogen atmosphere of 500 Pa until the preset treatment temperature of 470 °C was attained. Then a reactive gas mixture of 2% CH_4 + 98% H_2 was introduced into the chamber and the treatment was conducted for 15 h.

Concentration-depth profiles for Ni and C, determined by Glow Discharge Optical Emission Spectroscopy (GDOES), are shown in Fig. 1. High concentration of carbon in the superficial layer (depth of about a few nanometers) might result from the atmospheric contamination. Carbon diffused into Ni down to the depth of about 0.8 μm. Its presence in small amounts in surface layer can be inferred from a slight increase of surface hardness ($HV_{0.05}$, measured under 50 g load, average of 5 measurements) from 250 for untreated Ni to 255 for carburised Ni.

Electrochemical measurements were carried out on samples of three types:

(a) Nickel (composition as given above), designated “Ni untreated”. The samples were polished with 1 μm diamond spray.
(b) The as-carburised surfaces which contained carbon soot, designated: “Ni as-carburised (with soot)”. These samples contained carbon mainly in form of a deposit on the surface; effect of such carbon can be associated both with its possible catalytic action and with the large surface area.
(c) Carburised surface without soot (carbon soot was removed by rubbing on a microcloth wetted with ethanol); designated: “Ni carburised (without soot)”. Carbon can be present mainly in the solid solution in nickel. Carbon in this form can affect HER by changing catalytic activity and/or corrosion behaviour of nickel, but not by an increase of surface area.

Samples were ultrasonically cleaned in acetone and then mounted in a holder made of polychlorotrifluoroethylene (PCTFE). Exposed surface (0.36 cm^2) faced upward to avoid blocking by evolving hydrogen gas. The holder was inserted into a larger polytetrafluoroethylene (PTFE) cell (inner dia. 65 mm, height 100 mm) with the solution examined.

Measurements were carried out in a solution of 25 wt.% KOH at 80 °C. The solution was prepared from the reagent “Potassium Hydroxide 85% Pure P.A. Basic” made by POCH S.A. According to the specification, the content of heavy metals was max. 0.001 wt.%. 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 [21].This corresponded to pH 13.3 at 80 °C [22].

Supplementary measurements were performed in a high-purity solution prepared from the reagent “Potassium Hydroxide semiconductor grade, 99.99% trace metals basis” made by Sigma-Aldrich.

The solution was de-aerated by purging argon (99.99%) before and during the measurements. Electrochemical measurements involved potential sweeps, galvanostatic polarisation and potential jumps.

The electrode potential was measured and presented in this paper against mercury oxide electrode Hg|HgO|25wt% KOH which was held at room temperature (0.00 V vs. Hg|HgO|25wt% KOH = 0.06 V vs. SHE). Counter electrode was made of Ni wire which was placed inside an open tube to hamper entry of gaseous oxygen from the anode to cathode compartment.

Typically three measurements were performed for each experimental parameter. Figures present the most representative data.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) examinations were made with Nova NanoSEM 450.

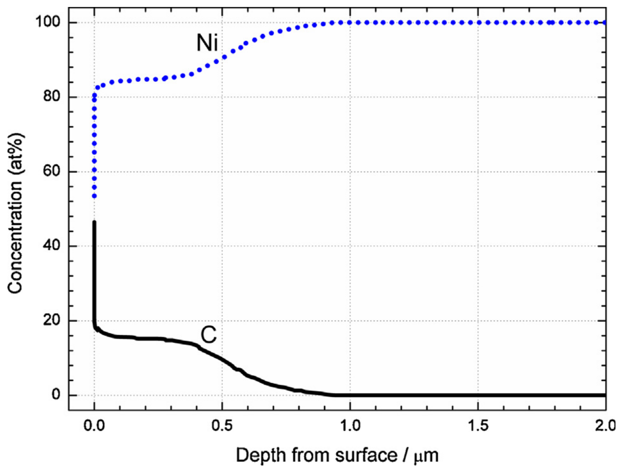

Fig. 1. GDOES concentration-depth profiles for carburised nickel. Carburising conditions: 470 °C for 15 h.

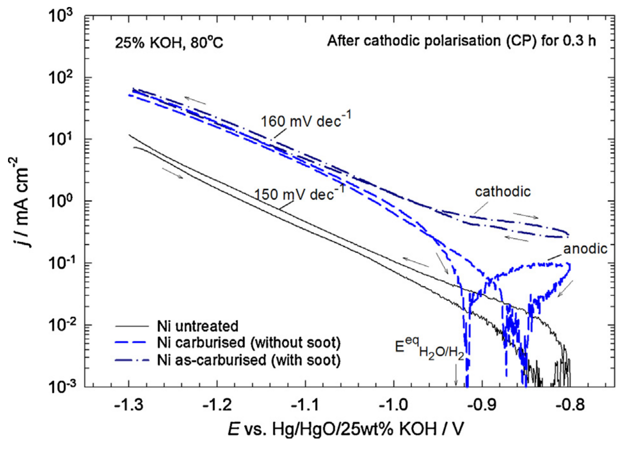

Fig. 2. Voltammograms for Ni untreated, Ni as-carburised (with soot) and Ni carburised (without soot) in 25% KOH at 80 °C, sweep rate 1 mV s^{-1}, after 0.3 h of cathodic polarisation (CP). Value of $E^{eq}_{H_2O/H_2}$ was evaluated from data in [23].