# 704. *The Anodic Oxidation of Metals at Very Low Current Density. Part II.* Nickel.*

By S. E. S. El Wakkad and (Miss) Sayeda H. Emara.

The conflicting results of various workers on the variation of the anode potential with the quantity of electricity passed when the nickel electrode is forced from evolution of hydrogen to that of oxygen, as well as on the type of oxides formed on the surface of the metal before oxygen evolution, have been clarified by carrying out the anodic oxidation of nickel in solutions of different pH values at very low current density. It is shown that the oxides formed on the anode before evolution of oxygen depend on the polarising current; at extremely low current density the oxides NiO, $Ni_3O_4$, $Ni_2O_3$, and $NiO_2$ are formed before oxygen is evolved, but at higher current density only the oxides NiO, $Ni_2O_3$, and $NiO_2$ appear. The primary anodic products are, however, the oxides NiO and $NiO_2$, $Ni_3O_4$ and $Ni_2O_3$ being formed from a secondary reaction between NiO and $NiO_2$. The higher oxides are unstable, decomposing to NiO, the most stable oxide in contact with the metal.

But little work has been carried out on the anodic oxidation of nickel. The results obtained are conflicting, and information on the type of oxide formed on the passive nickel is obscure. For instance, early observations on the nickel electrode in the Edison accumulator (Zender, *Z. Elektrochem.*, 1905, **11**, 809; 1906, **12**, 463; 1907, **13**, 572; Bellucci and Clavari, *Atti R. Accad. Lincei*, 1905, **14**, ii, 234; Grube and Vogt, *Z. Elektrochem.*, 1907, **13**, 572; 1938, **44**, 352; Foerster, *ibid.*, 1907, **13**, 414; 1908, **14**, 17, 285; 1910, **16**, 461) threw some doubt on whether $Ni_2O_3$ is formed primarily, and suggested that the main oxides formed on the nickel electrode are NiO and $NiO_2$, the oxides $Ni_2O_3$ and $Ni_3O_4$ being formed as solid solutions arising from interaction of NiO with $NiO_2$. On the other hand, the general conclusion reached from passivity studies (Evans and Stockdale, *J.*, 1929, 2651; Transtad, *Z. physikal. Chem.*, 1929, **142**, 272; Müller, *Monatsh.*, 1927, **48**, 559; Müller, Cameron, and Machu, *ibid.*, 1932, **53**, 73; Georgi, *Z. Elektrochem.*, 1932, **38**, 681, 714; 1933, **39**, 736) is that when nickel becomes passive it is covered with a protective film probably of the oxide $Ni_2O_3$ or the hydroxide $Ni(OH)_3$. Recently, Hickling and Spice (*Trans. Faraday Soc.*, 1947, **43**, 762), using the oscillographic method, showed that this oxide is the only one formed upon the metal anode before evolution of oxygen, and Besson (*Compt. rend.*, 1946, **223**, 28) showed that on nickel anodes NiO, $Ni_3O_4$, and $Ni_2O_3$ were formed but he found no evidence for $NiO_2$. VolchKova, Antonova, and Krasil'Shchikov (*J. Phys. Chem., U.S.S.R.*, 1949, **23**, 714) showed also that $Ni(OH)_2$ and $Ni_2O_3$ were formed on nickel anodes and that at high voltages oxygen is liberated on $Ni_2O_3$.

This matter has now been clarified by studying the anodic oxidation of nickel at very low current density, the technique and procedure developed for platinum (Part I, *loc. cit.*) being used. In this case attention has been directed primarily to the behaviour of nickel in alkaline solutions, where passivity is set up almost at once. From this study it is shown that, when nickel is forced from the hydrogen-evolution potential to the value for oxygen evolution, the oxides formed on the anode before oxygen is evolved depend on the polarising current. Although at extremely low current density the oxides NiO, $Ni_3O_4$, $Ni_2O_3$, and $NiO_2$ were formed before oxygen evolution, yet at higher current density only NiO, $Ni_2O_3$, and $NiO_2$ appeared. The primary anodic products are, however, the oxides NiO and $NiO_2$, the other oxides being formed from them by a secondary reaction. The higher oxides are unstable, decomposing to NiO, which is the most stable oxide in contact with the metal.

## Experimental

The electrical circuit and the electrolytic cell used were as previously described (Part I, *loc. cit.*). The nickel electrodes used were prepared by electrodeposition at a current of 20 mA/electrode for 30 min. from a bath containing, per l., $NiSO_4,6H_2O$ (300 g.), NaCl (3 g.), and $H_3BO_3$ (6 g.) on a platinum plate of 1·95 sq. cm. apparent area. The same results were obtained

---

* Part I, *J.*, 1952, 461.

if nickel was deposited on platinum previously plated with copper. The electrode was washed several times in conductivity water and then with the solution in which it was to be studied, before it was placed in its compartment in the electrolytic cell. Each experiment was carried out with a freshly prepared electrode. The cathode was a platinum spiral placed in such a position as to ensure uniform distribution of the polarising current at the anode surface.

Measurements were carried out mainly in the alkaline solutions, 0·1N-sodium hydroxide (pH 13), N-sodium carbonate (pH 11·5), and 0·1N-borax (pH 9·2). Anodic polarisations were carried out also in acetate buffer mixture of pH 5·6 (Cohn, *J. Amer. Chem. Soc.*, 1927, **49**, 173; 1928, **50**, 696). The solution was boiled before use and cooled in an atmosphere of pure nitrogen to remove any dissolved oxygen.

The detailed experimental procedure for obtaining the anodic, the cathodic, and the decay curves was essentially as described in Part I (*loc. cit.*). Two different polarising currents were used in the anodic polarisation, namely, 5 and 15 μA per electrode. The e.m.f. measurements were carried out exactly as for platinum (*loc. cit.*).

*Measurements of the Oxide Potentials of Nickel.*—The reports of previous workers on the different oxides of nickel are not in agreement. Bellucci and Clavari (*loc. cit.*) found that the degree of oxidation of nickel depended on the nature of the oxidising agent used and that none of these reagents led to the formation of an oxide having a formula $Ni_2O_3$. On oxidation with bromine in the presence of excess of potassium carbonate at 0°, and on washing the precipitate with concentrated potassium carbonate solution, the ratio Ni : O was 1 : 1·907, *i.e.*, nearly that required for $NiO_2$. This oxide was found to lose oxygen, forming substances of composition varying with the conditions. When $NiO_2$ was dried over calcium chloride at 100°, it passed almost always into a substance in which the Ni : O ratio varied from 1 : 1·4 to 1 : 1·3. The authors therefore regarded the oxides $Ni_2O_3$ and $Ni_3O_4$ as mixtures of $NiO_2$ and NiO.

On the other hand, Howell (*J.*, 1923, **123**, 669, 1772), by following the rate of decomposition of the precipitate obtained by the action of alkali and hypochlorite on nickel sulphate solution, found that in general the precipitate consisted of the hydroxide $Ni(OH)_2$, the sesquioxide, and the dioxide, but with sufficient hypochlorite the whole of the nickelous hydroxide was oxidised to the other two oxides.

We prepared the oxides NiO, $Ni_3O_4$, and $NiO_2$ by recommended methods (Archibald, "The Preparation of Pure Inorganic Substances," New York, 1932, p. 349; Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 15, Longmans Green and Co., 1947, pp. 391, 392).

*Potential Measurements.*—For these measurements a portion of the oxide was shaken with 0·1N-sodium hydroxide solution, and in measuring the potentials of systems containing NiO, a short nickel electrode was wholly immersed in the sludge formed and the potential was measured against a saturated calomel electrode in an atmosphere of pure nitrogen. When the oxidation–reduction potential between the two oxides, $Ni_3O_4$ and $Ni_2O_3$, was measured, the oxides were mixed in the 0·1N-sodium hydroxide solution, and a short platinum wire electrode was wholly immersed in the sludge formed; the potential was also measured in an atmosphere of pure nitrogen against a saturated calomel electrode. All the electrical measurements were carried out in an air thermostat at 25° ± 0·01°.

## RESULTS AND DISCUSSION

In Fig. 1, curve *A* is the characteristic anodic polarisation curve of nickel at 25° with a polarising current of 5 μA per electrode in 0·1N-sodium hydroxide. Curve *A'* is the anodic polarisation curve in the same solution but with a polarising current of 15 μA per electrode. In Fig. 2, Curves *A* and *A'* are the same anodic polarisation curves in 0·1N-sodium carbonate solution of pH 11·5. From these curves it can be seen that nickel gives characteric anodic polarisation curves in which we can detect the following stages: (1) a rapid linear rise of potential; (2) a somewhat slow rise of potential accompanied by five or by four steps according as the polarising current is 5 or 15 μA per electrode.

The first stage can be attributed, as in previous cases (Hickling and Spice, *Trans. Faraday Soc.*, 1947, **43**, 762), to the charging of the double layer. Measurements from a large number of polarisation curves in 0·1N-sodium hydroxide gave an average value of the double layer capacity of about 900 μF per apparent sq. cm. for our nickel electrode, and in N-sodium carbonate the average value was about the same. The nature of the second stage is very important, since the number of steps depended upon the polarising current used.

*The Oxide Potentials of Nickel.*—In Table 1 are shown the results obtained for the potentials of the different systems of nickel oxides on the hydrogen scale in 0·1N-sodium hydroxide. The potentials of the first three systems are our direct experimental measurements, that of the fourth system is a calculated value at the corresponding pH from a knowledge of the potential of the systems $Ni(OH)_2$–$NiO_2$ (Foerster, *loc. cit.*) and $Ni(OH)_2$–$Ni_2O_3$ (Hickling and Spice, *loc. cit.*), and that of the last system is due to Foerster (*loc. cit.*).

TABLE 1.

| System | Ni–NiO | $NiO$–$Ni_3O_4$ | $Ni_3O_4$–$Ni_2O_3$ | $Ni_2O_3$–$NiO_2$ | $NiO$–$NiO_2$ |
|---|---|---|---|---|---|
| Potential (v) in 0·1N-NaOH | −0·60 | −0·35 | +0·15 | +0·47 | +0·55 |

FIG. 1.

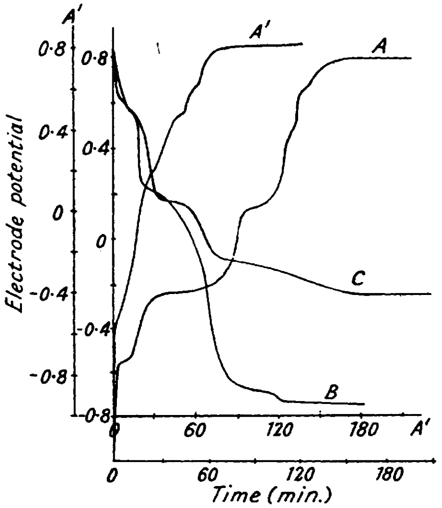
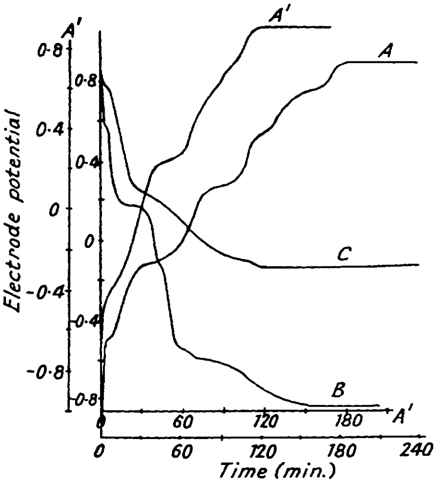


FIG. 2.



In Table 2 the starting potentials of the various steps observed under different polarising conditions (see above) are compared with the potentials of the same five systems at the corresponding pH values. The agreement between the determined equilibrium potentials and the starting potentials of the first four steps in our polarisation curves when using a polarising current of 5 μA per electrode suggests that these steps correspond to the consecutive formation of the oxides NiO, $Ni_3O_4$, $Ni_2O_3$, and $NiO_2$ on the nickel anode before evolution of oxygen. The nature of the fifth step is discussed on p. 3507.

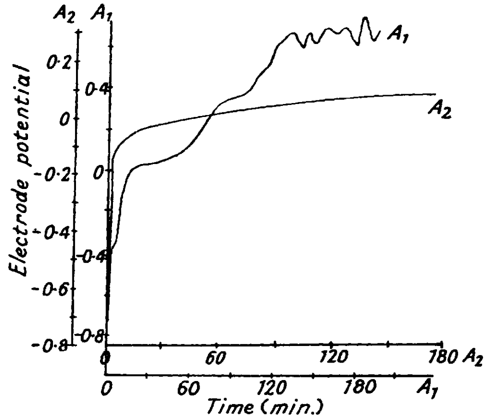
TABLE 2.

| Solution | Ni–NiO | $NiO$–$Ni_3O_4$ | $Ni_3O_4$–$Ni_2O_3$ | $Ni_2O_3$–$NiO_2$ | $NiO$–$NiO_2$ |
|---|---|---|---|---|---|
| | | Equilibrium potentials | | | |
| 0·1N-NaOH | −0·60 | −0·35 | +0·15 | +0·47 | +0·55 |
| N-$Na_2CO_3$ | −0·51 | −0·26 | +0·24 | +0·56 | +0·64 |
| | | Starting potentials (v) of steps with polarising current of 5μ amp. | | | |
| 0·1N-NaOH | −0·58 | −0·32 | +0·13 | +0·45 | +0·61 |
| N-$Na_2CO_3$ | −0·51 | −0·20 | +0·24 | +0·50 | +0·70 |
| | | Starting potentials (v) of steps with polarising current of 15μ amp. | | | |
| 0·1N-NaOH | −0·58 | — | +0·15 | +0·45 | +0·60 |
| N-$Na_2CO_3$ | −0·48 | — | +0·20 | +0·55 | +0·67 |

The quantity of electricity passed in the first step was about 1200 μcoulomb/apparent sq. cm., which would correspond to the formation of $3·75 \times 10^{15}$ atoms of oxygen; the density of nickel being taken as 8·8, the diameter of the nickel atom may be calculated as approximately $2·2 \times 10^{-8}$ cm., and hence there would be about $2 \times 10^{15}$ atoms of metal per true sq. cm. A rather crude estimate of the ratio of the real to the apparent area of our nickel electrode can be obtained from the value of the capacity of the double layer at the electrode in 0·1N-sodium hydroxide solution. The capacity of the double layer at platinum anodes before formation of oxide as obtained from previous studies (Hickling, *Trans. Faraday Soc.*, 1945, **41**, 333; Part I, *loc. cit.*) can be estimated as 100 μF per true sq. cm. If the difference between the capacity of our nickel electrode and the platinum electrode is assumed to be due only to the difference in the area, the ratio of the real to the apparent area of our nickel electrode will be about 9. This shows that the quantity of electricity passed in the first step corresponds to the formation of less than a unimolecular layer of NiO on the surface of the nickel. In this respect nickel is similar to cobalt (El Wakkad and Hickling, *Trans. Faraday Soc.*, 1950, **46**, 820). This fact may explain the agreement between the potential of the second step when using a polarising current of 5 μA per electrode with the experimentally determined value of the system NiO–$Ni_3O_4$ when using a nickel electrode.

The quantity of electricity passed in the second step was about 6000 μcoulomb/apparent sq. cm., which would liberate about $9 \times 10^{15}$ atoms oxygen; this suggests that an approximately unimolecular film of $Ni_3O_4$ is formed. The quantity of electricity passed in the third step was about 13,500 μcoulombs/apparent sq. cm., which is enough for the liberation of $4{\cdot}2 \times 10^{16}$ atoms of oxygen. This suggests that nickelic oxide is about two molecules thick. The nickelic oxide is further oxidised to the dioxide $NiO_2$.

FIG. 3.



On the other hand when using a polarising current of 15 μA/electrode (Figs. 1 and 2, curves *A'*) we get in the second stage four steps instead of five. From Table 2, the first three steps correspond to the formation of the oxides NiO, $Ni_2O_3$, and $NiO_2$. The nature of the last step is discussed on p. 3508.

The interesting fact that the numbers of steps differ according as the polarising current is 5 or 15 μA/electrode can be explained by consideration of the work of Bellucci and Clavari and of Foerster (*locc. cit.*), in which they considered that the oxide $Ni_3O_4$ is a solid solution or an oxide formed from a secondary reaction between NiO and $NiO_2$; for, at the very low current density, where the rate of discharge of hydroxyl ions is very small compared with the rate of combination between the oxides to form $Ni_3O_4$, this oxide will appear on the anodic polarisation curve. On the other hand, when the polarising current is increased to 15 μA/electrode and the rate of discharge of hydroxyl ions becomes higher than the rate of combination, the formation of the oxide $Ni_3O_4$ is greatly suppressed, and we get directly $Ni_2O_3$. The oxide $Ni_2O_3$ was considered also (Bellucci and Clavari, *loc. cit.*) to be a mixture of NiO and $NiO_2$; the results obtained, however, indicate that the rate of its formation must be higher than the rate of discharge of hydroxyl ions when a polarising current of 15 μA/electrode is used. If the polarising current is increased further, so that the rate of discharge of hydroxyl ions becomes still higher, a stage may be reached at which $Ni_2O_3$ will not appear and the anodic process will lead directly to the formation of $NiO_2$ after

NiO. We attempted an experiment at such a higher current density, but unfortunately the changes in the anodic potential were too rapid to be recorded by our direct potentiometric method.

The nature of the last step in the anodic polarisation curves is very interesting and may throw some light on this point, for comparison of the potential of this step with all the known oxidation–reduction potentials between the different oxides of nickel shows it to be near that of the system $NiO$–$NiO_2$, thus confirming the view that the NiO and $NiO_2$ are the primary oxidation products at a nickel anode. The oxide $Ni_3O_4$, and to some extent $Ni_2O_3$, are formed in secondary reactions between NiO and $NiO_2$.

The cathodic curves (*B* in Figs. 1 and 2) indicate reduction of the oxides $NiO_2$,$Ni_2O_3$, and NiO. There is no step corresponding to the reduction of the oxide $Ni_3O_4$.

The decay curves (*C* in Figs. 1 and 2) indicate clear steps at the potential of +0·60 and +0·15 v in the 0·1N-sodium hydroxide solution and at +0·70 and 0·25 v in N-sodium carbonate. Thus decay curves indicate that both $NiO_2$ and $Ni_2O_3$ are unstable. The decay curves in all cases approach very slowly the Ni–NiO potential, which is reached after about 24 hr. This shows that the latter oxide is the most stable one on the metal surface.

In the borate solution (curve *A*, Fig. 3) the potentials of the steps formed after the charging of the double layer indicate the formation of NiO, $Ni_3O_4$, and $Ni_2O_3$ on the electrode surface, after which the potential became irregular, indicating that the film formed subsequently (which may be a basic borate) is non-adherent and peals away. In more acid solutions, *i.e.*, in acetate buffer of pH 5·6 (curve $A_2$, Fig. 3) the electrode potential never rises to that of oxygen evolution, but the curve shows only anodic dissolution of the metal.

CAIRO UNIVERSITY, FACULTY OF SCIENCE, CAIRO, EGYPT.

[*Received, April* 13*th*, 1953.]