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The preparation of high surface area nickel oxide electrodes for synthesis

K. MANANDHAR, D. PLETCHER

Department of Chemistry, The University, Southampton, UK

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A study of the electrodeposition of nickel onto copper and graphite is described; the objective was to prepare high surface area, i.e. microrough, but stable deposits which could be used as nickel oxide anodes in aqueous base. It is shown that such electrodes may be prepared by electrodeposition at a high current density (200 mA cm^{-2}) from a Watts bath and that they give useful apparent current densities for a model synthetic reaction, the oxidation of ethanol to acetic acid.

1. Introduction

Some earlier papers have described a number of interesting synthetic reactions employing nickel oxide anodes in aqueous base [1–5]. These reactions are generally dehydrogenations, e.g. primary amines to nitriles, primary alcohols to aldehydes or carboxylic acids and secondary alcohols to ketones. It has been shown [1, 2] that these reactions take place via a mechanism such as

$$Ni(OH)_2 - e \rightarrow NiO(OH) + H^+$$

$$NiO(OH) + CH_3CH_2OH \rightarrow Ni(OH)_2 + CH_3\dot{C}HOH$$

$$CH_3\dot{C}HOH \xrightarrow[\text{oxidation}]{\text{further}} \text{products}$$

The oxidation of the nickel (II) hydroxide surface layer to a higher valency surface oxide has been widely studied [1, 6–12]. It is, however, the nature of the chemical reaction between the oxide and the organic molecule, i.e. hydrogen abstraction, which determines that the products are totally different from those at an anode where the initial reaction is electron transfer from the organic substrate. In practice these oxidations have the disadvantage that they can only be carried out at very low current densities, typically < 1% of the calculated diffusion-controlled current.

Hence, in order to make these reactions practically feasible we have sought to prepare high surface area nickel oxide electrodes where greatly increased apparent current densities may be obtained. In this paper we report some studies of the electrodeposition of nickel onto copper and graphite where the objective has been to form microrough but stable deposits; the nickel oxide electrodes were then prepared by immersion and polarization in aqueous potassium hydroxide.

2. Experimental

All electrochemical experiments were carried out with a Hi-Tek Potentiostat DT2101 and Pulse Generator PPR1 and *I–E* curves were recorded on a Hewlett Packard recorder 7015A.

The electrodepositions were performed at constant current in a two electrode cell. The working electrodes were copper or graphite discs surrounded by PTFE sheaths and these were introduced onto the side of the glass cell so that the face of the disc was vertical and any gas evolved left the electrode surface. The second electrode was a Pt gauze placed parallel to the working electrode. Before deposition, the discs (area 0·2 cm^2) were cleaned with fine emery paper and polished on a cloth with 1 μm and 0·05 μm alumina (Banner Scientific). The Watts bath contained, except where otherwise stated, 300 g l^{-1} nickel sulphate (GPR grade), 35 g l^{-1} nickel chloride (AR grade) and 40 g l^{-1} boric acid (AR grade) and the pH was adjusted with either sulphuric acid or ammonia.

All other electrochemical experiments were carried out in 1 M potassium hydroxide in a three

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electrode–two compartment cell. The working electrode prepared above was mounted so that it could be rotated and the counter electrode was a Pt coil in the base of the working electrode compartment. The reference electrode was mercury/mercuric oxide in 1 M KOH and was in a second compartment separated from the working electrode by a Luggin capillary and tap.

The current efficiency for the nickel depositions was estimated by dissolving the nickel in 10:1 HNO_3 : HCl and determining the nickel by atomic absorption spectroscopy (Varian model 1100).

The nickel deposits were also examined using a Cambridge S-150 Stereoscanning Microscope and a JEOL JXA-50A Electron Probe Microanalyser.

3. Results and discussion

The electrodeposition of nickel onto copper has, of course, been widely studied [13], and for this reason the experiments carried out in this investigation were limited to conditions likely to lead to high surface area deposits. Each of the electrodes thus prepared were subjected to the following set of experiments:

(a) Cyclic voltammograms were run at a series of potential scan rates with the electrodes in 1 M KOH.

(b) *I–E* curves were recorded at several rotation rates of the deposited nickel disc electrode in a solution of ferricyanide (10^{-2} M) in 1 M KOH.

(c) A steady state *I–E* curve was recorded for a solution of ethanol (10^{-2} M) in 1 M KOH. The electrode was stationary in this experiment.

(d) The current efficiency for the electroplating of the nickel was determined by dissolving the deposit in acid and determining the total nickel by atomic absorption spectroscopy.

(e) The morphology of selected deposits was investigated by electron microscopy and the surfaces were analysed with an electron probe microanalyser.

The results from such experiments are well illustrated by the data obtained with an electrode prepared at 293 K by deposition of nickel onto copper from a standard Watts bath, pH 3·5, at a current density of 200 mA cm^{-2} for 50 s (total charge 10 C cm^{-2}).

The cyclic voltammograms in 1 M KOH, run between 0·0 V and + 0·7 V are shown in Fig. 1. Well-formed peaks are observed for the oxidation of the nickel hydroxide layer to a higher valency oxide at $E_p \simeq 0{\cdot}47$ V and for the reverse process at $E_p = +\,0{\cdot}38$ V; oxygen evolution commences at + 0·7 V. The peak currents are proportional to the square root of the potential scan rate. This relationship was also found [8] for other nickel electrodes prepared by electroplating at a much lower current density (1 mA cm^{-2}) although at polished nickel electrodes the peak currents for these reactions are proportional to the potential scan rate. The cyclic voltammograms for our electroplated nickel electrodes also differed from those obtained with polished nickel [1, 6, 10, 11] in two other respects. Firstly, the peak current densities and hence the charges associated with the oxidation and the reduction are much higher. Secondly, the ratio of charges Q_{ox}/Q_{red} is larger than one and increases with increasing potential

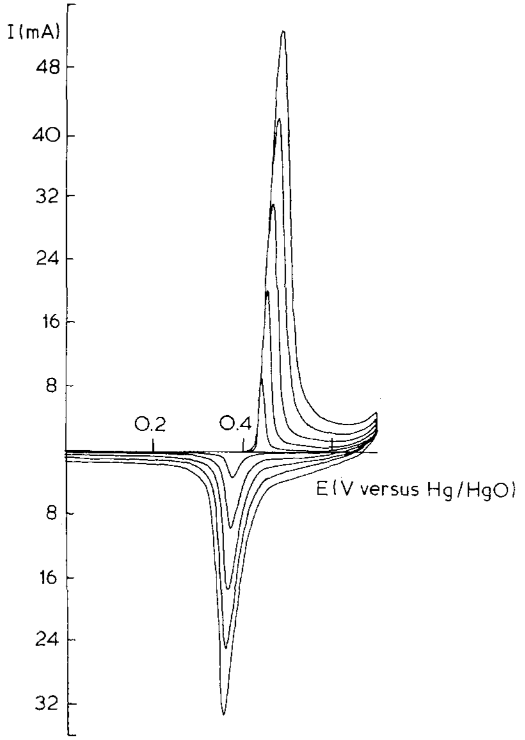

Fig. 1. Cyclic voltammograms for Ni on Cu electrode in 1 M KOH run between 0·0 V and 0·7 V versus Hg/HgO electrode. Potential sweep rates 0·01, 0·04, 0·09, 0·16 and 0·25 V s^{-1}. Ni deposited onto Cu (0·2 cm^2) at 200 mA cm^{-2} from a Watts bath pH 3·5, chloride 0·3 M. Deposition charge 10 C cm^{-2}.

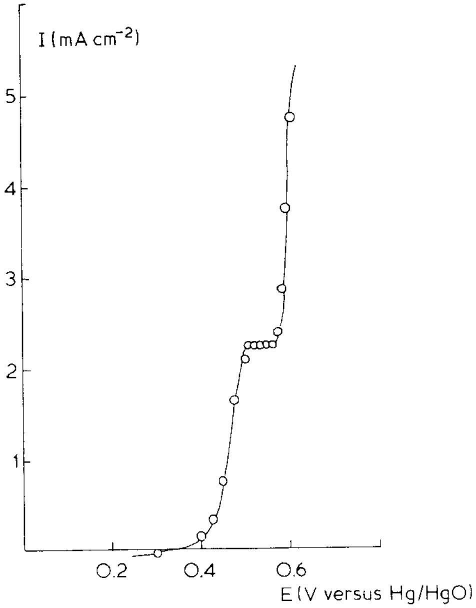

Fig. 2. Steady state *I–E* curve for ethanol (10^{-2} M) in 1 M KOH. Electrode as in Fig. 1.

scan rate; with polished nickel the ratio is always one. Since the cyclic voltammograms may be recorded repetitively without changes, $Q_{ox}/Q_{red} > 1$ probably indicates that the nickel (III) oxide can react to some extent with water or hydroxide ion.

The reduction of ferricyanide gives a simple *I–E* curve and at both a polished nickel electrode and an electrodeposited nickel electrode, the limiting current density is the same and is proportional to the square root of the rotation rate of the disc electrodes. Hence the reaction is mass transfer controlled. The *I–E* curves for the oxidation of ethanol also show well-formed waves, $E_{1/2} = +\ 0{\cdot}46$ V (see Fig. 2) but in this case the limiting current density using the electrodeposited nickel electrode (2·25 mA cm^{-2}) is much larger than that obtained with a polished nickel anode (0·17 mA cm^{-2}). Finally the dissolution into acid of the nickel from the copper disc and the determination of the nickel (II) in the solution showed the current efficiency for nickel deposition to be very low, 4·3%. The electrode thus prepared is stable to handling and prolonged electrolysis although the nickel deposit is readily removed with emery paper.

The results of several series of such experiments designed to elucidate the effects of the various parameters in the electrodeposition on the properties and performances of the nickel electrodes are summarized in Table 1. The following trends may be noted.

3.1. *Current density*

There are apparently two types of nickel deposit. With the electrodes prepared at the lower current densities, the charges associated with the charging and discharging of the nickel oxide layers are relatively low (see $Q_{\mathrm{NiOOH}\rightarrow\mathrm{Ni(OH)}_2}$) and the current efficiency for the deposition of nickel is high. At the highest two current densities, the charges for the oxide charging are much higher and the current efficiency for nickel deposition is very low owing to co-hydrogen evolution and leading to thinner nickel deposits. The increased charges for the charging and discharging of the oxide layer may be due to an increase in real surface area or to oxidation to a greater depth. Both factors may be important since although the limiting current for ethanol oxidation increases with $Q_{\mathrm{NiOOH}\rightarrow\mathrm{Ni(OH)}_2}$, the relationship between these quantities is not simple. Furthermore in the cyclic voltammogram for these two electrodes in 1 M KOH, the peak currents for the charge and discharge processes are proportional to the square root of potential scan rate. This would not be the case for a surface oxidation and reduction and probably indicates control of the current by a diffusion process within the oxide layer [8]. At all current densities and, indeed, for all electrodes prepared during this study, the limiting current for ferricyanide reduction is almost the same; this is to be expected for a mass transfer-controlled process provided the roughness of the surface is small compared with the diffusion layer thickness. There is no advantage in using a deposition current larger than 200 mA cm^{-2}.

3.2. *Charge for deposition of nickel*

For this series of electrodes all prepared at 200 mA cm^{-2}, the results were similar; for the lowest deposition charge, however, the charge $Q_{\mathrm{NiOOH}\rightarrow\mathrm{Ni(OH)}_2}$ and the limiting current for alcohol oxidation were slightly lower. The current efficiency for nickel deposition decreases with increasing deposition time. The electrode prepared

Table 1. Data taken from nickel electrodes prepared by electrodeposition onto copper under various conditions

Parameter varied	$Q_{NiOOH\rightarrow Ni(OH)_2}$[*] (mC cm^{-2})	I_L[†] *for* *10^{-2} M $Fe(CN)_6^{3-}$* (mA cm^{-2})	I_L[‡] *for* *10^{-2} M C_2H_5OH* (mA cm^{-2})	*Current efficiency*[§] *for Ni deposition* (%)
polished Ni	0·26	2·5	0·17	–
(a) *Current density, I, (mA cm^{-2}) varied, Q_{Ni} = 10 C cm^{-2}, pH 3·5, [Cl$^-$] = 0·3 M, T = 293 K*				
I = 100[‖]	1·8	3·0	0·56	99
I = 125[‖]	1·3	2·9	0·76	97
I = 150[‖]	1·2	3·1	1·01	85
I = 175	34	2·9	1·58	5·6
I = 200	38	2·7	2·25	4·3
I = 300	32	2·9	0·86	8·2
(b) *Deposition charge, Q_{Ni}(C cm^{-2}) varied, I = 200 mA cm^{-2}, pH = 3·5, [Cl$^-$] = 0·3 M, T = 293 K*				
Q_{Ni} = 1·0	8·7	2·8	1·42	13·2
Q_{Ni} = 3·0	32	2·6	2·30	6·9
Q_{Ni} = 10	38	2·6	2·29	4·3
Q_{Ni} = 50	40	2·5	2·24	1·3
(c) *pH varied, I = 200 mA cm^{-2}, Q_{Ni} = 10 C cm^{-2}, [Cl$^-$] = 0·3 M, T = 293 K*				
pH = 1·0	1·0	3·2	0·29	49
pH = 2·0	37	2·6	1·63	8·2
pH = 3·5	34	2·7	2·29	4·3
pH = 5·0	24	2·5	1·45	1·6
pH = 6·0	23	2·5	0·92	18
(d) *Chloride concentration varied, I = 200 mA cm^{-2}, Q_{Ni} = 10 C cm^{-2}, pH = 3·5, T = 293 K*				
[Cl$^-$] = 0	35	–	1·58	1·6
[Cl$^-$] = 0·03	34	–	1·58	2·5
[Cl$^-$] = 0·3	38	–	2·29	4·3
[Cl$^-$] = 1·5[‖]	1·8	–	0·47	95
[Cl$^-$] = 2·6[‖]	1·7	–	0·59	99
(e) *Temperature (K) varied, I = 200 mA cm^{-2}, Q_{Ni} = 10 C cm^{-2}, pH = 3·5, [Cl$^-$] = 0·3 M*				
T = 278	92	–	2·90	4·4
T = 293	38	–	2·30	4·3
T = 313[‖]	2·4	–	0·44	92
T = 333[‖]	2·8	–	0·38	96

[*] Charge associated with surface reduction peak on reverse sweep of cyclic voltammograms in 1 M KOH, $\nu = 0·1$ V s^{-1}.
[†] Limiting current density for reduction of ferricyanide (10^{-2} M) at a rotation rate ω = 400 rev min^{-1}.
[‡] Limiting current density for ethanol oxidation. Stationary electrode [C_2H_5OH] = 10^{-2} M.
[§] Current efficiency for nickel deposition calculated from AA analysis.
[‖] In 1 M KOH the oxidation and reduction peak currents, $I_p \propto \nu$. All other electrodes $I_p \propto \nu^{1/2}$.

with 10 C cm^{-2} was of higher stability than the others and this charge was therefore used in all other experiments.

3.3. *pH*

The most active electrode for ethanol oxidation was obtained at a pH of 3·5 and the best correlation is again between the limiting current for ethanol oxidation and the current efficiency for nickel deposition. This suggests that hydrogen evolution has a role in creating the high surface area electrodes. It should be noted, however, that there is no simple relationship between the pH of the deposition bath and efficiency for nickel deposition.

3.4. *Chloride ion concentration*

High concentrations of chloride ion clearly cause a levelling of the deposit even at this high current density. Some chloride ion in the bath does, however, lead to more active nickel electrodes.

3.5. *Temperature*

A low temperature leads to roughening of the nickel surface but at 5° C the deposit is uneven and not as stable as that at 20° C. At 40° C and above, the deposition process is efficient and the electrode gives only low current densities for ethanol oxidation.

Hence it is clear that electrodes with good activity for ethanol oxidation are formed under conditions where the current efficiency for nickel deposition is poor and hence there is copious hydrogen evolution. There is also some correlation between the charge for the oxidation and reduction of the oxide surface and the limiting current for ethanol oxidation. The optimum conditions were a Watts bath, pH 3·5 containing 35·5 g l^{-1} of nickel chloride, a temperature of 20° C and a current density of 200 mA cm^{-2}.

The oxidation of ethanol was investigated further at an electrode prepared under these conditions. The limiting current was proportional to ethanol concentration (10^{-3}–10^{-1} M) and showed a marked dependence on rotation rate when the electrode was rotated. A plot of I_L versus $\omega^{1/2}$ was, however, non-linear showing the ethanol oxidation to be partially mass transfer controlled. The limiting current was measured at such an electrode for a period of three hours and there was no loss in performance of the electrode.

The nickel deposits were examined by electron microscopy. Typical photographs are shown in Fig. 3 for deposition current densities of 100 and 200 mA cm^{-2}; at the same magnification, the polished nickel surface is featureless. The nickel deposit prepared at high current density exhibits a highly cracked, 'jigsaw' appearance as if the surface layer had contracted at some stage during its preparation. One possibility is that hydrogen atoms enter the lattice at the extreme conditions used for the deposition [14] (note low current efficiency for nickel) and when the electrode is returned to the open circuit potential the hydrogen is lost with a contraction of the nickel lattice. The electron probe microanalyser showed the surface to be free of chlorine but to contain a trace of sulphur and considerable oxygen although this may result from aerial oxidation.

An electrode prepared at 200 mA cm^{-2} was also used for a preparative scale oxidation of benzyl alcohol. A 5 cm x 3½ cm copper sheet encased in PTFE was covered with nickel (10 C cm^{-2}) and used for an electrolysis of 1·5 g of benzyl alcohol in 1 M KOH (150 cm^3). The electrolysis proceeded at a reasonable rate, initial current 300 mA, and led to benzaldehyde (2%) and benzoic acid (98%) as products.

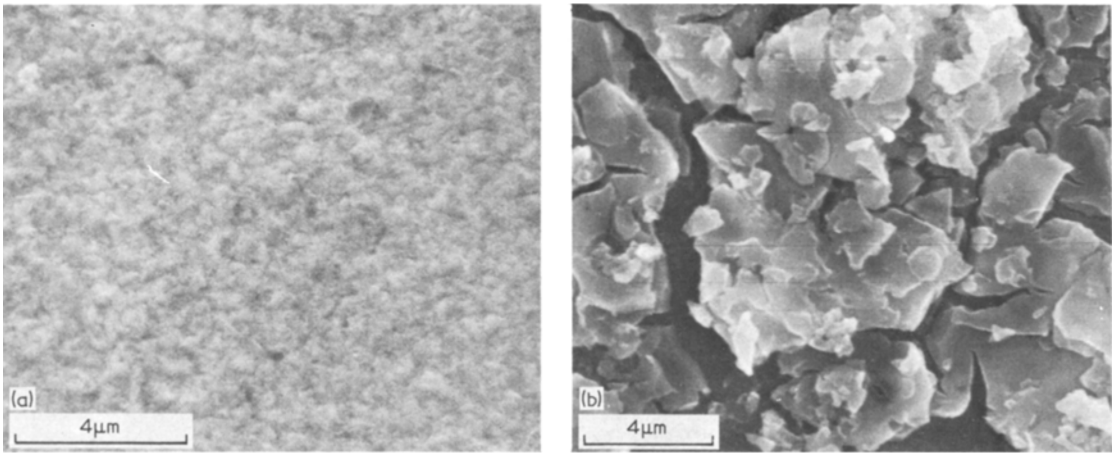

Fig. 3. Electron micrographs of Ni deposits on Cu. Deposition from a Watts bath, pH 3·5 containing chloride (0·3 M). Deposition charge 10 C cm^{-2}. Current density: (a) 100 mA cm^{-2}, (b) 200 mA cm^{-2}.

Table 2. Data taken from nickel electrodes prepared by electrodeposition onto graphite under various conditions (symbols as for Table 1)

Parameter varied	$Q_{NiOOH \rightarrow Ni(OH)_2}$ (mC cm^{-2})	I_L *for* 10^{-2} *M* $Fe(CN)_6^{3-}$ (mA cm^{-2})	I_L *for* 10^{-2} *M* C_2H_5OH (mA cm^{-2})	*Current efficiency for Ni deposition* (%)
polished Ni	0·26	2·5	0·17	–
(a) *Current density, I,* (*mA cm*$^{-2}$) *varied,* $Q_{Ni} = 25$ *C cm*$^{-2}$*,* $pH = 3{\cdot}5$*,* $[Cl^-] = 0{\cdot}3$ *M,* $T = 293$ *K*				
I = 100	3·3	2·9	0·97	90
I = 200	37·1	2·8	1·81	74
(b) *pH varied,* $I = 200$ *mA cm*$^{-2}$*,* $Q_{Ni} = 25$ *C cm*$^{-2}$*,* $[Cl^-] = 0{\cdot}3$ *M,* $T = 293$ *K*				
pH = 1·0	2·3	3·4	0·63	48
pH = 3·5	37·1	2·8	1·81	74
pH = 5·0	94·6	2·1	2·52	7

Some electrodes were also prepared by deposition of nickel onto graphite and these electrodes were used in the series of experiments (a)–(e) in Section 3. A typical set of results are summarized in Table 2. While the stability of these electrodes was always very good (aggressive use of emery paper is necessary to remove the deposit) and it can be seen that electrodes of high activity for ethanol oxidation can be prepared, there is a problem of reproducibility. Electrodes prepared under nominally the same conditions gave different results probably because of problems in preparing the graphite surface before deposition. There is not the same correlation between current efficiency for nickel deposition and the limiting current for ethanol oxidation. Fig. 4 shows an electron micrograph of the nickel deposit on graphite and this confirms that the form of the

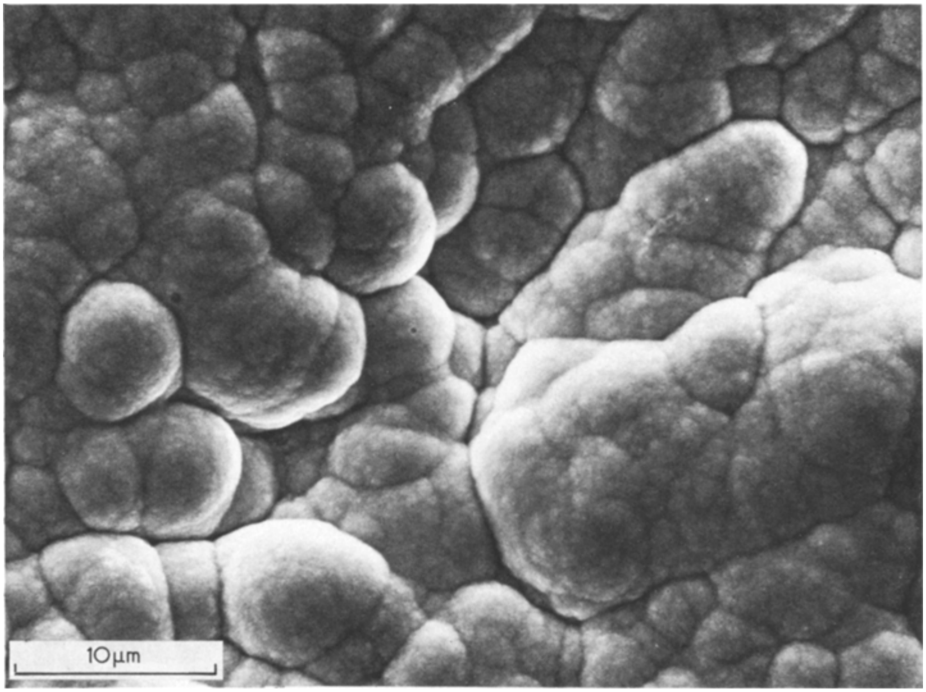

Fig. 4. Electron micrograph of Ni on graphite. Deposition from Watts bath, pH 3·5 containing chloride (0·3 M). Deposition charge 25 C cm^{-2}, current density 200 mA cm^{-2}.

deposit and the cause of the enhanced area is totally different from that with the copper substrate. Hydrogen does not have the same role in creating surface roughness.

Hence it can be seen that electrodes may be prepared by electrodeposition of nickel onto both copper and graphite which lead to greatly enhanced current densities for alcohol oxidation and which are of satisfactory stability. This type of procedure for enhancing limiting currents for kinetically-controlled reactions is likely to be general for other metals and, although only a simple variation of ideas widely used in fuel cell technology, could prove useful in synthetic electrochemistry.

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