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# RATE OF DIFFUSION OF PROTONS IN NICKEL OXIDES AND OXYGEN OVERPOTENTIAL AT A NICKEL OXIDE ELECTRODE

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Previous papers<sup>1,2</sup> have given results for the variation of the rate of diffusion of protons in nickel oxides with potential and solution composition in LiOH, NaOH, and KOH. The present paper reports a further study by the previous technique of the diffusion of protons in nickel oxides, in particular of the effect of impurities present in solution on the rate of diffusion of protons and on the overpotential accompanying the evolution of oxygen.

## EXPERIMENTAL

Fig. 1 shows plots of  $\phi$  against  $\log i$  for the oxygen overpotential on nickel, coated with an oxide film, in 3.3 N KOH alone and containing respectively  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  (each at a concentration of 10 g litre<sup>-1</sup>). It is seen that at the more positive potentials the slope (the constant  $b$  in the Tafel equation) varies from 0.068 to 0.084 V, while at lower potentials inflections are observed on the curves, and  $b$  increases to 0.142 V in the case of pure KOH. Fig. 1 also shows that addition of  $\text{Zn}^{2+}$  increases the oxygen overpotential, and addition of  $\text{Al}^{3+}$  increases it still further.

Fig. 2 shows the dependence of the logarithm of the proton diffusion current through the nickel oxide film ( $i_H$ ,  $\mu\text{A}$ ) on potential ( $\phi$ , V) in the above three solutions†. In the presence of  $\text{Al}^{3+}$  the points are seen to deviate, throughout the potential range investigated, from the

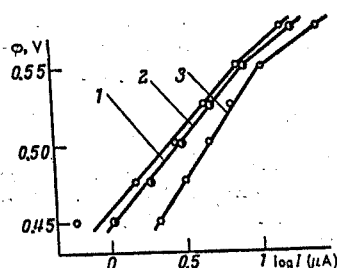


Fig. 1. Dependence of  $\phi$  on  $\log I$  in: 1) 3.3 N KOH + Al (10 g litre<sup>-1</sup>); 2) 3.3 N KOH + ZnO (10 g Zn litre<sup>-1</sup>); 3) 3.3 N KOH.

† In contrast to the previous work<sup>1</sup>, the cathode compartment contained 4 N KOH.

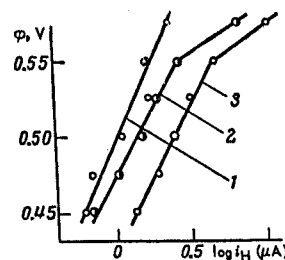


Fig. 2. Dependence of  $\phi$  on  $\log i_H$  (numbering of curves as in Fig. 1).

linear dependence of  $\phi$  on  $\log i_H$  of slope 0.21 V. In pure KOH and in the presence of  $\text{Zn}^{2+}$  the curves undergo a break, as in the case of the oxygen overpotential. At high potentials the slope of these curves varies from 0.066 V (for 3.3 N KOH +  $\text{Zn}^{2+}$ ) to 0.070 V (for 3.3 N KOH), whereas at lower potentials (below 0.55 V) the slopes increase to 0.176 and 0.183 V respectively. Fig. 2 also shows that, throughout the potential range investigated, the proton diffusion current is diminished by addition of  $\text{Zn}^{2+}$ , and still further by  $\text{Al}^{3+}$ .

Comparison of Fig. 2 with Fig. 1 shows a definite relation between proton diffusion current and oxygen overpotential, the greater the latter the smaller being the current through the nickel oxide film. The same rule was observed with 2 N solutions of LiOH, NaOH, and KOH.<sup>1</sup>

Great theoretical interest attaches to the effect of cations having a considerably higher charge than those ( $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Ni}^{4+}$ ) in the oxide under examination. For this purpose a study was made of the behaviour of the nickel oxide electrode in 3.3 N KOH containing  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$ . The oxygen overpotential curves in 3.3 N KOH with and without the addition of  $\text{MoO}_3$  and  $\text{WO}_3$  (10 g of Mo and of W respectively per litre) show (Fig. 3) that  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$  have almost the same effect on the oxygen overpotential at a nickel oxide electrode. They lower the overpotential at high potentials and increase it at low potentials. It is also seen that the slope of the  $\phi$ - $\log I$  curves is lower (0.052 V) at the more positive potentials, as in the pure 3.3 N KOH, and increases to 0.114 V at lower potentials.

Fig. 4 shows curves relating the logarithm of the proton diffusion current in nickel oxide with the potential in the above three solutions. As in the case of the oxygen overpotential (see Fig. 3), the curves consist of two sections having different slopes, varying at the higher potentials from 0.049–0.051 V (in the presence of  $\text{WO}_3$  and  $\text{MoO}_3$ ) to 0.070 V (for the 3.3 N KOH), and increasing to 0.176–0.183 V, practically the same in all three solutions, at lower potentials. It is also seen from Fig. 4 that, at higher potentials (above 0.54 V), the proton diffusion current is greater in the presence of  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$  than in 3.3 N KOH alone.

In Fig. 5 the proton diffusion current  $i_H$  (in  $\mu\text{A}$ ) at 0.550 V in 3.3 N KOH is plotted against the cathodic polarisation current on the other side of the foil. It is seen that the rate of diffusion of protons  $i_H$  increases practically linearly with increase in the polarisation current  $I_c$ .

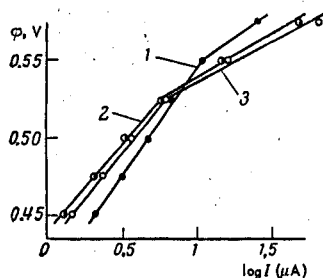


Fig. 3. Dependence of  $\phi$  on  $\log I$  in: 1) 3.3 N KOH; 2) 3.3 N KOH +  $\text{MoO}_3$  (10 g Mo litre $^{-1}$ ); 3) 3.3 N KOH +  $\text{WO}_3$  (10 g W litre $^{-1}$ ).

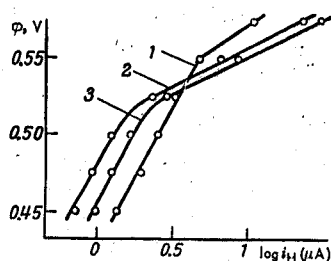


Fig. 4. Dependence of  $\phi$  on  $\log i_H$  (numbering of curves as in Fig. 3).

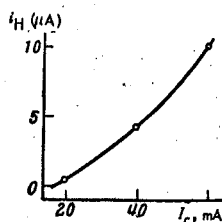


Fig. 5. Dependence of  $i_H$  (in  $\mu\text{A}$ ) on  $I_c$  (mA).

TABLE 1.

| Mono-layers        | 20  | 36   | 40  | 50  | 56   | 60  | 60  | 60  | 60   | 88  | 120  |
|--------------------|-----|------|-----|-----|------|-----|-----|-----|------|-----|------|
| $i_H, \mu\text{A}$ | 6.2 | 11.5 | 7.1 | 8.8 | 15.0 | 8.6 | 8.4 | 9.0 | 10.7 | 9.3 | 10.3 |

It was of interest to investigate the effect of the thickness of the oxide film on the rate of diffusion of protons in the film. Table 1 shows the diffusion currents  $i_H$  at 0.575 V and  $I_c = 40$  mA together with the corresponding film thickness in  $\text{NiO}(\text{OH})$  monolayers. It is impossible to detect any dependence of the proton diffusion current on film thickness. Irreproducibility in the value of the diffusion current probably exceeds variations due to differences in film thickness.

## DISCUSSION

Under the conditions of the present experiments, discharge of  $\text{OH}^-$  ions with subsequent evolution of oxygen and conversion of  $\text{NiO}(\text{OH})$  into  $\text{NiO}_2$  takes place at the electrolyte-oxide film interface. Therefore the layer of film in contact with the electrolyte is close to  $\text{NiO}_2$  in composition. At the metal-oxide film interface,  $\text{NiO}(\text{OH})$  is continuously reduced to  $\text{Ni}(\text{OH})_2$  by protons passing from the metal into the film. Therefore the layer of oxide film in contact with the metal is close to  $\text{Ni}(\text{OH})_2$  in chemical composition. Such a film can be arbitrarily regarded as  $\text{NiO}_2$  in which a proportion of the  $\text{O}^{2-}$  ions have combined with protons to form  $\text{OH}^-$ . Such a film not only differs in chemical composition at different depths but also has different mechanisms of conduction, since nickel hydroxide  $\text{Ni}(\text{OH})_2$  is a  $p$ -type semiconductor, while  $\text{NiO}_2$  is an  $n$ -type semiconductor.

The diffusion of protons through the film is probably accomplished by their transfer from  $\text{OH}^-$  ions to neighbouring  $\text{O}^{2-}$  ions with a corresponding transfer of electrons from one nickel ion to another. Independently of the mechanism of the diffusion of protons, the rate of this process will be proportional to the proton concentration gradient. Hence the rate of diffusion of protons will be determined mainly by the bulk properties of the film.

The effect of the cathodic polarisation current on the rate of diffusion of protons in the nickel oxide film is easily explained on the assumption that increase in the cathodic current produces an increase in the occlusion of hydrogen by nickel, with an increased concentration of protons in the layer of film in contact with the metal. This in turn increases the rate of diffusion of protons in the oxide film as a result of their increased concentration gradient.

It is a far more complicated task to explain the effect of the composition of the solution on the rate of diffusion of protons and on the oxygen overpotential at a nickel oxide electrode.

Let us examine the changes which may occur in  $\text{Ni}(\text{OH})_2$  and  $\text{NiO}_2$  on penetration of their lattice by alkali-metal ions from solution, for example  $\text{Li}^+$  ions, in exchange for nickel ions. The composition of an  $\text{Ni}(\text{OH})_2$  film with  $p$ -type conduction can be written



where  $\alpha$  is the concentration of Ni atoms in the film, and  $x$  the concentration of electron defects, which in the absence of any impurities is equal to the concentration of proton defects.

Let us suppose that, when this film is immersed in a solution of lithium hydroxide,  $\text{Li}^+$  ions replace  $\text{Ni}^{2+}$  ions

TABLE 2.

| Impurity         | Ni(OH) <sub>2</sub> , <i>p</i> -type   |                               |  | NiO <sub>2</sub> , <i>n</i> -type        |                               |                               |                                         |
|------------------|----------------------------------------|-------------------------------|--|------------------------------------------|-------------------------------|-------------------------------|-----------------------------------------|
|                  | concn.*<br>□H <sup>+</sup><br>(theor.) | <i>i</i> <sub>H</sub> (expt.) |  | concn. of<br>□H <sup>+</sup><br>(theor.) | <i>i</i> <sub>H</sub> (expt.) | conducti-<br>vity<br>(theor.) | oxygen<br>over-<br>potential<br>(expt.) |
| Li <sup>+</sup>  | —                                      | —**                           |  | —                                        | —                             | —                             | +                                       |
| Zn <sup>2+</sup> | —                                      | —                             |  | —                                        | —                             | —                             | +                                       |
| Al <sup>3+</sup> | +                                      | —                             |  | —                                        | —                             | —                             | +                                       |
| W <sup>6+</sup>  | +                                      | +***                          |  | +                                        | +***                          | +                             | +***                                    |

+ = increase in the corresponding quantities  $\alpha$ .

- = decrease in these quantities.

\* □H<sup>+</sup> = concentration of proton defects.

\*\* According to data in Ref. 1.

\*\*\* At high potentials.

in the film. After penetration of the Li<sup>+</sup> ions, the composition of the film will be†

$$[a - x - (1 + \gamma)y] \text{Ni}^{2+}(x + \gamma y) \text{Ni}^{3+}y \text{Li}^+ + [2a - x + (1 - \gamma)y] \text{OH}^- [x - (1 - \gamma)y] \text{O}^{2-}. \quad (2)$$

Comparison of Eqns. (1) and (2) shows that the penetration of  $y$  Li<sup>+</sup> ions in exchange for  $y$  Ni<sup>2+</sup> ions in the Ni(OH)<sub>2</sub> lattice having *p*-type conduction results in an increase in concentration of electron defects by  $\gamma y$  and a decrease in the concentration of proton defects by  $(1 - \gamma)y$ .

By examining the analogous changes accompanying penetration of Li<sup>+</sup> ions into the NiO<sub>2</sub> lattice in exchange for Ni<sup>4+</sup> ions, we can show that penetration of cations of lower valency (Li<sup>+</sup>) into an oxide lattice having *n*-type conduction diminishes the concentration of free electrons: *i. e.* it lowers the conductivity and increases the concentration of OH<sup>-</sup> ions or protons. Penetration of ions of higher valency (W<sup>6+</sup>) in exchange for Ni<sup>2+</sup> and Ni<sup>3+</sup> ions in the Ni(OH)<sub>2</sub> lattice must be expected to produce a decrease in the concentration of electron defects, *i. e.* a decrease in conductivity and an increase in the concentration of proton defects; while penetration of W<sup>6+</sup> ions into the NiO<sub>2</sub> lattice must be expected to increase the concentration of "free" electrons, *i. e.* to increase the conductivity and diminish the concentration of OH<sup>-</sup> ions or protons.

Let us compare the above results with experimental data on the effect of impurities on oxygen overpotential and the rate of diffusion of protons in nickel oxides. Table 2 shows that, for a layer of film having *n*-type conduction, a parallel exists between the experimental change in rate of diffusion of protons and oxygen overpotential and the expected change in concentration of proton defects and conductivity. A decrease in the rate of diffusion of protons is usually observed when penetration of the impurity into the oxide lattice should lower the concentration of proton defects (Li<sup>+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>), and an increase in the rate of diffusion occurs with impurities whose penetration into the lattice should increase the concentration of proton defects (W<sup>6+</sup>). The oxygen overpotential is observed to increase with impurities which should lower the conductivity (Li<sup>+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>), and to decrease with those whose penetration into the oxide lattice should increase the conductivity (W<sup>6+</sup>).

† Eqns. (1) and (2) require the observance of two conditions — (i) constancy of the concentration of positive and negative ions ( $\alpha$  and  $2\alpha$  respectively), and (ii) electrical neutrality.

A decrease in the concentration of proton defects in a layer having *n*-type conduction (NiO<sub>2</sub>) is equivalent to a diminution in the proton concentration gradient in the film, and conversely. This may be the reason for the decrease in the rate of diffusion of protons in the former case, and for its increase in the latter.

In contrast to the rate of diffusion of protons, which is determined by the bulk properties of the film, the rate of oxygen evolution will depend on the surface properties of the film at the boundary with the solution. The oxygen overpotential should depend on the conductivity of the surface layer when one of the electrochemical stages, for example the discharge of OH<sup>-</sup> or O<sup>2-</sup> ions, is rate-determining.

Comparison of theoretical deductions for films having *p*- and *n*-type conductance with experimental data on the effect on the rate of diffusion of protons indicates agreement for the film having *n*-type conduction. This probably indicates that the barrier layer to the diffusion of protons lies in a layer of the film having *n*-type conduction, *i. e.* closer to the oxide-solution interface, not in a *p*-type layer as we had previously supposed<sup>1</sup> from the dependence of the rate of diffusion of protons on the nature of the alkali-metal cation (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>). This barrier layer is apparently quite narrow. For this reason the proton diffusion current is not found to depend on the thickness of the film.

## SUMMARY

1. A nickel diffusion electrode coated on one side with an oxide film has been used to investigate the rate of diffusion of protons through the nickel oxide film and the oxygen overpotential on it in 3.3 *N* KOH solutions with additions of Zn<sup>2+</sup>, Al<sup>3+</sup>, W<sup>6+</sup>, and Mo<sup>6+</sup>.
2. Over the whole potential range investigated, additions of Zn<sup>2+</sup> and Al<sup>3+</sup> to KOH solution increase the oxygen overpotential and diminish the rate of diffusion of protons through the oxide film. Additions of W<sup>6+</sup> and Mo<sup>6+</sup> lower the oxygen overpotential and increase the rate of diffusion of protons at high potentials, but increase the oxygen overpotential and lower the rate of diffusion of protons at low potentials.
3. The rate of diffusion of protons is independent of the thickness of the oxide film. It increases with increase in the cathodic polarisation current on the reverse side of the nickel foil.
4. The observed regularities are explained on the hypothesis that the impurity ions can penetrate from the solution into the nickel oxide lattice in exchange for the nickel ions, and thereby change the semiconducting and electrochemical properties of the film.

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