JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 37–42

Electron conduction in passive films on nickel

H. YONEYAMA, S. TANABE and H. TAMURA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka, Japan

Received 26 July 1971

The electron conduction properties of the passive film on nickel in acid solution were studied by differential capacitance of nickel electrode in the passive condition, and by redox reactions of the Fe^{2+}/Fe^{3+} and Q/H_2Q systems. A large capacitance value of the passive electrode, which is possibly comparable to that of the double layer, can be ascribed to the space charge capacitance in the passive film which is highly nonstoichiometric. The redox reaction currents of these systems may be sustained by tunnelling of charge carriers through the space charge layer in the passive film, if it can be accepted that the 'tunnel effect' commences when the electric field strength in the space charge layer is of the order of 10^6 V/cm. Consequently, the passive film can not be an insulator, at least in acid solutions.

1. Introduction

It has been established that the passivation of nickel is brought about by anodic film formation [1–4]. The electronic properties of this passive film and its effects on the electrochemical reactions are still ambiguous because of the thinness of the film and its instability when removed from the electrolyte. Although the passive film seems to be electronically conductive [5, 6], this character may not be directly connected to the bulk properties. When an insulator film is very thin, of the order of 10 Å, in a metal/insulator/metal system, the film becomes electronically conductive via the 'tunnel effect' [7, 8].

In this paper, the electronically conductive character of the passive film is discussed on the basis of data concerning redox reactions and of the differential capacitance of passive nickel. If the film is a semiconductor as suggested by Bockris *et al.* [2], a semiconductive nickel oxide prepared by doping lithium may be representative of the passive film properties. Some information obtained previously on this electrode [9, 10] will be referred to later.

2. Experimental

2.1 *Electrode*

99·9% nickel sheet was polished with 2000 emery paper and then electrolytically polished for 30 min in 75% H_2SO_4 at 50°C. Before measurements, it was immersed in a mixture of conc. H_2SO_4 and conc. HNO_3(1:1), followed by washing with de-ionized water as a pretreatment. All procedures were carried out under wet conditions.

2.2 *Reaction current of the redox electrolyte*

A net reaction current of the redox electrolyte on the passive nickel electrode was estimated as follows. A steady state I-V curve was obtained in a medium solution such as 1N H_2SO_4 or 1N Na_2SO_4 using a saturated calomel reference electrode. Then, whilst holding a nickel electrode in the passive condition by means of a potentiostat, a redox solution was added to the electrolyte so as to attain a fixed concentration of the redox species. During this procedure, the solution was agitated with nitrogen. The I-V curve was then re-measured within the range of the passive potential. The net reaction current of the redox species was estimated by subtraction of the current measured in the background electrolyte from that in the redox electrolyte.

2.3 *Differential capacitance*

The capacitance of the passive nickel electrode was measured as a function of electrode potential by means of a impedance bridge during potentiostatic polarization as described in a previous paper [11]. A platinized platinum plate of large apparent area was used as a counter electrode.

The electrolytes were prepared with reagent grade chemicals and de-ionized water. A concentrated redox solution was dropped into the cell containing the background electrolyte. The SCE was connected to the electrolyte with an agar bridge. All measurements were carried out at 25±0·5°C in nitrogen.

3. Results and discussion

3.1 *Reaction rates of some redox systems*

The I-V curves of the passivated nickel electrode in 1N H_2SO_4 and in this solution containing quinone (Q) and hydroquinone (H_2Q) each of 5×10^{-3} M concentration are shown in Fig. 1.

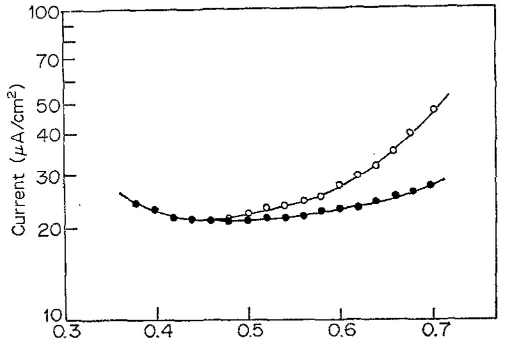

Fig. 1. I-V curves of the passive nickel electrode in 1N H_2SO_4 and in this solution containing quinone and hydroquinone each of 5×10^{-3} M. ● 1N H_2SO_4; ○ 1N H_2SO_4+Q/H_2Q.

The difference of the current values in these two electrolytes can be attributed to a net reaction current of the redox system. This was confirmed by comparison of the amount of dissolved nickel with that of charge passed during long periods of polarization at a passive potential of nickel in the two electrolytes above (Table 1). If an anticipated quantity of charge for the net reaction of Q/H_2Q system, 1·69 mAH, which was estimated as a product of the polarization time, and a net reaction current obtained by the subtraction at 0·7 V versus/SCE, is subtracted from the total quantity of electricity measured in the solution containing the Q/H_2Q system, the difference should be the charge associated with the dissolution of nickel. After this correction there is good agreement between the values of dissolved nickel per faraday for the two electrolytes.

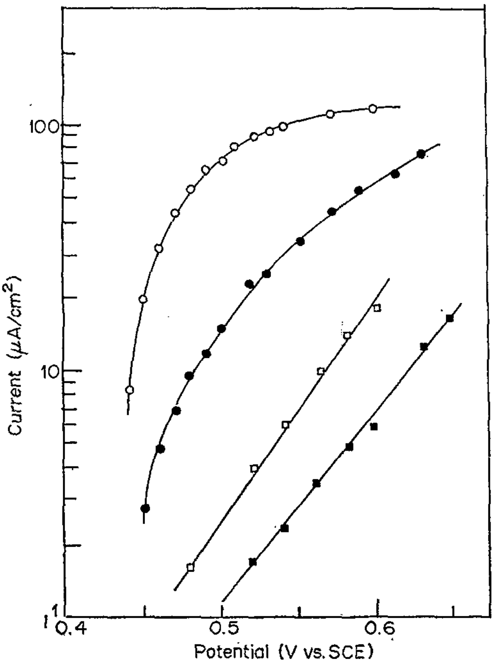

Fig. 2. I-V curves for the Fe^{2+}/Fe^{3+} system on various electrodes. ○ Pt; ● passive Ni; □ 580 Ω-cm NiO; ■ 3800 Ω-cm NiO. Solution: 1N H_2SO_4 containing Fe^{2+} and Fe^{3+} of 5×10^{-3}M each.

Fig. 2 shows typical I-V curves of the Fe^{2+}/Fe^{3+} system on platinum, passivated nickel and on lithiated nickel oxide electrodes. The I-V curve on the passive nickel was estimated by subtraction as described above, and those on the lithiated NiO electrodes are from a previous paper [10]. As described in [10], the current of

Table 1. Typical results for dissolved nickel per unit charge.

Electrolyte	*Charge*	*Fraction sustained by Q/H_2Q*	*Dissolved nickel*	*Dissolved nickel per net charge*
1N H_2SO_4	0·82 mA · H $(3{\cdot}06\times10^{-5}F)$	—	675 μg $(1{\cdot}1\times10^{-5}$ g-atom)	0·36 g-atom · F^{-1}
1N H_2SO_4 + Q/H_2Q	3·78 mA · H $(1{\cdot}41\times10^{-4}F)$	1·69 mA · H $(6{\cdot}3\times10^{-5}F)$	1580 μg $(2{\cdot}69\times10^{-5}$ g-atom)	0·35 g-atom · F^{-1}

Apparent surface area of the electrode: 2 cm^2.

Table 2. Apparent exchange current densities of Fe^{2+}/Fe^{3+} and of Q/H_2Q system on various electrodes.

System	*Medium*	*Electrode*	i_0 (A/cm^2)
5×10^{-3}M Fe^{2+} 5×10^{-3}M Fe^{3+}	1N H_2SO_4	Pt	$4{\cdot}6\times10^{-5}$
		passive Ni	$5{\cdot}0\times10^{-6}$
		NiO 580 Ω-cm	$2{\cdot}2\times10^{-6}$
		NiO 1600 Ω-cm	$1{\cdot}1\times10^{-6}$
		NiO 3800 Ω-cm	$8{\cdot}5\times10^{-7}$
5×10^{-3}M Q 5×10^{-3}M H_2Q	1N H_2SO_4	Pt	$5{\cdot}6\times10^{-5}$
		passive Ni	$9{\cdot}5\times10^{-8}$
	0·01N H_2SO_4+ 0·99N Na_2SO_4	Pt	$1{\cdot}6\times10^{-5}$
		passive Ni	$7{\cdot}8\times10^{-8}$
	1N Na_2SO_4	Pt	$1{\cdot}5\times10^{-6}$
		passive Ni	2×10^{-8}

the Fe^{2+}/Fe^{3+} system on a lithiated NiO electrode is controlled by the height of the potential barrier, which results from the space charge depletion layer in the electrode surface. In this case, the conductivity of the electrode affects the reaction current according to equation (1),

$$J = \sigma\,\{2qN(\phi\text{-}V)/\varepsilon\varepsilon_0\}^{\frac{1}{2}}\ \exp(q\phi/kT)\ \{\exp(qV/kT)-1\} \qquad (1)$$

where N, ϕ, V, and σ represents respectively carrier density, the potential barrier height which corresponds to a potential difference at a contact face between the Fermi level of the redox species [12] and an energy state containing charge carriers in the electrode, applied voltage on the space charge layer, and the conductivity of the semiconductor.

Apparent exchange current densities of this system on the various electrodes were estimated by a method due to Allen and Hickling [13] and are shown in Table 2. In Table 2, the results obtained on the Q/H_2Q system are also shown. It follows from these results that the passive film has a high electronic conductivity if the reaction current is not brought about by the 'tunnel effect' of the charge carrier.

3.2 *Differential capacitance of the passive nickel electrode*

To ascertain whether the passive film has a high electronic conductivity, the capacitance of the nickel electrode in a steady state condition was measured as a function of the electrode potential. If the film has a semiconductive character, a space charge layer will be formed in the film surface region in accordance with polarization potential as had already been observed on single crystal and poly-crystal lithiated NiO [10, 14]. In general, the space charge capacitance is so small compared with the Helmholz double layer capacitance that it is possible to obtain information about carrier density of a semiconductor by means of plots of reciprocal square of the measured capacitance *versus* V [15, 16]. Unfortunately, the measured capacitance of the passive nickel electrode was found to be comparable to the double layer capacitance (Fig. 3). This implies that the space charge capacitance is large enough if it were on the passive film, and hence it is impossible to obtain information about charge carrier density of the film directly from the measured capacitance.

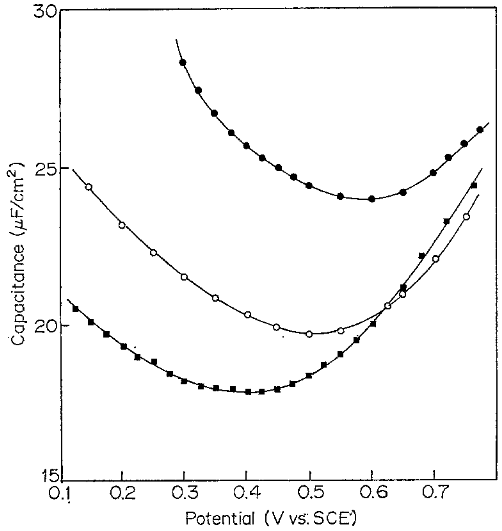

Fig. 3. Differential capacitance of the passive nickel electrode in selections of various pH. ● 1N HSO_4; ○ 0·01N H_2SO_4+0·99N Na_2SO_4; ■ 1N Na_2SO_4 (measuring frequency: 1 kc/s).

3.3 *Possibility of the passive film being an insulator*

According to published work the passive film in acid solution [2, 3] seems to be 40∼60 Å thick. If the film is an electronic insulator, the capacitance of the film, C_f, may amount to 2·65 μF/cm^2 (40 Å)∼1·77 μF/cm^2 (60 Å) if by estimation as a parallel plate condenser in which the dielectric constant of the film is the same as that of NiO [17]. Taking account of the double layer capacitance, C_H, to be 20∼40 μF/cm^2, the measured capacitance values shown in Fig. 3 cannot be due to a series connection of the C_f and C_H when the film is assumed to be an insulator of 40∼60 Å thickness, even if a roughness factor of 2∼3 is assumed.

3.4. *Semi-conductive properties of the passive film*

The observation that the measured capacitance is comparable to C_H may suggest that this large capacitance results from a large space charge capacitance in the passive film. According to a calculation of the capacitance value of the space charge depletion layer, such a condition will be met when the film has a large impurity concentration, i.e., is highly nonstoichiometric. The capacitance of the space charge depletion layer of a semiconductor can be approximately expressed [18] as;

$$C=(q\varepsilon\varepsilon_0 N/2\Psi)^{\frac{1}{2}} \qquad (2)$$

where Ψ represents the potential drop in the space charge layer in the semiconductor. If the flat-bend potential of the passive film is assumed to be analagous to that of NiO, i.e., 0·85 V *versus* SCE [10], a condition of creating the space charge depletion layer will be fulfilled in the passivation potential of nickel, because semiconducting NiO is p-type, the relation in equation (2) can then be applied. Fig. 4 shows the calculated space charge capacitance as a function of Ψ for film containing impurities of 5×10^{20}/cm^3∼5×10^{21}/cm^3, the impurities being mainly tri-valent nickel or di-valent nickel ion vacancies. The impurity concentration of 5×10^{20}/cm^3∼5×10^{21}/cm^3 is about 1/200∼1/20 times the total ion concentration in crystalline NiO. The assumption of such a high impurity concentration is not unusual and in agreement with the results of chemical analysis of the film formed anodically on nickel in an alkaline solution by Conway and Sattar [19]. The mobility of the charge carrier in the film is assumed to be that of 0·004 cm^2/V sec as in crystalline NiO [20], although the estimated mobility values are widely different [21, 22], and this gives a resistivity for the passive film containing the above content of impurity as 3–0·3 Ω-cm. It is evident from Fig. 4 that the space charge capacitance in the film is comparable to or larger than the double layer capacitance when the film contains such a high impurity content. Presumably, owing to such a high concentration,

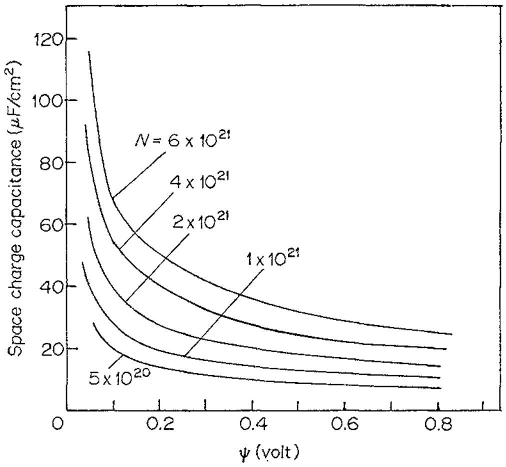

Fig. 4. Calculated space charge capacitance as a function of Ψ. N: impurity concentration ($1/cm^3$)

the measured capacitance will amount to 25~40 $\mu F/cm^2$.

3.5. *Current by 'tunnel effect' of charge carrier*

As was described in section 3.1, the I-V curve of the redox reaction is affected by a space charge depletion layer formed in the surface region of the semiconductor. However, there is another possible way for the current to be controlled when a semiconductor contains a high amount of impurities. It should be noted that the 'tunnel effect' of the charge carrier may occur through the space charge depletion layer in the semiconductor. In general, it is accepted that the 'tunnel effect' commences when the field strength in the insulating layer is of the order of 10^6v/cm. To ascertain whether this is likely in the passive film containing the impurity level estimated in section 3.4, the depth of the space charge layer was calculated according to equation (3),

$$d=(2\varepsilon\varepsilon_0\Psi/qN)^{\frac{1}{2}} \qquad (3)$$

The results are shown in Fig. 5 as a function of impurity concentration. If the polarization potential is assumed to be concentrated in the space charge depletion layer, the electric field strength on this layer E, can be estimated from equation (4).

$$E=\Psi/d \qquad (4)$$

The results are shown in Fig. 6. Actually, the field strength on the space charge layer will be smaller than the value shown in this figure, since a part of the applied potential may be across the double layer. Nevertheless, it is anticipated that the field strength of 10^6 V/cm is easily attained because the calculation for ideal conditions shows that the field strength amounts to 10^6 V/cm by polarization of 0·1 V or less from the flat-band potential. Thus, the current of the redox reaction in this study may be sustained by the 'tunnel effect' of charge carriers through the space charge layer on the passive film of nickel.

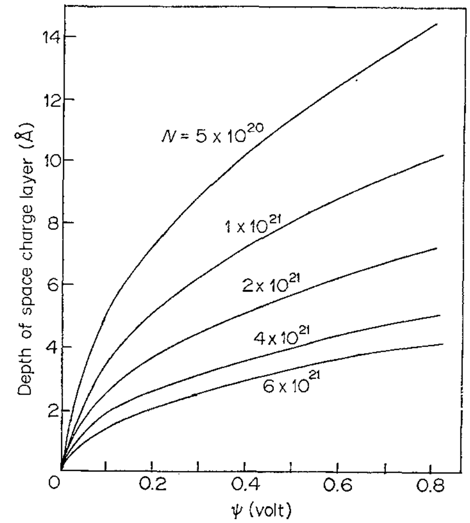

Fig. 5. Calculated depth of the space charge layer as a function of Ψ.

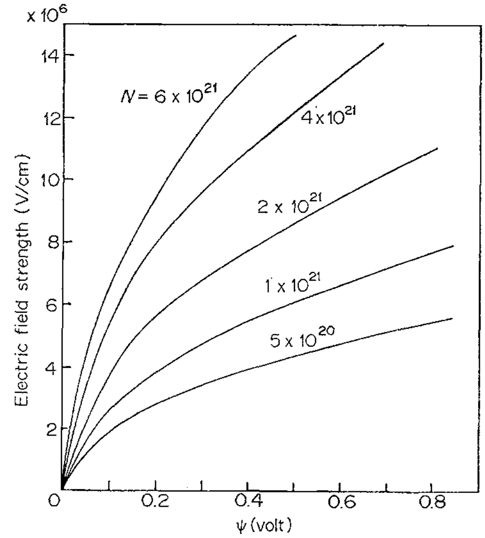

Fig. 6. Calculated electric field strength across the space charge in the electrode surface as a function of Ψ.

The small values of the apparent exchange current densities of the Q/H_2Q system on the passive nickel electrode compared with that of the Fe^{2+}/Fe^{3+} system on the same electrode, which are shown in Table 2, are presumably brought about by a slow reaction rate at a rate-determining step in the reaction sequence of this system and hence are unaffected by the transport properties of the charge carrier in the semiconductor electrode.

3.6. *Limitations on the validity of the proposed film property*

Recently, Kudo and Sato reported the film thickness of the passive film of nickel in pH=8·42 solutions to be 5∼15 Å [4]. This value is very different from those for acid solution found by Bockris *et al.* [2] and Arnold *et al.* [3]. If this were the case also in acid solution, the differential capacitance shown in Fig. 3 would be those observed with the assumption of a roughness factor of 2∼3 even if the film is an insulator. According to a theoretical analysis by Fisher and Giaever on the 'tunnel effect' through the insulating layer [7], there is a possibility that the current by 'electron tunnelling' is large enough to sustain the reaction current shown in Fig. 2 when the film thickness is 10 Å or so. The passive film cannot possess the proposed semiconducting property if the thickness is so small.

References

[1] N. Sato and G. Okamoto, *J. Electrochem. Soc.*, **112** (1965) 1064.
[2] J. O'M. Bockris, A. K. N. Reddy and B. Rao, *ibid.*, **113** (1966) 1133.
[3] K. Arnold and K. J. Vetter, *Z. Elektrochem.*, **64** (1960) 407.
[4] K. Kudo and N. Sato, Ext. Abs. of 17th Annual Symposium on Corrosion and Protection in Japan, Oct. 1970, p. 361.
[5] K. J. Vetter, *Z. Physik. Chem. N.F.*, **4** (1955) 165.
[6] K. G. Weil, *Z. Elektrochem.*, **62** (1958) 638.
[7] J. C. Fisher and I. Giaever, *J. Appl. Phys.*, **32** (1961) 172.
[8] R. Stratton, *J. Phys. Chem. Solid*, **23** (1962) 1177.
[9] H. Yoneyama and H. Tamura, *Bull. Chem. Soc. Jap.*, **43** (1970) 1603.
[10] H. Yoneyama and H. Tamura, *ibid.*, to be published.
[11] H. Yoneyama and H. Tamura, *ibid.*, **43** (1970) 350.
[12] H. Gerischer, *Z. Physik. Chem. N.F.*, **26** (1960) 223.
[13] P. L. Allen and A. Hickling, *Trans. Faraday Soc.*, **53** (1957) 1626.
[14] T. O. Rouse and J. L. Weininger, *J. Electrochem. Soc.*, **113** (1966) 184.
[15] J. F. Dewald, *Bell System Tech. J.*, **39** (1960) 615.
[16] P. J. Boddy, *J. Electrochem. Soc.*, **115** (1968), 199.
[17] R. Newman and R. M. Chrenko, *Phys. Rev.*, **114** (1959) 1507.
[18] V. A. Myamlin and Yu V. Pleskov, 'Electrochemistry of Semiconductors', p. 58, Plenum Press, New York (1967).
[19] B. E. Conway and M. A. Sattar, *J. Electroanal. Chem.*, **19** (1968) 351.
[20] F. J. Morin, *Bell System Tech. J.*, **37** (1958) 1047.
[21] S. van Houten, *J. Phys. Chem. Solid*, **17** (1960) 7.
[22] A. J. Bosman and C. Crevecouer, *Phys. Rev.*, **144** (1966) 144.