

811. *Effect of Various Anions on Thickness and Active-oxygen Content of Nickel Oxide Layers formed by Repeated Anodic-Cathodic Cycling; the Specific Effect of Chloride Ions and Its Dependence on the Nature of the Substrate.*

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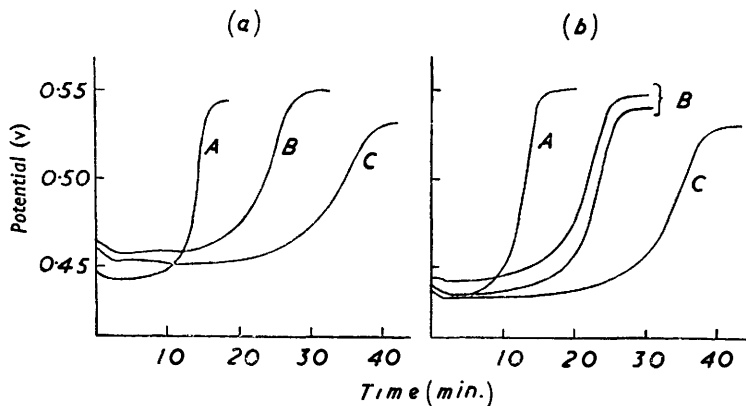
The effect of the fluoride, nitrate, perchlorate, and chloride anions on the thickness and active oxygen content of nickel oxide layers formed by repeated anodic-cathodic cycling on nickel and platinum substrates in a bath of a nickel salt was investigated. At concentrations from 10^{-4} to $10^{-3}N$ the first three ions had no effect, and on both substrates the thickness and active-oxygen content were essentially the same as for layers formed in the original bath alone. On a nickel substrate, chloride ions at or above $0.02N$ exhibited a specific effect, bringing about, though indirectly, considerable increase in layer thickness, and preventing almost completely the formation of active oxygen. On platinum these ions were ineffective. The specific effect of chloride ions is discussed and the advantage of repeated cycling in furnishing oxide layers of reproducible behaviour during anodic oxidation in $1.0M$ -sodium hydroxide over that of mere cathodic deposition illustrated.

THAT metals which tend to be passive can be activated by certain anions is well known. These anions are considered¹ somehow to hamper the progression of passivation

¹ Kabanov, Burstein, and Frumkin, *Discuss. Faraday Soc.*, 1947, **1**, 259; Hoar, *Trans. Faraday Soc.*, 1949, **45**, 633.

$\text{OH}^- \longrightarrow \text{OH} + e$ while allowing free anodic dissolution of the metal. However, the effect of such anions on anodic oxidation of a lower oxide when allowed to proceed on substrates of different materials with constant composition on the solution side of the interface has not previously been investigated. The preparation of nickel oxide layers by repeated anodic-cathodic cycling was described recently by Wynne-Jones and his co-workers;² with both nickel and platinum as substrates, the formed layer at the end of the last cathodic duration was shown³ by X-rays to be essentially $\text{Ni}(\text{OH})_2$, and contained measurable quantities of active oxygen whose presence is undoubtedly pertinent since nickelous hydroxide free from active oxygen can be formed by cathodic deposition under similar conditions.⁴

FIG. 1. Plot of electrode potential relative to that of a mercury-mercuric oxide electrode during anodic oxidation of layers of nickelous hydroxide deposited during (A) 5 min., (B) 10 min., and (C) 15 min. on (a) platinum and (b) nickel.



From a bath containing (cf. ref. 3) 0.1N-nickel sulphate, 0.1N-sodium acetate, and 0.001N-sodium hydroxide, nickelous hydroxide was cathodically deposited on nickel and platinum with a current efficiency of almost 100%: $\text{Ni}^{++} + 2\text{H}_2\text{O} + 2e \longrightarrow \text{Ni}(\text{OH})_2 + \text{H}_2$. Analyses of nickel in the formed layers agreed to within 3–5%; typical amounts of nickel (10^{-6} g.-atom/cm.²) on platinum at a constant current of 2.0 mA/cm.² of apparent area after various periods (min.) were 1.5, 0.9; 3.0, 1.9; 5.0, 2.9; 7.5, 4.4; 10.0, 6.1; 15.0, 9.2. The layers were pale green and did not contain active oxygen. When freshly deposited, then anodically oxidised in 1.0M-sodium hydroxide at 0.5 mA/cm.², they gave plots as shown in Fig. 1. Before the final resting stage corresponding to evolution of oxygen, each plot shows an arrest of length almost proportional to the layer thickness and, judged by the amount of electricity passed, such as to correspond to the oxidation of bi- to ter-valent nickel. However, it is conspicuous that the curves for layers of the same thickness on the different substrates do not coincide.

These results seem to support Wynne-Jones's suggestion that during repeated cycling oxide layers are formed mainly during the cathodic duration of the current. Oxidation of the deposited layer followed by evolution of oxygen, two processes due to the primary discharge of hydroxyl ions, would then occur during the anodic duration. As it appeared that this discharge might be hindered by the presence of other ions, we did the present work.

Produced by the eleven-cycle scheme² at a constant current of 2.0 mA/cm.² the oxide layer obtained on each of nickel and platinum in the original bath appeared dark grey or

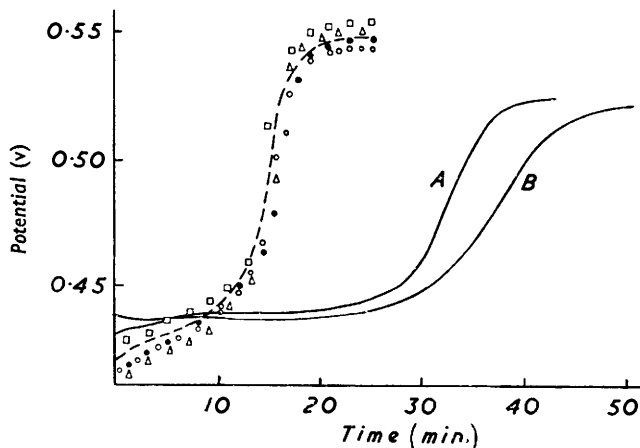
² Briggs, Jones, and Wynne-Jones, *Trans. Faraday Soc.*, 1955, **51**, 1433.

³ Briggs and Wynne-Jones, *ibid.*, 1956, **52**, 1272.

⁴ Salt, *Discuss. Faraday Soc.*, 1947, **1**, 169.

almost black. Its nickel and active-oxygen contents were $3.7\text{--}3.9 \times 10^{-6}$ and $4\text{--}6 \times 10^{-7}$ g.-atom/cm.² respectively, agreeing satisfactorily with previous results.² When oxidised anodically in 1.0M-sodium hydroxide at 0.5 mA/cm.², the metal gave a plot for such a layer as shown in Fig. 2 (broken line). With the bath made 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} N in each of F⁻, NO₃⁻, ClO₄⁻, and Cl⁻ ions successively by adding the potassium salts, and using a nickel substrate, the first three anions at all concentrations, and chloride ions up to 0.01N, had no effect on appearance, composition, or behaviour during anodic oxidation of the layer formed. At a critical concentration of 2.0×10^{-2} N, chloride ions brought about a

FIG. 2. Plot of electrode potential relative to that of a mercury-mercuric oxide electrode during anodic oxidation of layers of nickelous hydroxide.



The broken line refers to the bath alone, and the symbols O, ●, and Δ to the presence of 0.1N-fluoride, -nitrate, and -perchlorate ions respectively, all on nickel and on platinum. □ refers to 0.1N-chloride ion on platinum, and curves A and B to 0.02 and 0.04N-chloride ion, respectively, on nickel.

considerable increase in layer thickness. The nickel content increased to about 7.5×10^{-6} g.-atom/cm.², and that of active oxygen decreased to a trace; the layer appeared greyish-green. At 0.04N-Cl⁻, the layer formed was not easily visible; its nickel content was only slightly greater, *viz.*, 7.8×10^{-6} g.-atom/cm.², and it contained almost no active oxygen. With platinum no anion was effective, although the layer formed in presence of 0.1N-chloride ion resisted dissolution in dilute sulphuric acid somewhat. Some anodic plots are shown in Fig. 2.

The specific effect of chloride ions in increasing layer thickness on a nickel but not on a platinum substrate, while preventing almost completely the deposition of active oxygen is no doubt significant since it shows that the different processes involved must be intimately related. According to the adsorption theory of Kabanov *et al.*¹ and judged by the behaviour of the various anions at the mercury interface,⁵ the effect may be explained by the ready specific adsorption of chloride ions which so increase the field energy in the electrical double layer condenser that the nickel atoms of the substrate are loosened. The activated anodic process $\text{Ni} \longrightarrow \text{Ni}^{++} + 2e$ then proceeds in preference to the passivating process $\text{OH}^- \longrightarrow \text{OH} + e$. On a platinum substrate chloride ions up to 0.1N do not hinder the deposition of hydroxyl ions, nor do they on a nickel substrate below a critical concentration of 0.02N. The pH of the bath, with or without added salts, varied between 6.5 and 6.8. At the critical chloride-ion concentration, the ratio Cl⁻ : OH⁻ is then roughly 10,000 : 1. The same ratio causes change⁶ from preferential water-line

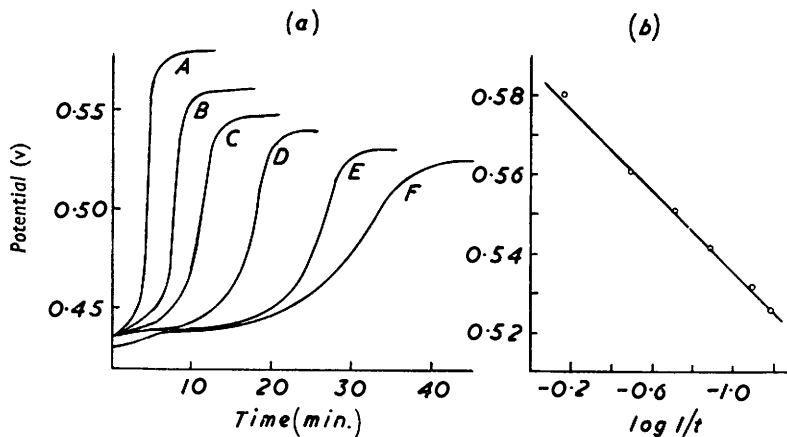
⁵ Grahame, *Chem. Rev.*, 1947, **41**, 441; Grahame, Poth, and Cummings, *J. Amer. Chem. Soc.*, 1952, **74**, 4422.

⁶ Peers, *Trans. Faraday Soc.*, 1955, **51**, 1748.

attack to general attack on oxide-bearing iron anodes. From our measurements of the differential capacity of mercury in an excess of a supporting electrolyte which did not exhibit specific adsorption and containing both anions, the same ratio caused the pseudo-capacity peaks on the anodic side of the electrocapillary maximum to coincide, thus indicating simultaneous dissolution of mercury as chloride and hydroxide.⁷

The activating effect of the chloride ions seems, however, to bear indirectly on the increase in layer thickness brought about in their presence. In a bath 0.1N with respect to Ni⁺⁺ ions and of pH almost equal to the precipitation pH value of nickelous hydroxide⁸ (6.7), the anodically released Ni⁺⁺ ions should be precipitated as Ni(OH)₂. If this happened, the hydroxide would be deposited probably some distance from the anode surface. This was supported by the fact that at a polished nickel substrate anodised first in the presence of 0.04N-chloride ions at 2.0 mA/cm.² for 15 min., then in 1.0M-sodium hydroxide at 0.5 mA/cm.², the oxygen-evolution potential in the latter solution reached, within 3 to 4 minutes from the start of polarisation, 0.594–0.600 v with respect to a mercury–mercuric

FIG. 3. (a) Plot of electrode potential relative to that of a mercury–mercuric oxide electrode during anodic oxidation of nickelous hydroxide layers deposited during (A) 1.5 min., (B) 3.0 min., (C) 5.0 min., (D) 7.5 min., (E) 12.0 min., (F) 15.0 min. on nickel. (b) Oxygen-evolution potential as a function of time of deposition, followed by cycling.



oxide electrode with no indication of previous separation of nickelous hydroxide on the electrode surface. The stimulating effect of chloride ions may therefore be considered as primarily due to the hindrance of hydroxyl-ion deposition so that the nickelous hydroxide formed during the successive cathodic intervals accumulates. For the eleven-cycle scheme used, the total duration of the cathodic current was 15.0 min., and cathodic deposition yields in this period approximately 9.2×10^{-6} g.-atom/cm.²; this agrees quite satisfactorily with that found experimentally for layers obtained on nickel by repeated cycling in presence of chloride ions.

It seems that the main advantage in preparing nickel oxide layers by repeated cycling² lies in the co-deposition of active oxygen. That the latter was essential for a well-defined and reproducible behaviour during anodic oxidation in alkali was substantiated as follows. After having been deposited cathodically on nickel, the layer, while still in the bath, was subjected to one cycle only, first anodically then cathodically, at the same current density and for the same period, *t*, as that of deposition. The formed layer appeared dark grey, and the active-oxygen content varied between 1 and 3×10^{-7} g.-atom/cm.², independently of thickness. The anodic plots for the so-treated layers in 1.0M-sodium hydroxide are shown in Fig. 3(a); the arrest indicating oxidation of bi- to ter-valent nickel occurs sharply

⁷ Unpublished results; also Moussa, Sammour, and Ghaly, *J. Phys. Chem.*, 1958, **62**, 1017.

⁸ Britton, "Hydrogen Ions," Chapman and Hall, London, vol. 2, 1942, p. 39.

at 0.442 v. Further, the plot of oxygen-evolution potential against $\log (1/t)$ [Fig. 3(b)], is almost straight, indicating that on such layers the relation between oxygen overpotential and current density is logarithmic, and that the effective current density is inversely proportional to the layer thickness as found by Jones and Wynne-Jones with layers formed by repeated cycling.⁹

EXPERIMENTAL

Nickel (Merck) was 99.8% pure. The substrates were in the form of sheets 1×2 cm. The nickel sheets were jammed into stiff wire wedges of the same material, and were kept tightly in position by slipping the wires into thick narrow-bored Polythene tubes. The platinum sheets were welded to short platinum wires which were then sealed into soda-glass tubes as usual. Before use, the nickel sheets were polished bright with 3/0 emery paper. The platinum sheets were first boiled in concentrated nitric acid for a few min., washed thoroughly, and then burnt in an alcohol flame. All other materials were "AnalaR."

Oxide layers were formed, cathodically and by repeated cycling, in a Haring cell with a middle compartment of about 80 ml. separated from the side compartments by sintered-glass discs. Platinum spirals served as auxiliary electrodes. The layers were anodically oxidised in a simple Pyrex cell with its lead-in capillary kept as close as possible to the anode surface. Polarisation and potential-measuring circuits were essentially the same as described before.¹⁰ Deposition and polarisation were made at $25^\circ \pm 0.1^\circ$ in an air-bath.

Active oxygen was determined iodometrically.⁹ Nickel was determined complexometrically; after the liberated iodine had been titrated the solution was made alkaline with ammonia, then titrated with 10^{-3} M-disodium ethylenediaminetetra-acetate dihydrate solution, with murexide as indicator.¹¹ The method gave very accurate results and the end-point was quite sharp.

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⁹ Jones and Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 1260.

¹⁰ Moussa, Embaby, and Sammour, *J.*, 1958, 2481.

¹¹ Flaschka, *Mikrochim. Acta*, 1952, **39**, 38.