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INFLUENCE OF HEAT TREATMENT ON THE ELECTROCHEMICAL BEHAVIOUR OF NICKEL

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ABSTRACT

Heat pretreatment of nickel in the temperature range 500–700 °C gives a non-stoichiometric nickel oxide which shows metallic conductivity and low activity for oxygen evolution; at higher temperatures (> 700 °C) a non-conducting NiO (p-type semiconductor) is formed.

INTRODUCTION

Nickel "metal" is the most suitable anode material for the processes involved in water electrolysis in alkaline solution to produce H_2 and O_2 [1,2].

Many studies have been carried out on the influence of nickel pretreatment on its electrochemical behaviour [3,4]. Recently, Liu and Conway [5] have shown that pretreatment of nickel by oxidation in aqueous NaOCl (active Cl_2 12%) at 75 °C produces a relatively thick black oxide film in which the rate of O_2 evolution is enhanced. The aim of this investigation is to study the influence of heat pretreatment of nickel (in the range 500–900 °C) on its electrochemical behaviour and on the kinetics of the oxygen evolution reaction.

EXPERIMENTAL

Thermogravimetric analysis (TGA)

Samples of nickel powder (Fluka No. 72 220) were heated in air (flow rate 6 l h^{-1}) in the temperature range 25–900 °C (heating rate 2 °C min^{-1}). The

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loss of weight was measured during heating using a Mettler TG 197 thermal balance.

Heat pretreatment of nickel

Nickel plates (AT 200) were treated in a well aerated furnace (Hereaus 15050 EK) at a given temperature for 30 min.

Electrochemical measurements

Cyclic voltammetry curves were obtained in 1 M NaOH using a standard Tacussel equipment.

Nickel (after heat treatment) was used as the working electrode, platinum was used as the counter electrode and $Hg/Hg_2SO_4 \cdot K_2SO_4$(sat.) was used as the reference electrode (the potential of which is 0.656 V relative to the standard hydrogen electrode). *

The temperature of the electrolyte was maintained at 20 °C during measurements and the potential scan rate was varied from 50 to 500 mV s^{-1}.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA)

Figure 1 shows the TGA data for nickel powder obtained in an air atmosphere. The increase in weight observed from 320 to 900 °C is due to the oxidation of nickel to nickel oxide.

$$Ni + O \rightarrow NiO \quad (1)$$

The experimental value of the weight increase (28%) is close to the theoretical value (27.3%) obtained from eq. (1).

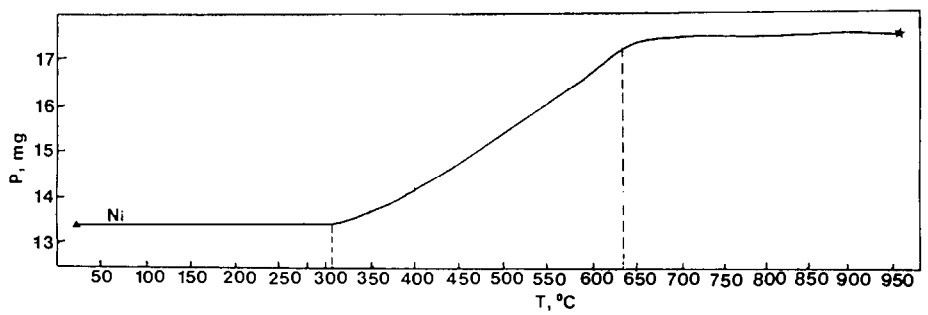

Fig. 1. Thermogravimetry curves of nickel in air. Heating rate, 2 °C min^{-1}.

* All potential values are referred to the standard hydrogen electrode.

Electrochemical measurements

The cyclic voltammogram of nickel "metal" in 1 M NaOH is shown in Fig. 2(I); the peaks a and b correspond to the oxidation of $Ni(OH)_2$ (nickel is known to be covered with a loose $Ni(OH)_2$ layer in NaOH solution) to $Ni \cdot O \cdot OH$ and re-reduction of the latter to $Ni(OH)_2$ according to the equation

$$Ni(OH)_2 \rightleftarrows Ni \cdot O \cdot OH + H^+ + e^- \quad (2)$$

Peak c is due to the reduction of $Ni(OH)_2$ to metallic nickel

$$Ni(OH)_2 \rightarrow Ni + 2e^- + 2OH^- \quad (3)$$

The influence of heat treatment on the cyclic voltammogram is shown in Fig. 2(II–IV). The heights of peaks a, b and c decrease with temperature of heat treatment and they completely disappear after treatment above 700 °C. The reason for the disappearance of peaks a, b and c after heat treatment is due to the formation of a compact layer of oxides which prevents formation of nickel hydroxide.

It was pointed out in ref. 6 that if a carbonyl nickel surface is covered by a thin layer of protective nickel oxide, this layer passivates the transformation of nickel to nickel hydroxide.

Figure 3A shows the steady state current–potential curves obtained for nickel pretreated in air at different temperatures. This figure shows that the

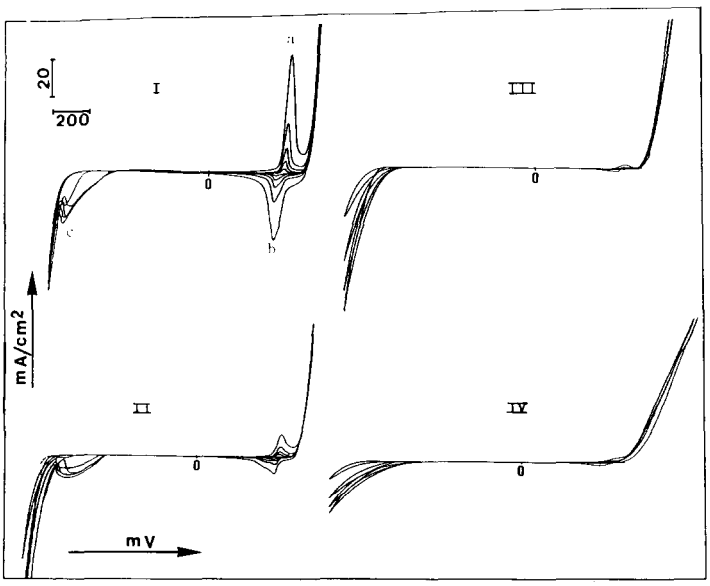

Fig. 2. Cyclic voltammogram of nickel obtained in 1 M NaOH at 20 °C (scan rate, 50–500 mV s^{-1}): I, nickel "metal" without heat pretreatment; II, after pretreatment at 500 °C; III, after pretreatment at 600 °C; IV, after pretreatment at 700 °C.

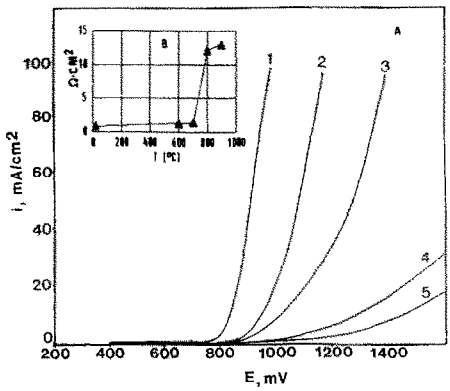

Fig. 3. A. Steady state current–potential curves of nickel obtained in 1 M NaOH at 20 °C: 1, nickel "metal" without heat pretreatment; 2, after pretreatment at 600 °C; 3, after pretreatment at 700 °C; 4, after pretreatment at 800 °C; 5, after pretreatment at 900 °C. B. Reported values of electrode resistance as a function of the temperature of heat pretreatment.

electrode resistance (slope of the linear part of the i–E curve) increases considerably when nickel is pretreated in air above 700 °C, indicating that a non-conducting nickel oxide is formed on nickel when treated above 700 °C. It was reported in ref. 7 that NiO prepared at 1000 °C is a p-type semiconductor.

For nickel pretreatment below 700 °C the electrode resistance (Fig. 3B) is low ($1 \pm 0.2\ \Omega\ cm^2$) but the rate of oxygen evolution at a given potential is considerably decreased (Fig. 3A). For nickel "metal" O_2 evolution occurs on an oxidized surface where the average oxidation state of the Ni ions is 3 + (formation of $Ni \cdot O \cdot OH$) which is very active for O_2 evolution [8]. Heat treatment of nickel below 700 °C covers the surface with a compact layer of a conductive non-stoichiometric nickel oxide [7] which is inactive for oxygen evolution.

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