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Phosphate-bonded composite electrodes for hydrogen evolution

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A new process of cementing metallic powders to produce high surface area cathodes for alkaline water electrolysis is described. The binding compound is a tridimensional polymer of aluminium phosphate ($AlPO_4$). Phosphate-bonded composite electrodes give a low-polarization performance for hydrogen evolution in 1 M KOH aqueous solution in the case of 95 wt % Pt and 98 wt % Ni. When electrode materials are prepared with nickel powder, the electrocatalytic activity for the hydrogen evolution reaction, the chemical stability and the electrical conductivity depend on the Ni content and morphology of the electrode. The best performance and chemical stability with Ni as the starting material are obtained for spiky filamentary particles produced by the decomposition of nickel carbonyl.

1. Introduction

Nickel-based electrodes are among the most active electrocatalysts for cathodic hydrogen production in alkaline solutions. The key to the successful development of a good electrocatalyst is to obtain a large surface area electrode to lower the overpotential associated with the hydrogen evolution reaction (HER). Many processes are reported to prepare such electrodes: plasma-spraying, vacuum deposition or sputtering of nickel [1–3] or nickel compounds such as NiAl (with subsequent leaching of Al) [4–6], NiMo [2], NiSi [2]; electrodeposition of Ni catalysts such as NiMo [5], NiMoCd [5, 7–9], NiS [10], NiZn [5, 6, 11, 12] with subsequent leaching of Zn or Cd (alternatively, the plating scheme can involve the codeposition of elements such as NiAl with Ni [13] with the leaching of Al); sintering a pressed Ni or Ni compound powder [1, 6, 14, 15] at high temperature, i.e. approximately 700° C under a reducing atmosphere. In the latter process, sintering can be preceded by coating the powders with compounds such as methylcellulose [15] or a polysilicate paint [16].

The new process of cementing metallic powders to produce high surface area electrodes, reported here, has the advantage that the cementation is done at low temperatures, i.e. 200 to 300° C and does not need a reducing atmosphere. For the first time, Ni particles of high specific surface area have been shaped into useful electrodes by binding them under pressure with a tridimensional inorganic polymer of aluminium phosphate, $AlPO_4$, a well known catalyst in heterogeneous and homogeneous catalysis, which has been used in important industrial processes such as dehydration, isomerization, cracking polymerization, condensation, alkylation and hydrogenation [17–21]. Although $AlPO_4$ is a non-conductive compound, mixing it with spiky filamentary nickel particles (fractal shape) produces electrodes of good electrical conductivity and chemical stability in alkaline aqueous solutions when the electrode material contains more than 90 wt % Ni, (the remainder being the binding agent).

This paper also deals with cathodic H_2 evolution on such electrodes by the electroreduction of water in 1 M KOH at 25° C.

2. Experimental

2.1. *Preparation*

2.1.1. The binder. An acid aluminium phosphate, combined *in situ* with a source of alumina, was used as the binding agent. This class of compound is prepared by the reaction of alumina with phosphoric acid at a temperature of around 100° C. For the electrodes under study, the aluminium/phosphate ratio can vary from 0.66 to 0.33 with a preferred value of 0.33, corresponding to the monoaluminium phosphate $Al(H_2PO_4)_3$. The advantage of using monoaluminium phosphate is that it can be heated at 150° C without undue intermolecular polymerization and can react further with an alumina source such as $Al(OH)_3$ in the presence of nickel powders to give the binding aluminium phosphate. The formation of the acid aluminium phosphate and its transformation into the tridimensional aluminium phosphate are described by

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the following equations

$$\tfrac{1}{2}\mathrm{Al_2O_3} + 3\,\mathrm{H_3PO_4} \longrightarrow \mathrm{Al(H_2PO_4)_3} + \tfrac{3}{2}\mathrm{H_2O} \quad (1)$$

$$\mathrm{Al(H_2PO_4)_3} + 2\,\mathrm{Al(OH)_3} \longrightarrow 3\,\mathrm{AlPO_4} + 6\,\mathrm{H_2O} \quad (2)$$

The $Al(H_2PO_4)_3$ was synthesised by heating 207.4 g H_3PO_4 85% with 30.6 g of Al_2O_3 (Al_2O_3 is produced by previously heating $Al(OH)_3$ for 24 h at 500° C). The rectangular Teflon cell of $10 \times 5 \times 5\,cm^3$, used as the reactor, was slowly heated at boiling temperature in a water bath while the reaction mass was stirred constantly. An exothermic reaction occurred after about 30 min and the temperature rose to 130° C. After a further 20 min, the temperature dropped to 97° C. The reaction mass was a viscous semitransparent liquid. As this reaction is autocatalytic, the same proportion of reactants and cell surface must be used to promote the exothermic reaction.

The cell containing the reaction mass was subsequently heated in an oven at 150° C for 6 to 24 h. A Teflon cell was used because an intermediate compound in the heating step reacts with glass. The $Al(H_2PO_4)_3$ formed was then crushed in a blender and sifted to obtain particles of less than 38 μm. $Al(H_2PO_4)_3$ is highly hygroscopic and must not come into contact with an atmospheric humidity over 4% during manipulation; if necessary, a glovebox can be used.

2.1.2. The electrodes. A homogeneous mixture of the nickel powder, binder $Al(H_2PO_4)_3$ and $Al(OH)_3$ was prepared using a ball mill. The three compounds were sifted to obtain particles of less than 38 μm diameter. The nickel powder was previously degreased with CH_2Cl_2 in a Soxhlet for 24 h. Anhydrous conditions were maintained throughout the preparation because of the hydroscopic nature of $Al(H_2PO_4)_3$. The shaping was done in a vacuum mould 1.3 cm in diameter under a presure of $7000\,kg\,cm^{-2}$ for 10 min at 25° C. The electrode was then heated for 3 h at 300° C under argon to allow polymerization to the tridimensional $AlPO_4$. The 3 mm thick electrode was coated with an epoxy resin on one face and on the sides to obtain a working disk area of $1.33\,cm^2$. Electrical contact was made by a nickel wire embedded in the electrode during the shaping stage.

The influence of the particle shape of nickel powders on electrode preparation and performance for the HER was studied. A nickel powder with an open filamentary structure and an irregular spiky surface produced by the thermal decomposition of nickel tetracarbonyl [22] was tested. The powder was supplied by Anachemia and by Inco Company (Inco Ni 255). Other Ni powders with different morphologies were considered: spheroidal particles with a mean diameter (m.d.) of 5 μm from Alfa Product, nodular particles (m.d. < 1 μm) from Aldrich, and cauliflower-like particles made by precipitation Ni salt with hydrogen in solution [22] from AESER. Co, Cu and Pt were also used as starting materials.

2.2. *Electrochemical measurements*

The measurements were made in a three-electrode cell with two glass compartments divided by a Nafion membrane separator. The main compartment was held at a constant temperature of 25° or 70° C by circulating thermostated water. A high surface area Raney nickel was used as the counterelectrode; the working electrode, with a geometric surface of $1.33\,cm^2$, was fixed in a vertical position at a distance of 0.5 mm from the Luggin capillary connected to the outside reference electrode of Hg/HgO. The reversible potential for the HER in a 1 M KOH solution w.r.t. Hg/HgO was -927 mV. The solutions of KOH were prepared from Fisher-certified ACS reagent grade with MilliQ water (16 MΩ resistivity). Before each

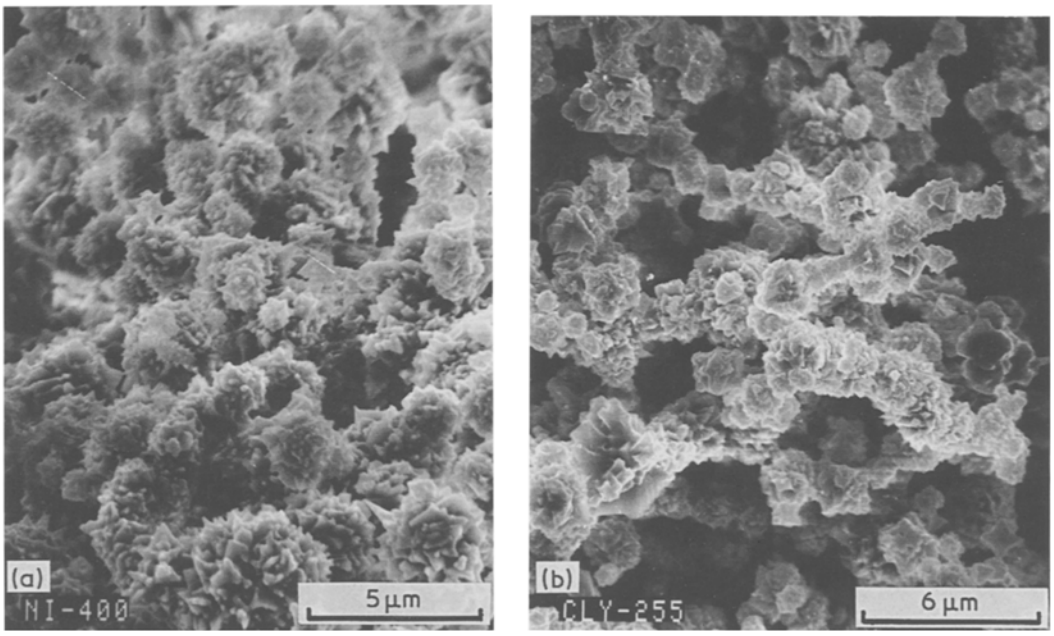

Fig. 1. Spiky filmentary nickel particles produced by decomposition of nickel carbonyl, supplied by (a) Anachemia (b) Inco Company, (length: 38 μm).

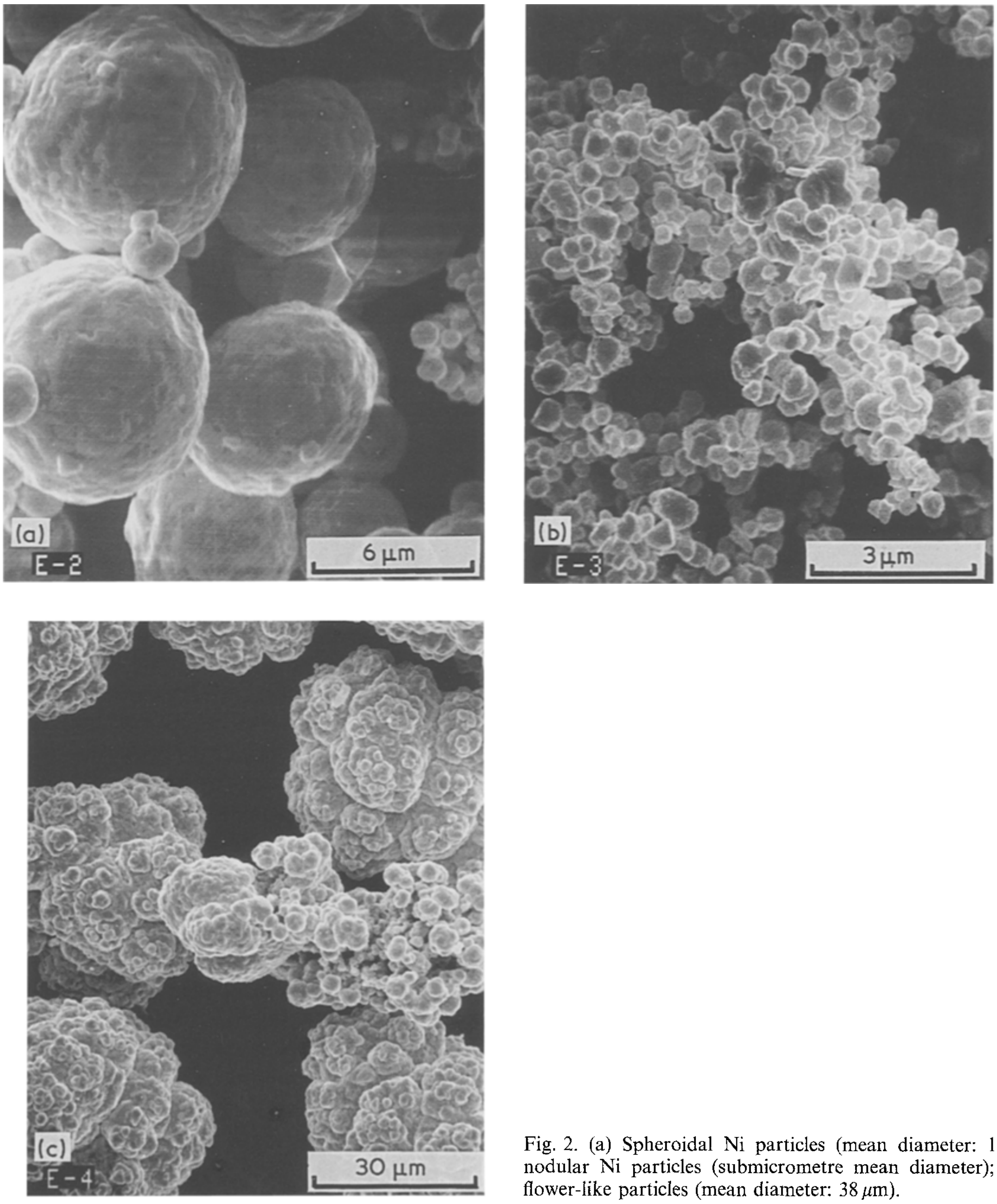

Fig. 2. (a) Spheroidal Ni particles (mean diameter: 10 μm); (b) nodular Ni particles (submicrometre mean diameter); (c) cauliflower-like particles (mean diameter: 38 μm).

experiment, the oxygen was removed by nitrogen bubbling.

Experimental polarization curves were obtained by galvanostatically reducing the applied current from 300 mA cm^{-2} at which c.d. it was kept for 0.5 h to activate the surface) to 0.01 mA cm^{-2}. The current was applied by a galvanostat–potentiostat PAR model 273 controlled by a Commodore PC2 microcomputer. The potential values were corrected for the ohmic drop by a linear regression method [23].

3. Results

3.1. *Mechanical strength and chemical stability of the electrodes*

Scanning electron micrographs (SEM) of the different powders used in the electrode preparation are presented in Figs 1 and 2. The nickel powder particles produced by the carbonyl decomposition (Fig. 1) have a length/width ratio (38 μm to 3 μm) of approximately 13 and a spiky filamentary shape. Powders from two different supplies were tested. The other nickel particles have a roughly spherical shape (Fig. 2) and differ in size: the spheroidal particles (Fig. 2a) present a relatively smooth surface with a mean diameter of 10 μm; the nodular particles (Fig. 2b) have a rounded shape and a submicrometre mean diameter; and the cauliflower-like particles produced by reducing an aqueous solution of a nickel salt by hydrogen (Fig. 2c) also have a rounded shape but a rough surface and a mean diameter of about 38 μm. The mechanical strength and chemical stability of electrodes in alkaline media are strongly related to the shape of the nickel particles. Electrodes of Ni–AlPO$_4$ made with spiky filamentary nickel particles, i.e. Inco 255 and Anachemia powders, require as little as 2% by weight binder material for good mechanical strength, but a higher percentage is

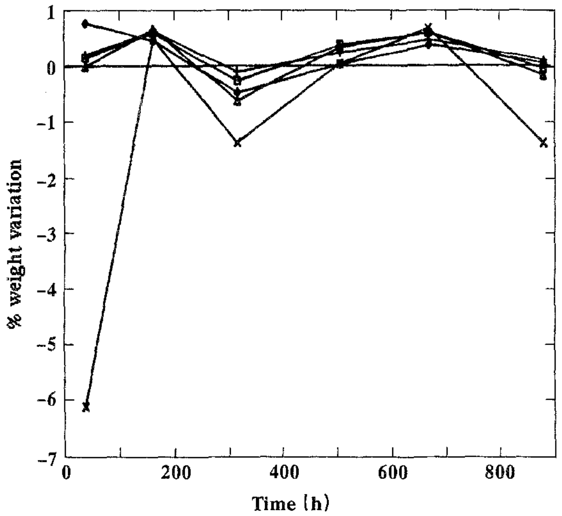

Fig. 3. Chemical stability test of spiky filamentary shape Ni powder electrodes in 30 wt % NaOH at 70° C of (□) 98 wt % (+) 97 wt %, (◇) 96 wt %, (△) 95 wt %, (x) 90 wt % Ni content.

needed with spherical powders to attain the equivalent mechanical strength (Fig. 2a, b, c).

Electrodes made with all four types of nickel particles and having a ranging content from 80 to 98 wt % were tested to determine the chemical stability by the weight loss method in 30 wt % NaOH solution at 70° C at open-circuit potential. Those with spheroidal, nodular and cauliflower-like particles were destroyed in 30 wt % NaOH at 70° C after a few minutes, but the spiky filamentary powder electrodes showed good stability in this highly aggressive medium as the Ni content increased from 80 to 98 wt %. Figure 3 shows the percentage weight loss of 90 to 98 wt % Ni electrodes after 900 h immersion in 30 wt % NaOH at 70° C. Electrodes with a content of 95 to 98 wt % showed a percentage weight variation of less than 1% after 900 h while an electrode of 90 wt % Ni lost 6% in weight in the first 30 h of immersion, indicating an attack by the alkali. The observed weight increase is probably due to the formation of oxides, whereas the increased chemical stability with the lower $AlPO_4$ content, in the range 10 to 2 wt %, is explained by the poor stability of the polymer in contact with alkaline solutions.

Following optimization of the chemical stability and mechanical strength of the Ni-$AlPO_4$ electrodes, these new electrocatalysts were tested for hydrogen production by the reduction of water in 1 M KOH at 25° and 70° C.

3.2. *Morphology of Ni electrodes studies by SEM*

Scanning electron micrographs of spiky filamentary nickel particle electrodes with 98 wt % Ni are presented in Figs 4 and 5. The micrographs show that the two electrodes, when compared and the powder used in their formulations (Fig. 1a and b) have essentially the same morphology, i.e. deep pores and a spiky filamentary particle shape, resulting in a very rough surface. It can be seen that the new process to cement metallic powders does not radically change the morphology of the initial particles and that the low pressure needed to mould the electrode does not compact the powders excessively. The real surface area determined by BET analysis is 1 $m^2 g^{-1}$, i.e. a working surface of 10 000 cm^2 per centimeter of geometric surface.

3.3. *Electrochemical results*

The kinetic parameters for the HER on electrodes containing 80 to 98 wt % spiky filamentary nickel particles were measured in 1 M KOH at 25° C. A typical Tafel plot obtained for a 98 wt % Ni electrode is shown in Fig. 6. The values of the Tafel slope and the exchange current density were 84 mV $decade^{-1}$ and 10.5 mA cm^{-2}, respectively. An overpotential of 116 mV was obtained for a current density of 250 mA cm^{-2}. The polarization curve was corrected

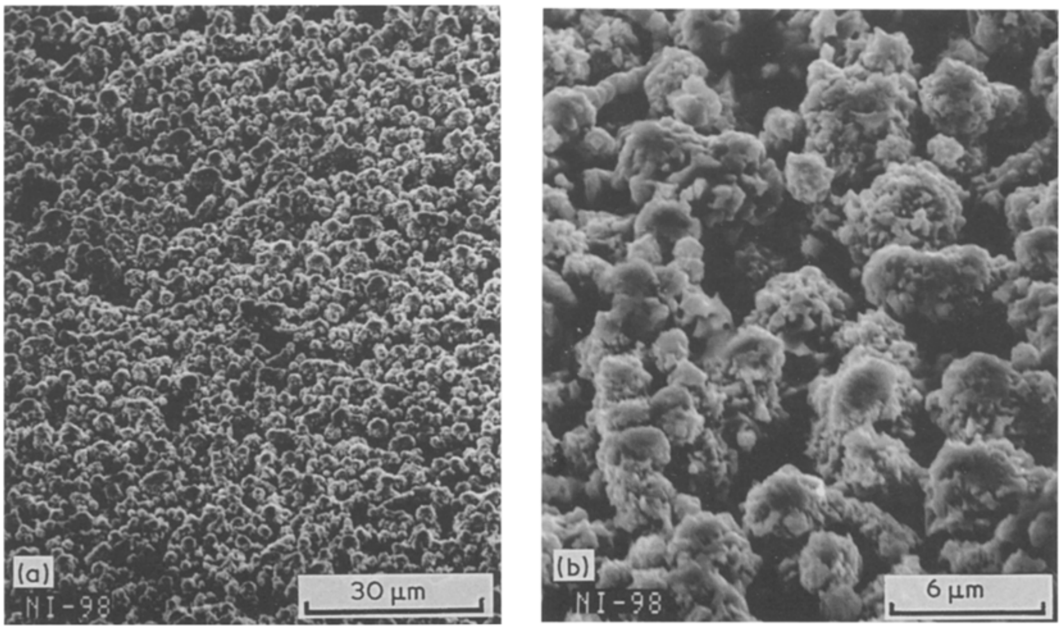

Fig. 4. Electrode at 98 wt % Ni prepared with spiky filamentary nickel particles supplied by Anachemia.

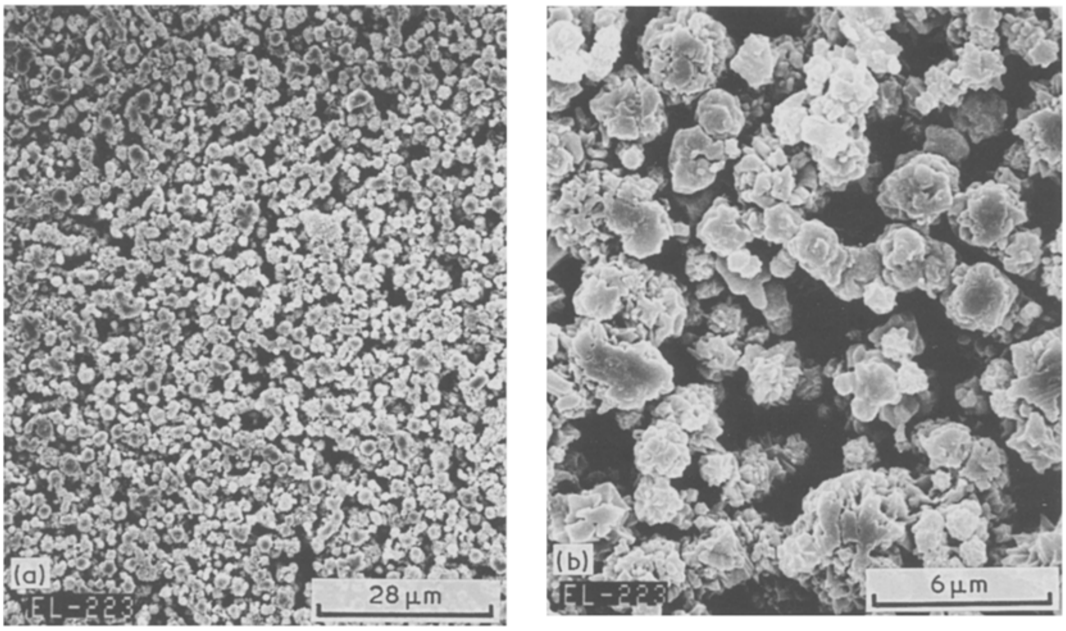

Fig. 5. Electrode of 98 wt % Ni prepared with the spiky filamentary nickel particles supplied by Inco Company.

for the ohmic drop by a linear regression program [23]. Table 1 shows the variation in the kinetic parameters for several electrodes made with two different supplies of Ni spiky filamentary particles (Inco Company and Anachemia) together with their chemical and physical properties. Electrodes with 98 wt % Ni showed the lowest hydrogen overvoltage ~ 122 mV at 250 mA cm^{-2}; a decrease in the content of Ni to 90 to 70 wt % was detrimental to both electrocatalytic activity of the HER and the chemical stability and electrical resistivity. A significant improvement of the 98 wt % Ni electrodes towards hydrogen evolution was observed as the temperature was increased from 25° to 70° C, i.e. the hydrogen overvoltage at 250 mA cm^{-2} decreased from ~ 122 mV at 25° C to ~ 60 mV at 70° C.

Experiments were conducted in an attempt to increase the porosity and the working surface of the cathodes by introducing a leachable compound such as 2 wt % aluminium powder (Table 1, example 5) or 1 wt % sodium chloride salt (example 6) into the electrode materials. The Ni–Al electrode was leached in 30 wt % NaOH at 70° C for 4 h and the Ni–NaCl electrode in hot water for 4 h. As seen in Table 1, these electrodes are less active than the Ni 98 wt % and the Ni 90 wt % electrodes. Cu, Co and Pt powders were also used as starting material. The particle diameter is typically 30 μm in the case of Cu (Fig. 7a); 2.5 μm in the case of Co (Fig. 7b) and 0.4 μm in the case of Pt (Fig. 7c). Amongst these materials, the best performance for the HER was observed for platinum cathodes (Table 1), the hydrogen overpotential at 250 mA cm^{-2} being only 27 mV.

A constant cathodic current of 100 mA cm^{-2} was applied to 98 wt % Ni electrodes for several hours. The curve of the hydrogen overpotential is plotted

Table 1. Chemical, physical and electrocatalytical properties of phosphate bonded composite electrodes

Metallic composition (wt %)	*Chemical stability to alkaline media*	*Electrical resistivity (Ω cm)*	*Kinetic parameters for HER** *Temperature (° C)*	*Tafel slope (mV decade⁻¹)*	*Exchange current density (mA cm⁻²)*	*Overpotential at 250 mA cm⁻² (mV)*
Ni 98	good	8.9×10^{-5}	25	74–86	6.5–11.0	116–128
			70	36–41	5.8–8.9	60
Ni 90	good	2.4×10^{-4}	25	81	0.4	229
Ni 80	poor	1.5×10^{-4}	25	75	0.2	238
Ni 70	poor	2.4×10^{-4}	25	–	–	–
Ni 95 Al 2	good	–	25	99	3.7	180
Ni 96 NaCl 1	good	–	25	112	3.8	203
Co 98	good	2.5×10^{-3}	25	186	1.8	400
Cu 98	good	–	25	155	0.4	431
Pt 95	good	–	25	40	52.7	27

* The performances for hydrogen evolution have been tested in 1 M KOH.

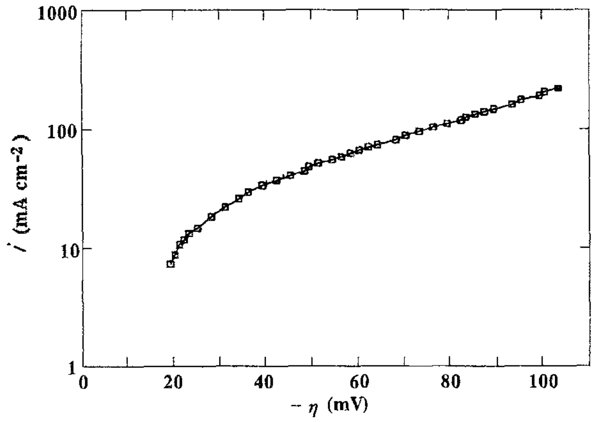

Fig. 6. Polarization curve for HER of 98 wt % Ni electrode in 1 M KOH at 25°C.

against time in Fig. 8 for the case of 1 M and 30 w/o KOH aqueous solution at 70°C. A long-time degradation of performance is manifested as an increase in η of ~ 50 mV during the first 20 h of polarization, the potential variation with time being negligible after 20 h of polarization.

4. Discussion

The three generally accepted reaction steps for hydrogen evolution in alkaline solution are

$$H_2O + M + e = M - H + OH^- \quad \text{(VOLMER)} \quad (3)$$

$$M - H + H_2O + e = M + H_2 + OH^- \quad \text{(HEYROVSKY)} \quad (4)$$

$$2M - H = H_2 + 2M \quad \text{(TAFEL)} \quad (5)$$

It is generally agreed [24–27] that the Volmer–Tafel mechanism applies to nickel cathodes in alkaline solution. The slope of Tafel plots of 120 mV decade^{-1} obtained at high overpotentials is attributed to a slow discharge step mechanism at 25°C [24, 26, 27].

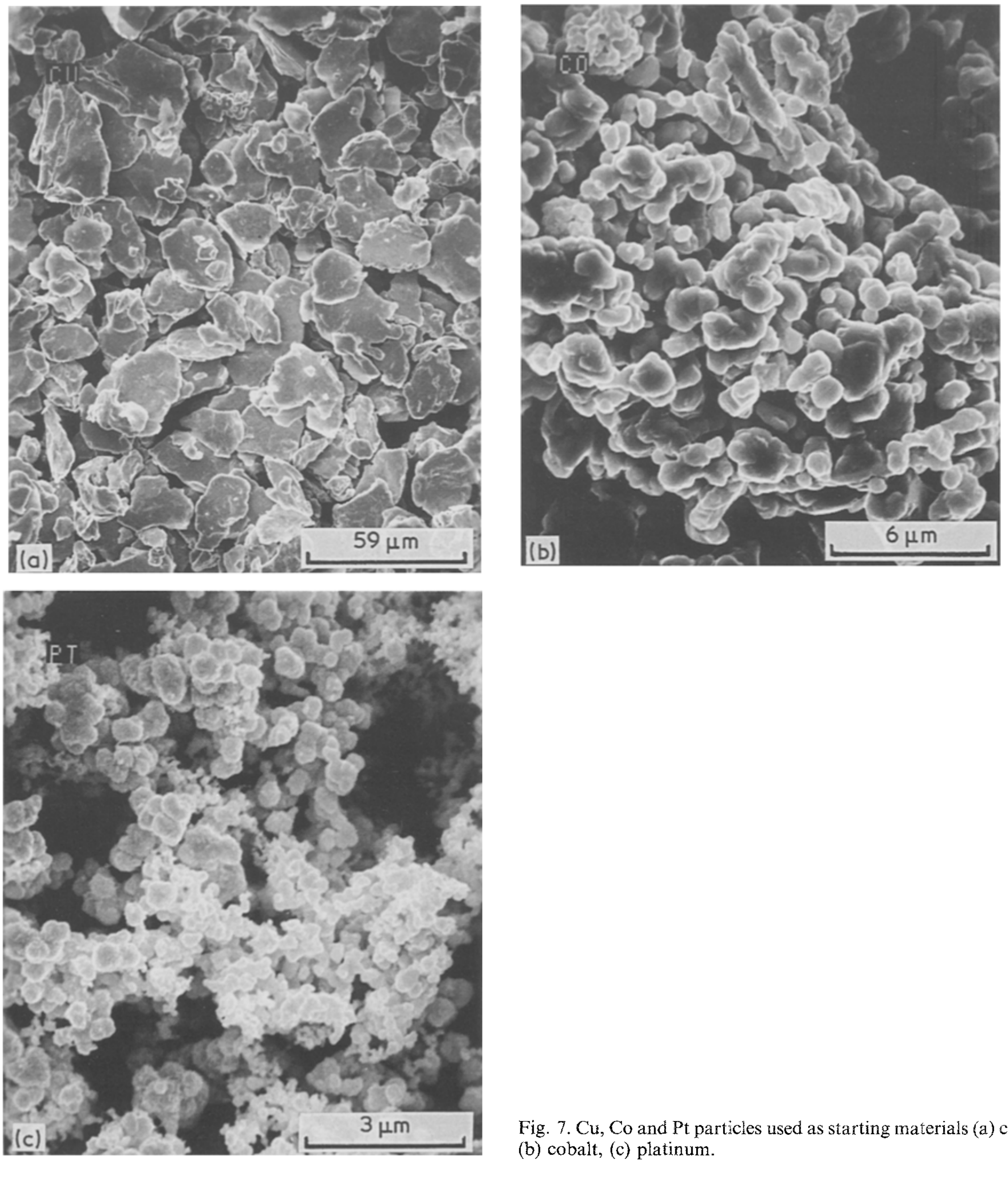

Fig. 7. Cu, Co and Pt particles used as starting materials (a) copper, (b) cobalt, (c) platinum.

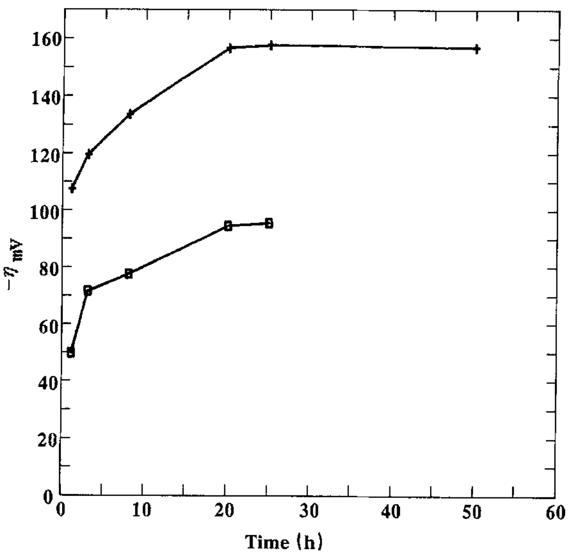

Fig. 8. 98 wt % Ni cathode behaviour as a function of time under galvanostatic control at 100 mA cm^{-2} (70° C) (□) 1 M MOH (+) 30 wt % KOH. η is IR corrected.

Low b values occur in the HER when some step other than the primary discharge step (Equation 3) is rate-controlling in the overall process of H_2 evolution [28], a condition that arises with some transition metals where relatively strong hydrogen chemisorption occurs.

Two aspects are involved to obtain high-performance materials for the discharge of hydrogen from highly alkaline media: 1. Selection of materials with high i_0 and low b; 2. increase in the surface area.

Generally, in hot concentrated alkali, electrodes of nickel alloys and intermetallic nickel compounds such as NiAl, NiZn, NiMoCd, NiMo, NiSi, NiS [5–8, 10–13] present an enhanced catalytic activity for hydrogen discharge because of their extended surface and different reaction pathway, which result in low Tafel slopes. Some of these electrodes have an overpotential of 60 to 70 mV at 200 mA cm^{-2} [5, 13]. Electrodes made from pure Ni powders have less effect on lowering the hydrogen overvoltage [1–4, 14, 16], partly because of their high Tafel slopes.

The composite Ni($AlPO_4$) cathodes have low hydrogen overvoltages in 1 M KOH solution at 25° and 70° C. The new in-house process produces Ni electrodes with a high surface area, as shown by the apparent exchange-current densities (5.8 to 8.9 mA cm^{-2}). A current density of 250 mA cm^{-2} is attained with an overpotential of only 60 mV in 1 M KOH at 70° C before deactivation. This is a very satisfactory performance, comparable to those observed by Hall [1] on plasma-sprayed Ni 123 and Brossard [29] on Electrolyser Inc. catalysts. The good performance of the composite Ni($AlPO_4$) electrodes are tentatively attributed to their high surface area. The mechanism of the HER on 98 wt % Ni cathodes is under investigation by the open-circuit potential decay method to clarify this matter [30].

5. Conclusions

The principtal advantage of the newly developed process to cement metallic powders to produce high surface area electrodes for alkaline water electrolysis is the low temperature cementation of the metallic particles. In the case of 95 wt % Pt and 98 wt % Ni, phosphate-bonded composite electrodes give low polarization overpotentials for the hydrogen evolution reaction in 1 M KOH aqueous solution. In the case of electrode materials prepared with nickel powder, the electrocatalytic activity for the HER, the chemical stability and the electrical conductivity depend on the Ni content and morphology of the particles. The 98 wt % Ni electrodes show a loss of efficiency for the hydrogen evolution which takes the form of increases in the cathodic overpotential at constant current density of 100 mA cm^{-2}.

Acknowledgments

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