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EFFECT OF SURFACE PRETREATMENT ON THE
GALVANOSTATIC OXIDATION OF NICKEL

B. MacDougall and M. J. Graham

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R9

Abstract—The open-circuit, cathodic reduction and anodic charging characteristics of oxide films on both electropolished and electropolished + HNO_3 etched nickel electrodes have been studied in aqueous Na_2SO_4 solutions. While the oxide film thicknesses are approximately the same, the film on etched nickel dissolves much more rapidly than that on electropolished nickel. To galvanostatically passivate etched nickel at charging rates in the range 20–200 $\mu A \, cm^{-2}$ in pH 2.8 Na_2SO_4, the rate of oxide chemical dissolution has to be substantially decreased and this is achieved by lowering the electrolyte temperature from 25°C to 5°C. The transient anodic passivation charge thus observed for etched nickel is ~2x larger than that for electropolished nickel. With either pretreatment, the current efficiency for oxide formation is low (~20%), the majority of the transient charge (~80%) accounted for by Ni^{2+} in solution. Chemical dissolution of the oxide alone cannot explain the observed charging differences between etched and electropolished nickel since the individual charges and oxide formation current efficiencies are not influenced by anodic charging rate or solution aggressiveness. The results are best explained in terms of a continual breakdown and repair of the oxide film at defect areas during anodic charging, with most of the charge consumed by inefficient film repair. The influence of the oxide defects and the reason for the differences in behaviour between electropolished and etched nickel are discussed.

INTRODUCTION

Galvanostatic charging techniques have frequently been employed to study the anodic behaviour of nickel in both neutral and acid electrolytes[1–7]. The objective of these investigations is usually to clarify the nature of the passivation process and in particular the role of the passive oxide film in retarding corrosion. In most investigations, the nickel electrodes are given a particular pretreatment prior to anodic charging, *eg* chemical polishing, electropolishing, abrading, cathodic reduction, pre-anodizing or various combinations of these. The importance of surface pretreatments on the nature of anodic charging curves, and therefore on the passivation process itself, is not generally studied. In contrast, extensive studies on the thermal oxidation of nickel in O_2 have considered this effect and the results indicate that the oxidation rate is highly dependent upon the surface pretreatment[8–12]. This dependency arises because the different pretreatments produce structurally different prior nickel oxide films with different densities of easy diffusion paths[12–15]. The most rapid oxidation occurs on surfaces with the film of highest density of easy diffusion paths since these paths facilitate more rapid outward transport of cations.

In the present paper, the effect of different surface pretreatments on the galvanostatic oxidation of nickel is examined. Two procedures are used to form the prior oxide film: (i) electropolishing in H_2SO_4, and (ii) electropolishing in H_2SO_4 followed by etching in 5 % HNO_3 for 30 s. The pretreated nickel electrodes are galvanostatically anodized and the differences in the anodic charging results are correlated with anticipated differences in the nature of the prior oxides. The current efficiency for oxide growth is obtained directly from solution analysis of trace amounts of Ni^{2+} at various stages of anodic charging. The influence of anodic charging rate, solution pH and temperature on the galvanostatic charging results provide information on the roles of chemical dissolution and breakdown/repair of the oxide. The results permit a more detailed interpretation of the anodic charging of nickel and the role of the oxide film in the passivation process.

EXPERIMENTAL

Polycrystalline specimens, $1 \times 2.5 \, cm \times 0.025 \, cm$ thick, were prepared from zone-refined nickel sheet of 99.996 % purity as described elsewhere[16]. Briefly, they were degreased with benzene, chemically polished, electropolished for 2 min at 23°C in a 57 vol. % (v/o) sulphuric acid solution at 0.5 A cm^{-2}, and then annealed at 800°C in a vacuum of 10^{-8} torr. The specimens were electropolished again immediately before use in an experiment and some specimens were given a 30 s chemical etch in 5 % HNO_3. Surfaces after both electropolishing and etching were analysed using Auger electron spectroscopy. Extremely small amounts of impurities were found in the oxide films: $< \sim 0.5$ at % S following the sulphuric acid electropolish and ~ 4 at % N after the nitric acid etch.

Electrode potentials are referred to the Hg–Hg_2SO_4 reference electrode in 0.15N Na_2SO_4 (+0.665 V with respect to the standard reversible hydrogen electrode). Experiments were conducted in deaerated solutions of 0.15N Na_2SO_4 at pH 2.8 and 6.0 and at temperatures of 25 and 5°C. Nickel electrodes were immersed in solution either on open circuit or with a constant applied cathodic current and the change in potential with time was recorded. Surface activities were measured by switching the potential to some value in the passive region (*eg* 0V) and measuring the

anodic charge passed during the first two seconds, as reported elsewhere[17–19]. Both electropolished and etched nickel electrodes were immersed in solution with applied anodic currents of 20, 80 and 200 $\mu A\,cm^{-2}$ and the galvanostatic anodic charging profiles recorded. Solutions were analyzed for Ni^{2+} by carbon rod atomic absorption spectroscopy, the lower limit of detection by this method being $0.2\,\mu g\,cm^{-2}$ (sample area $= 5\,cm^2$; cell volume $= 50\,ml$). X-ray emission spectroscopy was used to determine oxide film thickness[16, 20–22].

RESULTS

(i) *Anodic charging of electropolished and etched nickel*

Figure 1 shows the galvanostatic charging profiles in pH 2.8 Na_2SO_4 at 25°C of both electropolished and etched nickel electrodes. In both cases, the electrodes were immersed in the solution with an applied anodic current of 80 $\mu A\,cm^{-2}$. The conditions are sufficient to ensure the passivation of electropolished nickel but not the etched sample, the latter undergoing activation after a brief potential arrest at −0.3V. The results indicate that the oxide on etched nickel dissolves more rapidly (in pH 2.8 Na_2SO_4 at 25°C) than it is formed (at 80 $\mu A\,cm^{-2}$) so that the surface quickly becomes oxide free and the anodic current is consumed by active nickel dissolution ($Ni \rightarrow Ni^{2+} +2e$). The result of this is the potential plateau at −0.65V. In contrast, the corresponding rate of dissolution of the oxide on electropolished nickel is sufficiently low for oxide growth and passivation to occur.

(ii) *Open-circuit and cathodic reduction behaviour*

As anticipated, open-circuit potential decay profiles at 25°C showed that the oxide on electropolished nickel breaks down more slowly than that on etched nickel, the breakdown times being ~ 60 s and ~ 1 s, respectively. To decrease the aggressiveness of the solution and thereby increase the oxide breakdown times, experiments were performed at the lower

solution temperature of 5°C. Figures 2 and 3 show both open-circuit and cathodic reduction behaviour in pH 2.8 Na_2SO_4 at 5°C of electropolished nickel and etched nickel, respectively. As seen in Fig. 2a, breakdown of the oxide on electropolished nickel takes more than 40 min at 5°C compared with ~ 1 min at 25°C. In the same way, the lower temperature also retards the open-circuit dissolution of the oxide on etched nickel, this now requiring more than 60 s (Fig. 3a) compared with ~ 1 s at 25°C. While the oxide reduction transient is more distinct for electropolished nickel (*cf* Figs. 2b and 3b), the charge in each case is approximately the same and corresponds to ~ 7 Å of NiO. These results are in good agreement with the oxide thicknesses of 6–7 Å for both electropolished and etched nickel determined by X-ray emission spectroscopy[20–22].

(iii) *Anodic charging at different temperatures, pH's and charging rates*

The rate of dissolution of the oxide on etched nickel is sufficiently low at 5°C for passivation to occur at 80 $\mu A\,cm^{-2}$ in pH 2.8 Na_2SO_4 (Fig. 4). Also shown in Fig. 4 is the anodic charging profile for electropolished nickel at 5°C. The transient charge, Q_a^t, defined as the anodic charge passed from the time of immersion to the potential plateau, can be determined from the point of intersection of extrapolated lines defining the beginning and the end of the charge transient (2). Q_a^t for electropolished nickel is found to be almost half that for etched nickel and the transition to the plateau region is more distinct.

Current efficiency measurements made in the transient region indicate a value of only ~ 20 per cent for oxide growth at 20 $\mu A\,cm^{-2}$ in pH 2.8 Na_2SO_4 (5°C) for both electropolished and etched nickel (Table 1), the majority of the anodic charge being accounted for by Ni^{2+} in solution. In an attempt to increase the current efficiency for oxide growth during galvanostatic oxidation of nickel, the charging rate was increased by a factor of ten times to 200 $\mu A\,cm^{-2}$ and, in a separate experiment, the solution pH was increased from 2.8 to 6.0. Figure 5 shows that the anodic charging profile for etched nickel is independent of
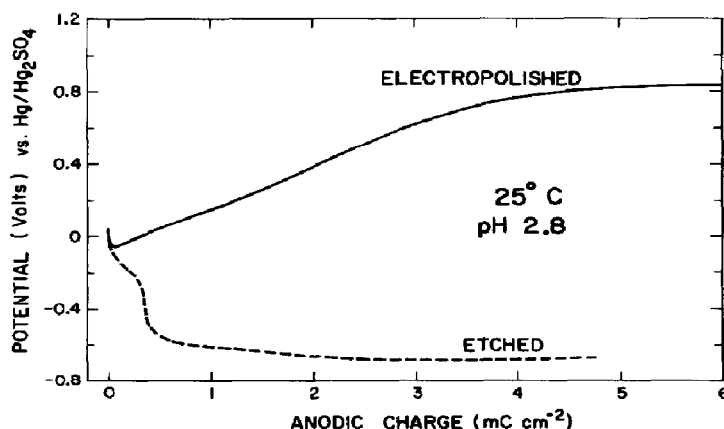

Fig. 1. Galvanostatic charging profiles, at 80 $\mu A\,cm^{-2}$ in pH 2.8 Na_2SO_4 at 25°C, for electropolished nickel (——) and etched nickel (– – –), the etch treatment being 30 s in 5% HNO_3.
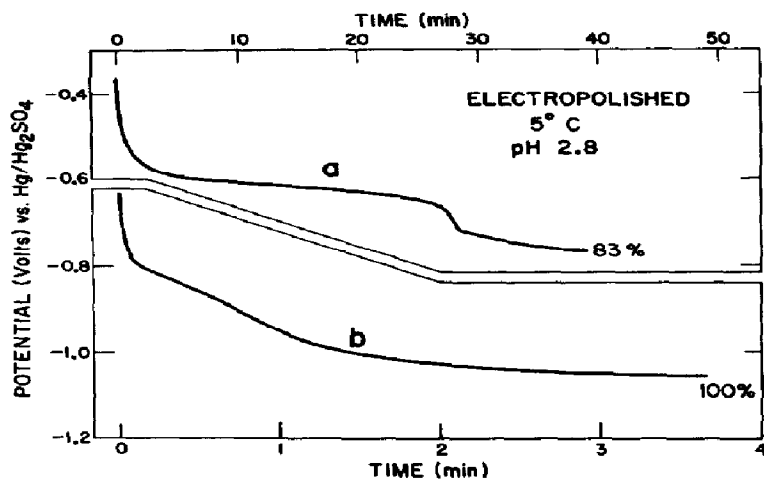
Fig. 2. Open-circuit decay profile (a) and galvanostatic reduction profile at $80 \mu A cm^{-2}$ (b) for elec-tropolished nickel in pH 2.8 Na_2SO_4 at 5°C. Recorded surface activities (in %) give an indication of the extent of oxide removal.
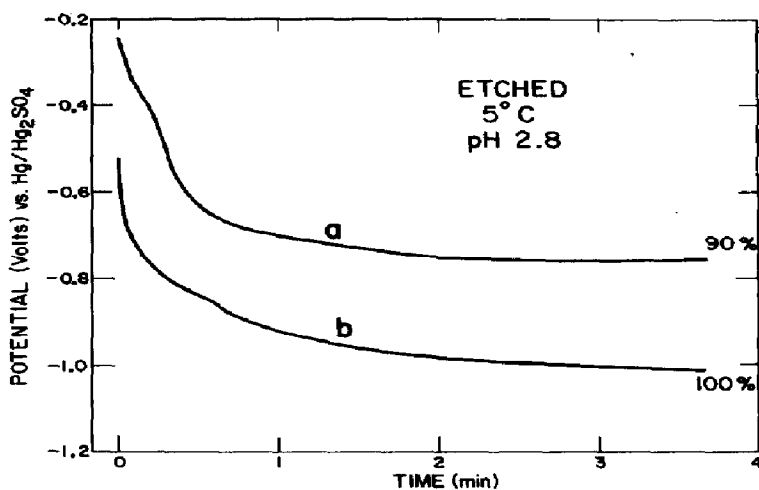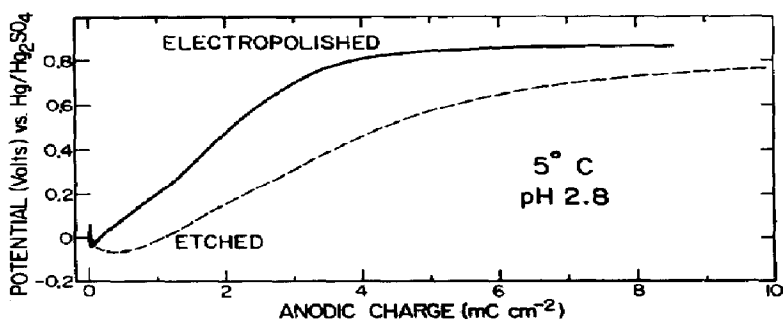

Fig. 3. As in Fig. 2, but for etched nickel.

Fig. 4. Galvanostatic anodic charging profiles, at $80 \mu A cm^{-2}$ in pH 2.8 Na_2SO_4 at 5°C, for electropolished nickel (———) and etched nickel (———).

Table 1. Quantity of Ni^{2+} in solution as a function of anodic charge passed during the galvanostatic oxidation of nickel electrodes after either electropolishing or etching for 30 s in 5% HNO_3. The anodic charge has been converted to μg Ni^{2+} cm^{-2} of electrode by assuming a current efficiency of 100%. All experiments were performed at 5°C

Electrode Treatment	Solution pH	Charging rate (μA cm^{-2})	Charging time (s)	Anodic transient charge Q_a^t (μg Ni^{2+} cm^{-2}) ±5%	$[Ni^{2+}]$ in solution (μg m^{-2}) ±5%	Current efficiency for Ni^{2+} production (%) ±10%
Electro- polished	2.8	20	150	0.91	0.70	77
	6.0	20	126	0.76	0.59	78
	2.8	20	290	1.76	1.38	80
	2.8	20	59	0.36*	0.31	86
	2.8	80	65	1.58	1.32	84
Etched	2.8	200	31	1.88	1.60	85
	2.8	200	26.5	1.60	1.30	81
	6.0	20	273	1.66	1.34	81
	6.0	20	73	0.44*	0.35	80

* Experiments stopped at an earlier time than corresponds to Q_a^t.

anodic charging current between 20 and 200 μA cm^{-2}, the only change being the anticipated anodic shift in potential of the entire profile at the higher charging rate. Also, the rate of anodic charging does not appear to alter the low oxide growth current efficiency, this remaining at $\sim 20\%$ (Table 1). The influence of an increase in solution pH to 6.0 on the anodic charging characteristics of both electropolished and etched nickel is shown in Fig. 6. In both cases, while the value of Q_a^t was somewhat less than that obtained at pH 2.8, the oxide growth current efficiencies were still only $\sim 20\%$ (Table 1). Solution analysis at earlier charging times in the transient region than corresponding to Q_a^t indicated that the oxide growth current efficiency was still $\sim 20\%$ (Table 1), ie the processes giving rise to this low current efficiency are at work from the beginning of anodic charging.

DISCUSSION

The results indicate that while etched nickel is less stable towards chemical dissolution than electropolished nickel, whenever passivation is achieved by galvanostatic charging the transient charge, Q_a^t, is not much influenced by pH (cf. Figs 4 and 6), temperature

(cf. Figs 1 and 4), or charging rate (Fig. 5). Furthermore the current efficiency for oxide growth is always found to be low ($\sim 20\%$) with most of the charge contributing to nickel dissolution (Table 1). If chemical attack of the oxide was the major contributor to nickel dissolution during galvanostatic oxidation, then Q_a^t should be strongly dependent on the transition time and the aggressiveness of the solution. With increasing charging rate, i_a^0, or decreasing solution agressiveness, the contribution of oxide chemical dissolution towards Q_a^t should decrease and the current efficiency for oxide growth should eventually approach 100 per cent. This is certainly not the case here, and a model involving more than simply chemical dissolution must be proposed to explain the results. Alternative models would include: (i) potential dependent oxide dissolution as previously proposed by other workers for bulk oxides[23–27]; (ii) electrochemical dissolution of cations under the influence of a high field across the oxide[28, 29]; (iii) local breakdown and repair of the oxide at defect sites within the film, these being the areas which are most susceptible to chemical dissolution[2, 17–19, 30, 31]. Consistent with previous work[2], model (iii) will be adopted as the most probable explanation for the present results.

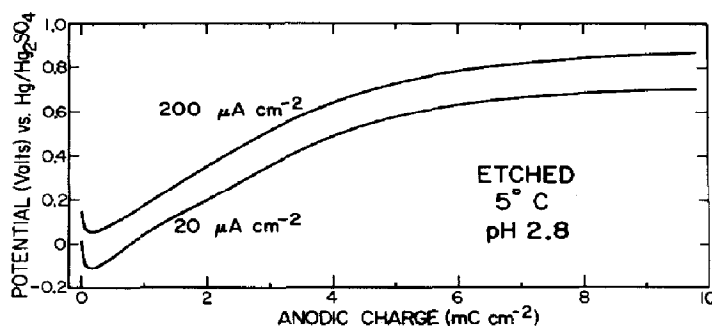In terms of the defect model, repair of the oxide is

Fig. 5. Anodic charging profiles for etched nickel electrodes in pH 2.8 Na_2SO_4 at 5°C at 20 μA cm^{-2} and 200 μA cm^{-2}.

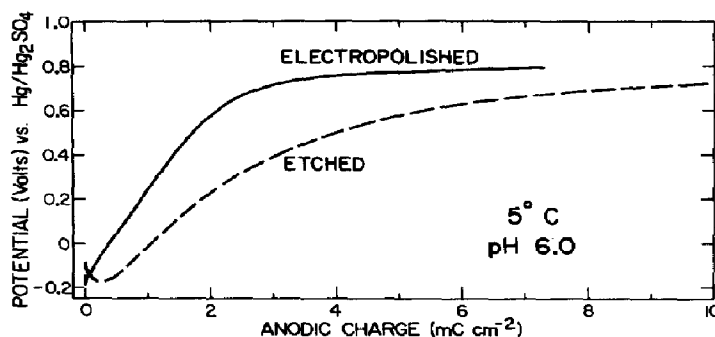Fig. 6. Anodic charging profiles, at 20 μA cm^{-2} in pH 6.0 Na$_2$SO$_4$ at 5°C for electropolished nickel (———) and etched nickel (———).

an inefficient process involving both oxide formation, $Ni + H_2O \rightarrow NiO + 2H^+ + 2e$, and metal dissolution, $Ni \rightarrow Ni^{2+} + 2e$, two potential dependent reactions. The increase in anodic potential, V_a, through the transient region when charging at a constant i_a^0 is due to an increase in oxide film stability with amount of charge passed, ie the fewer breakdown and repair events which occur, the higher must be V_a to achieve the same rate of nickel dissolution. Since the rate of increase of V_a with anodic charge Q_a, (dV_a/dQ_a), is almost constant, and the defect density is decreasing, the current efficiency for oxide growth (or perfection) must be decreasing so that the same anodic current can be handled by the reduced active area[2]. The reason for the constancy of Q_a^t at widely different charging rates (Table 1) is related to the fact that the entire charging profile is shifted to higher anodic potentials at the higher charging rates (Fig. 5). In terms of the defect model, these higher anodic potentials result in a more rapid rate of nickel dissolution in comparison with oxide formation, for any particular condition of the surface, so that the same Q_a^t can pass even at widely different transition times. The same reasoning explains the observations that pH and temperature have little influence on Q_a^t. While these parameters have a very major influence on the rate of oxide chemical dissolution and therefore the ability of a particular charging current to passivate a surface (as opposed to activating it), once passivation has been achieved the charge Q_a^t reflects the influence of anodic potential on the repair kinetics of the oxide. Any change in the breakdown kinetics associated with the different solution aggressiveness is compensated for by a change in anodic potential which alters the repair kinetics and thereby keeps the overall efficiency of film development approximately constant $(cf[2])$.

In the above discussion it was noted that once the solution pH and temperature and the anodic charging rate have been adjusted so that galvanostatic passivation occurs, dV_a/dQ_a is generally independent of these parameters for both electropolished nickel and etched nickel. However, under the same solution and charging conditions, dV_a/dQ_a is substantially different for electropolished nickel compared with etched nickel (Fig. 4). It is not simply that the oxide on etched nickel chemically dissolves more rapidly than that on electropolished nickel since it has been shown that chemical dissolution by itself does not explain the current

efficiency in the transient region. The large increase in Q_a^t for etched nickel is also not due to an increase in electrode roughness or to the formation of a thicker oxide film. An electropolished electrode given a similar etch by open-circuit treatment in pH 2.8 Na$_2$SO$_4$ at 25°C showed only a small (< 10 %) increase in Q_a^t, and X-ray emission film thickness measurements and electron microscopy[12] indicate an increase in roughness of etched nickel over electropolished nickel of < 20 per cent. Furthermore, in the present study, film thickness measurements on specimens removed after the transient region indicate that the oxide is ~ 12 Å thick on both electropolished and etched nickel. Thus, the most likely interpretation of the difference of dV_a/dQ_a between electropolished and etched nickel is that following film breakdown, film repair and the associated increase in oxide perfection occurs with a lower current efficiency on etched nickel. Indeed, the increased rate of open-circuit breakdown of the oxide on etched nickel can be interpreted in terms of a lower current efficiency for local film repair as well as an increase in the density of defects. The question arises as to why repair and development of the oxide on etched nickel is such an inefficient process and what is the difference between electropolished and etched nickel which leads to the substantial difference in charging behaviour.

On nickel single crystals it is found that both electropolishing and etching produces epitaxed oxide films of similar particle size and lattice parameter, but of varying ratios of twin-related oxide orientations[12]. During thermal oxidation incoherent twin boundaries present in the film are considered to be effective paths for cation diffusion[12–15], and the increased oxidation rate of etched single crystal and polycrystalline nickel over electropolished nickel can be explained in terms of an increased number of easy diffusion paths in the oxide[12, 9]. By analogy, those boundaries which facilitate nickel diffusion during thermal oxidation could well permit the most nickel to dissolve during anodic polarization, and the more rapid open-circuit breakdown of the oxide on etched nickel can also be explained on this basis. Clearly, to understand more fully why different types of defects in an oxide are repaired and perfected at different rates, further information is needed about the nature of these oxide defects and the influence on them of time and potential of anodization. The present results do in-

dicate, however, that structurally different prior oxide films formed as a consequence of different surface pretreatment can lead to differences in passivation behaviour.

SUMMARY

The rate of chemical dissolution of NiO films is dependent on their stability as well as the aggressiveness of the solution, the latter being determined by electrolyte pH and temperature. The oxide on HNO_3 etched nickel is less stable towards chemical dissolution than that on electropolished nickel, and galvanostatic passivation can only be achieved by operating at a low electrolyte temperature and/or a high solution pH. When the conditions are adjusted so that passivation is achieved by galvanostatic charging, the transient charge is not much influenced by pH, temperature or charging rate. The current efficiency for oxide growth, however, is low (~ 20 per cent) with most of the charge contributing to nickel dissolution. The results suggest that this low current efficiency is not due solely to chemical dissolution of the oxide but can be best explained in terms of breakdown and inefficient repair of the oxide during anodic charging, the transient charge being a measure of the efficiency of oxide growth and development. The transient anodic passivation charge is $\sim 2x$ larger for etched nickel than electropolished nickel which can be explained in terms of structural differences in the two prior oxides influencing the way the film grows and perfects.

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