# KINETICS OF ELECTRODEPOSITION OF NICKEL FROM WATTS BATHS

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Abstract—Tafel slopes and reaction orders for the electrodeposition of nickel from Watts type baths onto a vitreous carbon electrode have been determined by both steady state and transient methods. After correcting the currents for concurrent hydrogen evolution, and taking the composition of the deposit into account, the following kinetic parameters have been obtained: Tafel slope 120 mV decade<sup>-1</sup>, reaction orders with respect to nickel and chloride both +1. The agreement between the two methods was excellent. No dependence of cathodic rate constants on pH could be found. The cathodic results do not therefore support the widely held opinion that an adsorbed complex involving a hydroxide ion is an intermediate in active dissolution.

Results for the nucleation constant are given in the Appendix. The nucleation constant for nickel on vitreous carbon is found to depend on potential and concentration of nickel ions, and to be independent of pH and concentration of chloride ions.

## INTRODUCTION

The electrolytic oxidation and reduction of nickel and its ions has been the subject of numerous and extensive studies, but as yet no reaction mechanism has been found that can account for all aspects of the observed behaviour.

In this paper we shall concern ourselves primarily with the determination of the kinetic constants for the cathodic process. The parameters sought are the Tafel slope and the reaction orders with respect to the various components in the solution participating in either the rate-determining step or in equilibria preceding it. The mechanism of nickel dissolution will be treated in a subsequent paper.

Most authors assume the mechanism to involve two consecutive one-electron charge transfers, and the participation of an anion with formation of an adsorbed complex. This mechanism can be represented in a general form as:

$$Ni^{2+} + X^{-} \rightleftharpoons NiX^{+} \tag{1}$$

$$NiX^+ + e^- \rightleftharpoons NiX_{ads} \tag{2}$$

$$\operatorname{Ni}X_{\operatorname{ads}} + e^{-} \rightleftharpoons \operatorname{Ni} + X^{-}.$$
 (3)

The anion  $X^-$  has been variously assumed to be OH<sup>-</sup> or Cl<sup>-</sup>.

The Tafel slopes and reaction orders for the above general mechanism depend on:

- (a) which of the reactions constitutes the ratedetermining step,
- (b) whether the coverage  $\theta$  of the electrode with the adsorbed complex obeys a Langmuir isotherm for either low ( $\theta < 0.1$ ) or high ( $\theta > 0.9$ ) coverage, or an isotherm like the Temkin isotherm for intermediate coverage ( $0.2 < \theta < 0.8$ ).

The Tafel slopes and reaction orders that can be calculated for the various rate-determining steps and ranges of coverage are given in Table 1.

In the work reported here the kinetic parameters for nickel deposition have been obtained by both steady state methods and from potentiostatic transients for deposition onto vitreous carbon electrodes. The current-time relationships which have been derived for the model of right circular cones in the case of nucleation of a single phase followed by shape-

Table 1. Calculated values for the cathodic and anodic kinetic parameters for the reaction mechanism (1)-(3)

		Tafel slope		$\frac{\partial \log k}{\partial \log \left( X^{-} \right)}$		$\frac{\partial \log k}{\partial \log [\operatorname{Ni}^{2+}]}$	
rds	Coverage	cathodic	anodic	cathodic	anodic	cathodic	anodic
	$\theta < 0.1$		30	+ 1	+ 1	+1	0
(1)	$0.2 < \theta < 0.8$	æ	30	+ 1	+ 1	+1	0
•	$\theta > 0.9$	8	60	+ 1	0	+ 1	0
	$\theta < 0.1$	120	40	+1	+1	+ 1	0
(2)	$0.2 < \theta < 0.8$	120	60	+1	+0.5	+0.5	0
	$\theta > 0.9$	120	120	+1	0	0	0
	$\theta < 0.1$	40	120	+1	+1	+1	0
(3)	$0.2 < \theta < 0.8$	60	120	+0.5	+1	+0.5	0
1-7	$\theta > 0.9$	120	120	0	+ 1	0	0

preserving three-dimensional growth, are as follows[1]:

(a) for progressive nucleation:

$$i = nFk'a\left\{1 - \exp\left[\frac{-\pi M^2 k^2 A N_o t^3}{3\rho^2}\right]\right\}$$
(4)

(b) for instantaneous nucleation:

$$i = nFk'a\left\{1 - \exp\left[\frac{-\pi M^2 k^2 N_{\rm o} t^2}{\rho^2}\right]\right\}$$
(5)

in which *i* is the current (A), *nF* the charge per mole (C mole<sup>-1</sup>), *a* the surface area of the electrode (cm<sup>2</sup>), *M* the molecular weight (g mole<sup>-1</sup>),  $\rho$  the density (g cm<sup>-3</sup>), *k* the rate of lateral growth (mole cm<sup>-2</sup>s<sup>-1</sup>), *k'* the rate of outward growth (mole cm<sup>-2</sup>s<sup>-1</sup>), *A* the nucleation constant (s<sup>-1</sup>), N<sub>0</sub> the number of active sites (cm<sup>-2</sup>) and *t* the time (s).

However, the deposition of nickel does not obey these relationships. The transients exhibit a maximum before approaching a stationary plateau. Explanations include the assumption of cessation of growth ("death") combined with renewed nucleation ("rebirth")[2, 3], and the theory of non-shape preserving outward growth of growth centres which have the shape of spherical caps [4, 5]. The latest interpretation argues that a mixture of interstitial hydrogen alloys of nickel is deposited [6].  $\alpha$ -Nickel is a solid solution containing very little interstitial hydrogen; it obeys the laws for progressive nucleation and three-dimensional growth.  $\beta$ -Nickel, however, is rich in interstitial hydrogen. It is primarily formed in the early stages of deposition, and its formation is favoured by low pH, low temperature and high cathodic overpotential. At longer times mass transfer of H<sup>+</sup> ions restricts further growth.  $\beta$ -Nickel is held responsible for the occurrence of the maximum in the potentiostatic transient.

In view of this, the kinetic information obtained with the aid of Equations (4) and (5) must be viewed with some reservation. In particular the interpretation of the steady state current, ie

$$i = nFk'a \tag{6}$$

is ambiguous, since one actually has an unknown proportion of  $\alpha$ - and  $\beta$ -nickel on the surface, and these phases have different rates of growth.

In transient studies the slopes of plots of  $i vs t^3$  for single pulse, and of  $i vs t^2$  for double pulse experiments, at the base of the transients where overlap effects are still negligible, are used to obtain kinetic information. Only those transients have been used in which the deposit consists of  $\beta$ -nickel alone. This composition can be proved by anodic linear sweep voltammetry;  $\beta$ -Ni has a dissolution peak at about -0.2 V, while  $\alpha$ -Ni has a peak at about -0.1 V vs sce. If we assume that changes in the composition of the solution or in the potential have no, or at most a small effect on the ratio between the rate constants k and k', the slopes for single pulse ( $S_{SP}$ ) and double pulse ( $S_{DP}$ ) experiments can be witten as:

$$S_{\rm SP} = \frac{i}{t^3} = \frac{K N_{\rm o} k^3 A}{3}$$
(7)

$$S_{\rm DP} = \frac{i}{t^2} = K N_{\rm o} k^3 \tag{8}$$

in which all the common constants have been combined into a single constant K. The quantity which has been used in plots against the variables under study has been  $\frac{1}{3} \log S$ :

$$\frac{1}{3}\log S_{\rm SP} = \log k + \frac{1}{3}\log K + \frac{1}{3}\log \frac{A}{3} + \frac{1}{3}\log N_{\circ}$$
(9)  
$$\frac{1}{3}\log S_{\rm DP} = \log k + \frac{1}{3}\log K + \frac{1}{3}\log N_{\circ}.$$
(10)

Provided the value of  $N_0$  remains reasonably constant in a series of experiments, plots of  $\frac{1}{3} \log S_{\rm DP}$  vs either the potential or the logarithm of a concentration should be linear, and yield the required kinetic information from the slopes. Similar results can only be obtained from single pulse experiments if the nuclation constant A is independent of the variable under consideration. The parameters which have been determined in this study are the cathodic Tafel slope and the reaction orders with respect to Ni<sup>2+</sup>, Cl<sup>-</sup> and OH<sup>-</sup> ions.

Appendix 1 gives a survey of literature values for these kinetic parameters, as well as reaction mechanisms which have been proposed for the electrolytic reduction of nickel ions. It can be seen that a number of these mechanisms bear little relation to the experimental observations, in particular as regards the involvement of  $OH^-$  ions.

#### **EXPERIMENTAL**

Lengths of vitreous carbon rod (grade GC 30, Tokai, Japan) were scaled into glass tubing to serve as working electrodes. The electrode surface was mechanically polished with successively finer grades of emery paper and alumina on Metron polishing cloth (Metallurgical Services Laboratories, Ltd) to a mirrorbright finish free from scratches and pits.

In one experiment the steady state current on a massive nickel electrode was used. The nickel (Koch-Light, 99.998 % Ni) was held in a tightly fitting PTFE sleeve and was mechanically polished before use.

A conventional three-compartment cell with a vitreous carbon counter electrode and a saturated calomel electrode (Radiometer, Denmark) as reference electrode was used. All potentials are quoted with respect to the *sce*.

All solutions were made with AnalaR reagents and triply-distilled water. They were chiefly based on the Watts bath, *ie* 0.85 M NiSO<sub>4</sub> + 0.15 M NiCl<sub>2</sub> + 36 gl<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>. The baths were operated at room temperature and were deaerated before use by bubbling oxygen-free nitrogen.

Measurements were made using a Hi-Tek 2101 potentiostat and PPRI waveform generator and either a Hewlett-Packard 7015B X-Y recorder or a Servoscribe RE541.20 potentiometric recorder. Coulometric measurements were made with a Hi-Tek gated integrator. All cathodic currents were corrected, first for background current, then for hydrogen evolution (HER) current. Bulk pH was measured with a Philips PW9410 digital pH meter with a glass electrode.

The kinetic parameters sought were obtained from logarithmic plots; the linear relationships were all calculated by the method of least squares.

The dimensions of the working electrode surface were measured with the aid of a travelling microscope.

#### RESULTS

#### (I) Steady state methods

In evaluating steady state currents, the following points must be taken into consideration.

- (a) The hydrogen evolution reaction (HER). All steady state currents must be corrected for the concurrent HER. These HER currents have been determined in blank experiments on a nickel electrode and are functions of time, potential and pH.
- (b) Surface pH. Due to the concurrent HER, the surface pH will differ from the bulk pH. For the reaction order  $(\partial \log k)/(\partial pH)$  it is the surface pH which matters, not the bulk pH. Also, for Tafel slopes and other reaction orders the surface pH should be kept constant, not the bulk pH. Various authors have measured the pH in a thin surface layer during nickel deposition from the Watts bath[7, 8, 9, 10]. The surface pH is in general dependent on bulk pH, current density, time, hydrodynamic conditions and the amount of the boric acid buffer. In an unstirred Watts bath, the surface pH was found to increase gradually from 4.0 to 6.5 during the first 120 s of nickel deposition at 1 mA cm<sup>-2</sup>[8].
- (c) Composition of the deposit. Due account must be taken of the proportions of α- and β-nickel[6].

(A) Tafel slope. Tafel slopes for nickel deposition, after correcting for the HER, were usually found to be high and irreproducible. Time and solution pH appeared to play a role. This variability in Tafel slopes has been attributed to variation in the composition of the surface layer of deposit. One can write

$$i = Fa(n_a k'_a \psi_a + n_\beta k'_\beta \psi_\beta) \tag{11}$$

where  $\psi_{\alpha}$  and  $\psi_{\beta}$  stand for the proportion of the surface covered with  $\alpha$ - and  $\beta$ -nickel. Since  $\psi_{\alpha} + \psi_{\beta} = 1$  at steady state, Equation (11) becomes

$$i = Fa\{n_{\alpha}k'_{\alpha} + (n_{\beta}k'_{\beta} - n_{\alpha}k'_{\alpha})\psi_{\beta}\}.$$
 (12)

Initially  $n_{\beta}k'_{\beta} > n_{\alpha}k'_{\alpha}$  and  $\psi_{\beta} > 0$ , and as a result currents exceeding the steady state value for  $\alpha$ -nickel alone are found. As depletion of hydrogen ions at the surface increases with time, both  $n_{\beta}k'_{\beta}$  and  $\psi_{\beta}$  decrease, and eventually the current will approach the steady state current for deposition of  $\alpha$ -nickel:

$$i = n_a F k'_a a. \tag{13}$$

The nature of the substrate plays a role in the initial stage of nucleation and growth. On a metal with a low hydrogen overvoltage, less hydrogen is available for formation of  $\beta$ -nickel than on a vitreous carbon electrode, since in the former case there is linear diffusion of hydrogen ions to the entire electrode, in the latter hemispherical diffusion to the growing centres only. Thus one would expect more  $\beta$ -nickel on vitreous carbon than on nickel. Furthermore epitaxy would favour  $\alpha$ -nickel on nickel.

The variation in the composition of the nickel deposit as a function of time and pH was investigated by comparing steady state currents on a vitreous carbon electrode  $(0.083 \text{ cm}^2)$  and a nickel electrode  $(0.136 \text{ cm}^2)$ , *ie* area ratio 0.610. The composition of the

solution was 0.5 M NiSO<sub>4</sub> + 0.5 M NiCl<sub>2</sub> + 36 gl<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>. The potential was -0.820 V vs sce.

Figure 1 shows the current ratio  $i_{vc}/i_{Ni}$  as a function of time for various values of the solution pH. It is apparent that the current ratio generally exceeds the area ratio. The deviation is largest for small values of the time and for low pH; these are exactly the conditions that favour formation of  $\beta$ -nickel. The current ratio approaches the area ratio at long times and high pH, and here deposition of  $\alpha$ -nickel alone can be expected. Dependable values for the Tafel slope and reaction orders should therefore be sought at high pH and long times.

Figure 2 shows the Tafel slopes obtained from



Fig. 1. The current ratio for steady state currents on a vitreous carbon electrode as compared to those on a nickel electrode, as a function of time and pH, for deposition of nickel at -0.82 V from 0.5 M NiSO<sub>4</sub> + 0.5 M NiCl<sub>2</sub> + 36 g l<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>.



Fig. 2. Apparent Tafel stopes, obtained for nickel deposition at i = 10 min, in the potential interval -0.82 to -0.86 V vs sce, as a function of the pH of the bath.

steady state currents at t = 10 min on vitreous carbon and nickel, as a function of pH. The more dependable values lie at high pH where the curve connecting the points in Fig. 2 approaches the value 120– 130 mV decade<sup>-1</sup>. The result is in agreement with the value  $120 \pm 5$  mV decade<sup>-1</sup> reported by Arvia *et al.*[11] who state that the cathodic Tafel line could only be evaluated in the pH range from 4 to 6.

(B) Reaction order with respect to  $OH^-$  ions. Optimum conditions for the steady state deposition of  $\alpha$ -nickel alone are again high pH and long times. Figure 3 shows the dependence of the steady state current at -0.860 V, after correcting for the HER, on the pH in the interval 3.37 < pH < 4.65. The current is independent of the pH.

As one proceeds to lower pH values, increasing amounts of  $\beta$ -nickel are to be expected. In addition, the correction for the HER becomes considerable, eg at pH = 2.3 at -0.84 V it amounts to around 30% of the total current. No dependable results can therefore be expected at pH < 3.0.

Strictly speaking, the fact that the steady state current for  $\alpha$ -Ni appears independent of pH can be interpreted in two ways:

- (a) the surface pH varies, but the reaction order with respect to OH<sup>-</sup> ions is zero and
- (b) the reaction order with respect to OH<sup>-</sup> ions is not equal to zero, but the surface pH in the steady state is constant, even if the bulk pH varies.

(C) Other reaction orders. The reaction order with respect to Ni<sup>2+</sup> ions has been determined in Watts type solutions in which part of the Ni<sup>2+</sup> ions had been replaced by Mg<sup>2+</sup> ions. A logarithmic plot of the steady state current at t = 10 min, corrected for HER, against the Ni<sup>2+</sup> concentration is shown in Fig. 4. The linear plot yields for the reaction order:

$$\frac{\partial \log i}{\partial \log[\mathrm{Ni}^{2+}]} = +0.875.$$

The steady state current is moreover markedly affected by the concentration of  $Cl^-$  ions in the solution. From the logarithmic plot shown in Fig. 5 the following reaction order has been calculated:

$$\frac{\partial \log i}{\partial \log [\mathrm{Cl}^-]} = +0.85.$$

#### (II) Transient methods

The advantages of transient over steady state methods are that

- (a) if measurements are confined to very low currents at the foot of the transient, the surface pH will not yet have deviated markedly from the bulk pH and
- (b) the composition of the deposit becomes apparent as soon as one dissolves the deposit anodically. The anodic charge thus obtained is used to determine the current efficiency, and so correct for the HER. The main disadvantages of transient methods are:
- (a) because of the high rate of nucleation of  $\beta$ -Ni (see Appendix 3) and the mass transfer limitations for H<sup>+</sup> ions required for further growth, there is only a small time interval where *i* is proportional to  $t^3$ , usually at currents less than 1% of steady state



Fig. 3. Dependence of the steady state current for nickel deposition on pH in the interval 3.37 < pH < 4.65. Electrode, vitreous carbon;  $a = 0.083 \text{ cm}^2$ ; potential, -0.860 V vs sce; solution, Watts bath; time, 10 min.



Fig. 4. Dependence of the steady state current for nickel deposition on the concentration of Ni<sup>2+</sup> ions. Electrode, vitreous carbon;  $a = 0.083 \text{ cm}^2$ ; potential, -0.820 V vs sce; solution, Watts bath in which 0, 20, 40 and 60% of the Ni<sup>2+</sup> ions had been replaced by Mg<sup>2+</sup> ions; time, 10 min.



Fig. 5. Dependence of the steady state current for nickel deposition on the concentration of Cl<sup>-</sup> ions. Electrode, vitreous carbon; a = 0.083 cm<sup>2</sup>; potential, -0.820 V vs sce; solution, x M NiCl<sub>2</sub> + (1.0 - x) M NiSO<sub>4</sub> + 36 gl<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>; time. 10 min.

values; here the background current constitutes a major source of error and

(b) the value of  $N_0$  may not be constant in the course of successive depositions and dissolutions.

Kinetic parameters have been obtained from plots of  $\frac{1}{3} \log S$  for single (SP) and double pulse (DP) depositions against the variable under consideration. A number of such plots are shown in Figs 6-9. The slopes of these plots are given in Table 2.

The following conclusions can be drawn from experiments using the double pulse method:



Fig. 6. Dependence of  $\frac{1}{3} \log S$  for DP and SP nickel deposition on the potential. Electrode, vitreous carbon;  $a = 0.083 \text{ cm}^2$ ; solution, Watts bath; pH = 2.95; prepulse, 20 ms at -1.20 V vs sce.



Fig. 7. Dependence of  $\frac{1}{3} \log S$  for DP and SP nickel deposition on the concentration of Ni<sup>2+</sup> ions. Electrode, vitreous carbon;  $a = 0.083 \text{ cm}^2$ ; potential, -0.820 V vs sce; solution, Watts bath with 0, 20, 40 and 60% of the Ni<sup>2+</sup> ions replaced by Mg<sup>2+</sup> ions; prepulse, 20 ms at -1.20 V vs sce.



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Fig. 8 Dependence of  $\frac{1}{3} \log S$  for DP and SP nickel deposition on the concentration of Cl<sup>-</sup> ions. Electrode, vitreous carbon; a = 0.083 cm<sup>2</sup>; potential, -0.820 V vs sce, solution, x M NiCl<sub>2</sub> + (1.0 - x) M NiSO<sub>4</sub> + 36 gl<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>; prepulse, 20 ms at -1.20 V vs sce.



Fig. 9. Dependence of  $\frac{1}{3} \log S$  for DP and SP nickel deposition on the pH. Electrode, vitreous carbon;  $a = 0.083 \text{ cm}^2$ ; potential, -0.820 V vs sce; solution, Watts bath; prepulse, 20 ms at -1.20 V vs sce.

- (a) the cathodic reaction order with respect to  $Ni^{2+}$  ions is +1,
- (b) the cathodic reaction order with respect to Cl<sup>-</sup> ions is + 1,
- (c) the cathodic reaction order with respect to H<sup>+</sup> and OH<sup>-</sup> ions is 0 and
- (d) the cathodic Tafel slopes obtained are 135, 108 and 100 mV decade<sup>-1</sup>, average value 114.5 mV decade<sup>-1</sup>.

The following conclusions can be drawn from the comparison of single and double pulse experiments:

- (a) the nucleation constant is independent of the concentration of Cl<sup>-</sup> ions and of the pH and
- (b) the nucleation constant is dependent on the potential and on the concentration of  $Ni^{2+}$  ions.

The dependence of the nucleation constant on the potential and the Ni<sup>2+</sup> ion concentration is discussed in more detail in Appendix 3. It is shown there that under the experimental conditions prevalent in this study active sites on the vitreous carbon surface act as critical clusters. Under these circumstances the dependence of A on the potential follows a relationship

$$A = A' \exp\left[\frac{-\beta FE}{RT}\right]$$
(14)

in which  $\beta$  is the apparent transfer coefficient. If one substitutes this value for A in Equation (9), it becomes apparent that the Tafel slope can be obtained directly from single pulse experiments:

Tafel slope = 
$$\frac{4}{3} \frac{d(-E)}{d(\frac{4}{3} \log S_{SP})}$$
. (15)

From the data for the SP experiments in Table 2 the values 109 and 97 mV decade<sup>-1</sup> are derived for the Tafel slope. These values are in reasonable agreement with those obtained from double pulse experiments.

#### REACTION MECHANISM FOR THE REDUCTION OF NICKEL IONS

Although steady state results apply to the deposition of  $\alpha$ -nickel, and transient methods to the deposition of  $\beta$ -nickel, the kinetic parameters obtained with the two methods are in remarkably good agreement. It must be concluded that the kinetic parameters for the

Solution	pH	Potential V vs sce	Method	Result
Watts bath	2.05	-0.80 to $-0.88$	DP	$\partial \frac{1}{4} \log S / \partial E = 7.41  \mathrm{V}^{-1}$
	2.78	-0.80 to $-0.84$	DP	= 9.23
	2.78	-0.80 to $-0.84$	SP	= 12.2
	2.95	-0.80 to $-0.90$	DP	= 9.97
	2.95	-0.80 to -0.90	SP	= 13.7
Watts bath, but part of the Ni <sup>2+</sup>		- 0.82	DP	$\partial \frac{1}{3} \log S / \partial \log [\text{Ni}^{2+}] = +1.09$
ions replaced by Mg <sup>2+</sup> ions		- 0.82	SP	= +1.61
Watts bath with varying		- 0.82	DP	$\partial \frac{1}{3} \log S / \partial \log [Cl^-] = +1.01$
proportions of NiCl <sub>2</sub> and		- 0.82	SP	= +0.95
$NiSO_4$ , $[Ni^{2+}] = 1.00 M$		- 0.82	DP	= +0.89
		-0.82	SP	= +0.99
Watts bath, various pH	2.18-3.22	- 0.82	DP	$\partial \frac{1}{3} \log S / \partial pH = +0.04$
· •	2.18-3.22	- 0.82	SP	= +0.02
	1.84-3.12	-0.82	DP	= -0.005
	1.84-3.12	-0.82	SP	= + 0.01
$1 \text{ M NiSO}_4 + 36 \text{ gl}^{-1} \text{ H}_3 \text{BO}_3$	2.60-3.41	-0.82	DP	$\partial \frac{1}{3} \log S / \partial \mathbf{pH} = +0.06$
various pH	2.60-3.41	- 0.82	SP	= +0.04

Table 2. Results for the kinetic parameters for nickel deposition obtained from potentiostatic transients

reduction of nickel ions are:

Tafel slope	120 mV decade <sup>-1</sup>
$\partial \log i / \partial \log [\mathrm{Ni}^{2+}]$	+1
$\partial \log i / \partial \log [C1^-]$	+1
$\partial \log i/\partial \log [OH^-]$	0

If one compares the obtained kinetic parameters with those calculated and listed in Table 1, one can deduce that, if a reaction mechanism of the general type (1)-(3) applies in the Watts bath:

- (a) the anion  $X^-$  involved must be the chloride ion and
- (b) the rate-determining step is reaction (2), *ie* the first-electron transfer step.

For confirmation of these conclusions, and for further information on the coverage, it is necessary to study the reverse process, *ie* the electrolytic oxidation of nickel metal. Unfortunately there is no agreement on the kinetic parameters for the oxidation of nickel, and a marked discrepancy between the results of cathodic and anodic experiments.

In Appendix 2 a number of reaction mechanisms has been listed which have been proposed for the oxidation of nickel (and the closely related metals cobalt and iron) on the basis of their observed anodic behaviour. For each of these proposed mechanisms it is possible to calculate the cathodic kinetic parameters that would follow; these have been tabulated in the right-hand section of the table.

A comparison of deduced and experimental cathodic parameters shows that there is no agreement between the two sets of values for any of the proposed dissolution mechanisms. The greatest discrepancy is found in the pH dependence and the involvement of  $H^+$  and  $OH^-$  ions. Clearly further investigations are required to elucidate the causes of this discrepancy.

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PENDIX
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Kethod	Electrods	Selution	-Teap.	뾥	Tafel slope (mV/dec)	<u>2 log 1</u> 2 log[N1 <sup>2+</sup> ]	3 10g 4 3 10g[0H]]	<u>a 106 1</u> a 10g[C1 <sup>-</sup> ]	Reaction mechanisms proposed	al l
State	XX.	chloride perchiorate	900 °	0 0 0 0 0	120 mV/dec for 4 < pH < 6	0'1+	ł	t	$N1^{2*} + H_{2} = \frac{1}{2} = \frac{1}{2} + H_{2}$ $N10H^{+} + H_{2} = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{1}{2} + \frac{1}{2} $	п
Steady State (galv)	Ni (electro- lytic)	NICIO4	ŝ	5-6	30	6°°¢+		1	R1 <sup>2+</sup> + 2 <sub>2</sub> 0	13
initial potentials	z	3	:	z	87 * *	ł	,	è	FRANK IN A REAL REAL FRANK FRANK FRANK	
Steady Siste (galv)	11	NiSO <sub>4</sub> bath NiCl <sub>2</sub> bath Watts bath	25 <sup>0</sup> (0-85 <sup>0</sup> )		2 2 80 90	1	į	•	M1 <sup>2+</sup> + H <sub>2</sub> O + e <sup>-</sup> <sup>m</sup> <sup>m</sup> M10H <sup>+</sup> + (H) <sup>ada</sup> NLOH <sup>+</sup> + e <sup>-</sup> <sup>-</sup> <sup>-</sup> <sup>-</sup> <sup>-</sup> <sup>-</sup> (H10H) <sup>ada</sup> (N10H) <sup>ada</sup> + (H) <sup>ada</sup> <sup>man</sup> H1 + H <sub>2</sub> O	t
Steady State	И	MICIZ	25°	4. 1	* * 8	7	¢	0)	N1 <sup>2+</sup> + e	13
Steady State (galv)	Ni ROE	N4C12+CaC12			21 (1. wol) 11 (1 ugh 1) 811	2 2	ş		Parallel intermediates Hi(H <sub>2</sub> O) <sub>5</sub> <sup>4</sup> and MiCi (H <sub>2</sub> O) <sub>5</sub> . Second step occurs on kink sites	4
Steady State (potent)	Cu RDE	Matts Dath	50 <sup>6</sup>	8 4	43(10% ŋ) 118(ḥigh n)	ŗ+	ð		$M_{1}^{2} + M_{2}^{0} \xrightarrow{d} M_{1}^{2} + H^{1} + H^{2}$ $H1OH^{1} + 6 \xrightarrow{d} (N1OH) A_{Als} BDS$ $H1OH^{1} + 4 \xrightarrow{d} - \frac{1}{2} + H^{2} + H^{2}$	15
potentio- static transfeuts	Y1tteous carbon	Watts bath Sulphate bath	room temp		93 mV/dec 108 (k) 120 (k')	about 1	1	B	•	81
State State	P.C RDE	Chloride Clo <sub>4</sub>	÷		51 (low 1) 98 (high i)	+1,2	o	¢.¢	M4 <sup>2+</sup> + C1 <sup>2</sup>	17
polaro. graphy	DME	Chloride			43 (10* 1) 170 (high 1)	ĩ	1	1+	$(XL(H_2O)_{B} ^{2^{4}} + C1^{-4 + x}(NL(H_2O)_{5}C1)^{4} + u_{2}^{0}O$ $[NL(H_2O)_{5}C1]^{4} + e^{\frac{2}{3}4my}NLC1 + 3H_{2}O$ $NLC1 + e^{\frac{2}{3}} - \cdots + NL + C1^{-}RDS$	28
linear swcep volt- annerry	kg hanging orop	Sulphate		5-5 9	114		0	and the second se	decomposition of complex rate-detormining	19

Kinetic parameters and reaction mechanisms for the electrolytic reduction of nickel ions, as reported in the literature.

The second se

APPENDIX 2

A survey of proposed reaction mechanisms for the electrolytic dissolution of nickel (and the closely related metals Co and Fe), and of cathodic parameters that can be derived from them.

<u>ц</u>	roposed reaction mechanisms for dissolution	af N <b>i</b> (Co, Fe)			Predicted values for t	he cathodic kin	etic parameter	ψĐ
	Mechanism.	RDS	σοl	Ref	<u>Tafe1</u> (mV/dec)	<u>а тов 1</u> д тов[и1 <sup>2+</sup> ]	<u>а log 1</u> а log[он <sup>т</sup> ]	<u>8 106 1</u> 3 108[C1 <sup>-</sup> ]
~	$N_{1} + H_{2}O  (N_{1}OH) + H^{+} + e^{-} (1)$ $(N_{1}OH)  N_{1}OH^{+} + e^{-} (2)$ $N_{1}OH^{+} + H^{+}  N_{1}^{2+} + H_{2}O (3)$	(1) (3) (3)	<0.1 <0.1 >0.5	20,21 11 20	60 120	1+ 1+	17 17 17 17 17 17 17 17 17 17 17 17 17 1	000
m	$N_1 + OH^{-} \longrightarrow (N1OH)_{ads} + e^{-} (1)$ $N_1 + (N1OH) \longrightarrow N1(N1OH) (2)$ $N_1 (N1OH) + OH^{-} \longrightarrow N1OH^{+} + (N1OH) + 2e^{-} (3)$ $N1OH^{+} + H^{+} \longrightarrow N1^{2^{+}} + H_2^{0} (4)$	(3)	40.1 ×0,9	81 7	(m) 60	(1+)	(+2) +1	*0 0
υ	$Fe(0H^{-}) + Fe(Cl^{-}) \stackrel{f}{\longrightarrow} Fe + Fe0H^{+} + Cl^{-} + 2e^{-} (1)$ $Fe0R^{+} + H^{+} \stackrel{f}{\longleftarrow} Fe^{2+} + H_{2}^{0} (2)$	Ð	40, İ	53	69	I+	1+	1+
a.	$NI + H_{2}O+CI \leftarrow (NICLON^{-}) + H^{+}+e^{-} (1)$ $(NICLON^{-}) \leftarrow NICLON + e^{-} (2)$ $NICLOR + H^{+} \leftarrow NI^{2+} + CI^{-} + R_{2}O (3)$	(2)	0,2 - 0,8	33	120	Ĩ+	l+	1+
pa	$NI + CI \xrightarrow{\leftarrow} (NICI) + e^{-} (1)$ $(NICIB^{+} + CI \xrightarrow{\leftarrow} NICIB^{+} (2)$ $NICIB^{+} + CI \xrightarrow{\leftarrow} NICI_{2} + B^{+} + e^{-} (3)$ $NICI_{2} \xrightarrow{\leftarrow} NI^{2+} + 2CI^{-} (4)$	(2)	<0.1	53	9	7	Ť	7
<u>94</u>	$N_{1}  N_{1} + e^{-} $ (1) $N_{1}  N_{1}^{2} + e^{-} $ (2)	(3)	ì	13	120	<b>r</b> +	o	0
o	$\begin{array}{c} \text{N1} + x \text{ H}_{2} 0  (\text{N1}(\text{H}_{2} 0)_{x}^{+}) + \mathbf{e}^{-} (1) \\ (\text{N1}(\text{H}_{2} 0)_{x}^{+}) + \text{c1}^{-} \underset{\text{N1}(\text{H}_{2} 0)_{x-1} \text{c1}^{+} \mathbf{e}^{-} (2a) \\ (\text{N1}(\text{H}_{2} 0)_{x}^{+})  \end{aligned}$	3		14	64	1+	٥	o



Fig. 10. The dependence of the nucleation constant A, obtained from double and single pulse potentiostatic transients, on the overpotential. Electrode, vitreous carbon; a = 0.083 cm<sup>2</sup>; solution, Watts bath; potential range, -0.80 to -0.90 V vs sce; prepulse, 20 ms at -1.20 V vs sce. (a) log A is plotted against  $1/\eta^2$ . (b) log A is plotted against the potential.

#### APPENDIX 3

double pulse transients:

According to the classical thermodynamic theory of nucleation the steady state rate of nucleation A is given by

$$A = A_{\rm o} \exp\left[\frac{-A_k}{kT}\right] \tag{16}$$

in which  $A_k$  is the work required for the formation of the critical cluster. The linear relationship between  $A_k$  and  $1/\eta^2$ , in which  $\eta$  is the overvoltage with respect to the equilibrium potential, gives information on  $n_c$ , ie the number of atoms involved in the formation of the critical cluster.

The classical theory characterizes the critical cluster in terms of macroscopic concepts such as surface energy. Surface energy has no physical meaning when  $n_c$  becomes very small. The atomistic treatment is more appropriate for very small clusters, for it involves instead the interaction between small clusters and their building elements. The atomistic treatment of nucleation[24-26] predicts for the steady state nucleation rate:

$$A = A_{o} \exp\left[\frac{-\phi(n_{c})}{kT}\right] \exp\left[\frac{-(n_{c}+\beta)eE}{kT}\right].$$
 (17)

Here  $\phi(n_c)$  is a measure for the energetic state of the critical cluster; it can be considered constant for nuclei of a given size. In this case a plot of log A vs potential gives direct information on  $n_c$ :

$$\frac{\mathrm{d}\log A}{\mathrm{d}E} = -\frac{n_{\mathrm{r}} + \beta}{0.060}.$$
(18)

The apparent transfer coefficient  $\beta$  for nickel deposition equals about 0.5 as was shown before.

Though in principle the classical theory applies to large clusters only, and the atomistic theory to small clusters, in practice it is usually found that experimental data fit both types of equations equally well; thus  $\log A$  can be plotted against  $1/\eta^2$  to give a straight line, as well as against E to give one or more straight line sections. The values found for *n*, have generally been low with both methods.

#### Experimental results

The nucleation constant A for nickel deposition on vitreous carbon has been obtained from the combination of single and

$$\frac{1}{3}\log S_{\rm SP} - \frac{1}{3}\log S_{\rm DP} = \frac{1}{3}\log \frac{A}{3}.$$
 (19)

Figure 10(a) shows a plot of log A vs  $1/\eta^2$ ; in Fig. 10(b) the same data for log A are plotted against the potential. The former gives values of  $n_c$  ranging from 0.50 at -0.80 V to 0.23 at -0.90 V; the latter gives a value for  $n_c$  of 0.09. A duplicate experiment gave  $n_c = 0.33-0.24$  in the range -0.80 to -0.84 V with the classical, and  $n_c = 0.02$  with the atomistic treatment. These results are in good mutual agreement and indicate that in this potential interval the active sites on the vitreous carbon substrate act as critical clusters, and that an active site with an adsorbed nickel atom is already a stable configuration.

The nucleation constant is independent of pH and Cl<sup>-</sup> ion concentration, as can be seen from the results in Table 2. The nucleation constant is, however, clearly dependent on the concentration of Ni<sup>2+</sup> ions. In the concentration interval 0.4-1.0 M Ni<sup>2+</sup> one obtains from the experimental data (Fig. 11):



Fig. 11. The dependence of the nucleation constant A on the concentration of  $Ni^{2+}$  ions. Electrode, vitreous carbon;  $a = 0.083 \text{ cm}^2$ ; solution, Watts bath, with part of the  $Ni^{2+}$  ions replaced by  $Mg^{2+}$  ions; potential, -0.820 V vs sce; prepulse, 20 ms at -1.20 V vs sce.

$$\frac{d \log A}{d \log [Ni^{2+}]} \simeq 1.6.$$

NB It should be borne in mind that the nucleation constants discussed above refer only to nucleation and

growth of  $\beta$ -nickel. The nucleation constant for  $\alpha$ -nickel is probably much lower, for  $\alpha$ -Ni obeys growth laws for progressive nucleation for extended periods of time. Apparent values for A, calculated from experiments in which a mixed deposit is involved, are usually several orders of magnitude lower than those for  $\beta$ -nickel alone.