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Redox Reactions on the Lithiated Nickel Oxide Electrode

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The redox reactions of the Ce^{3+}/Ce^{4+}, Fe^{2+}/Fe^{3+} and $Fe(CN)_6{}^{4-}/Fe(CN)_6{}^{3-}$ systems on lithiated nickel oxide electrodes in a H_2SO_4 medium were studied. For the Fe^{2+}/Fe^{3+} and $Fe(CN)_6{}^{4-}/Fe(CN)_6{}^{3-}$ systems, the reactions were controlled by an activation process when the electrode was polarized anodically, while the current tended to saturation as the current was increased in the cathodic direction. The apparent exchange current densities of these systems were distinctly dependent on the resistivity of the electrode. These phenomena were discussed qualitatively from a consideration of the energy states of the charge carriers in the electrode and redox systems, and it was concluded that all the reactions had proceeded through only hole transfer.

A large number of metallic oxides exhibit semiconductivity. For a catalytic reaction which proceeds in the presence of such kinds of oxides, it has often been found that the reactivity is affected by their semiconducting character. In such a case, the chemical reaction is supposed to be controlled by the behavior of the charge carriers in the oxides. More particularly, for the electrode of a semiconductor such as Ge it has been found that the behavior of the charge carriers clearly controls an electrochemical reaction.[1,2] Recently, studies of electrode reactions on semiconductors have been developed to cover oxide semiconductors.[3,4] Almost all of the semiconductors on which electrode reactions have been studied have, though, been ones with a clear energy-band scheme. In these electrodes, the current-potential curves are often affected by the behavior of the minority carrier in the electrode, and from these curves it is possible to estimate which carrier, electron or hole, participates in the reaction. This estimation is also possible from the study of the reactions of redox systems having various standard electrode potentials,[5,6] because the density of the electron or hole in the electrode-surface region is adjusted in accordance with the redox potential of the redox system.

In contrast to a usual band-type semiconductor such as Ge and ZnO, a hopping-type semiconductor is normally considered to have a different energy-band structure,[7] although this question has not yet been completely clarified. However, the kind of charge carrier participating in an electrode reaction on a hopping-type semiconductor electrode may be estimated by means of the experimental technique used in the study of the electrode reaction on usual band-type semiconductors, because a reaction should also proceed when the energy state of the charge carrier in the semiconductor almost coincides with that of ions in an electrolyte. Recently, Yohe and his co-workers studied the redox reactions on a lithiated nickel oxide electrode[8], which is classified as a typical hopping-type semiconductor.[7,9] However, they examined the behavior of the electrode over a wide pH range, and so the condition of the electrode surface may not have been always the same[10]; moreover, the effect of the resistivity of the electrode on the reactivity is not clear, either. Therefore, we studied the reactivity of the redox reactions on this electrode as a function of its resistivity. Experiments were carried out in an acid medium so as always to establish the same surface condition of the electrode.

Experimental

Electrode. High-purity Ni powder (99.99%) was dissolved in a H_2SO_4 solution, and $NiCO_3$ was precipitated by the addition of $NaHCO_3$ to the solution.

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[1] F. Beck and H. Gerisher, *Z. Elektrochem.*, **63**, 500 (1959).

[2] D. R. Turner, *J. Electrochem. Soc.*, **103**, 252 (1956).

[3] S. R. Morrison and T. Freund, *Electrochim. Acta*, **13**, 1343 (1968).

[4] F. Lohman, *Ber. Bunsenges. Phys. Chem.*, **70**, 438 (1966).

[5] F. Beck and H. Gerisher, *Z. Elektrochem.*, **63**, 943 (1959).

[6] H. Gerisher, *Ber. Bunsenges. Phys. Chem.*, **69**, 578 (1965).

[7] F. J. Morrin, *Bell System Tech. J.*, **37**, 1047 (1958).

[8] D. Yohe, A. Riga, R. Greef and E. Yeager, *Electrochim. Acta*, **13**, 1351 (1968).

[9] D. P. Snoden and H. Saltsburg, *Phys. Rev. Lett.*, **14**, 497 (1965).

[10] M. Pourbaix, "Atlas of Electrochemical Equilibra in Aqueous Solution," Pergamon Press, New York (1966), p. 330.

After several decantations, the precipitate was filtrated, washed thoroughly by de-ionized water, and then evaporated to dryness. It was finally decomposed to NiO by heating at 600°C for 4 hr in the air. The NiO powder prepared in this way was spectroscopically pure. Using this NiO powder, an electode was prepared by a method descirbed previously.[11] This electrode showed P-type semiconductivity when examined by the thermo-electromotive-force measurements.

Specific Resistivity. The specific resistivity of the electrode was measured by the four-probe method[12] at 25°C after completing the measurements of the polarization curves in various redox solutions. The electrode had a specific resistivity of 1.9—193 Ω-cm. The electrodes had the Li contents shown in Table 1. The Li contents in Table 1 were estimated from the relationship between the Li content and the resistivity, which had been obtained beforehand for various NiO's. In the previous investigation we estimated the resistivity from the voltage drop between platinum contacts on both faces of a disk-shaped electrode. The value estimated before was somewhat larger than that obtained by the four-probe method. Even if this difference had been caused by bringing Pt into contact with the lithiated NiO, Pt contact on the lithiated NiO did not have any serious effect on the electric conduction as will be discussed below.

TABLE 1. Li CONTENT IN TEST ELECTRODES

Resistivity at 25°C (Ω-cm)	1.9	5.0	13.3	44.0	192
Li content (atom %)	7.0	2.4	0.80	0.23	0.054

Electrode Area. The effective area of the electrode was estimated by a method described previously.[11] The area was fixed in a small part of the face of the disk-shaped electrode by covering it with epoxy resin in order to eliminate the voltage drop in the electrode, which would make the current-potential curves more complex. In the estimation of the surface area, the resistivity estimated by the method reported previously[11] was used, because the electrode always had Pt contact on the lithiated NiO.

Cell Equipment. Connection between the reference electrode (SCE) and the solution was made by an agar bridge containing a saturated KCl solution, but the agar bridge was not inserted directly into the electrolytic cell. The cell was convered with aluminum foils so as to shut off the light.

Current-potential Relation. Steady-state current-potential (*I*-*V*) curves were obtained potentiostatically by means of an electronic potentiostat. Electrodes were conditioned by successive pre-electrolysis in 0.1N H_2SO_4 at 1.6 V and −1.2 V each 10 min and finally at 0V for 5 min. Before and during measurements N_2 gas was bubbled into the electrolyte so as to remove any dissolved oxygen and stir the solution. All the measurements were carried out at 25±0.5°C.

Chemicals. All the chemicals used in this study were of a G.R. grade. Three kinds of redox systems were used in this study. They are indicated in Table 2. The concentrations of the ions were determined by analysis, if necessary. The Fe^{2+}/Fe^{3+} and Ce^{3+}/Ce^{4+} systems were prepared by their sulfates, while potassium salts were used to prepare the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system.

TABLE 2. REDOX SYSTEMS STUDIED

System	Medium
5 mM Ce^{3+} 5 mM Ce^{4+}	0.17N H_2SO_4
5 mM Fe^{2+} 5 mM Fe^{3+}	0.1N H_2SO_4
5 mM Fe $(CN)_6^{4-}$ 5 mM $Fe(CN)_6^{3-}$	0.1N H_2SO_4

Results

Steady-state *I*-*V* curves in 0.1N H_2SO_4 are shown in Fig. 1 for 1.9, 5.0, 13.3, 44, and 192Ω-cm electrodes. *I*-*V* curves for $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, Fe^{2+}/Fe^{3+}, and Ce^{3+}/Ce^{4+} systems are shown in Figs. 2, 3, and 4 respectively. For the Ce^{3+}/Ce^{4+} system, a saturation current was observed when the anodic

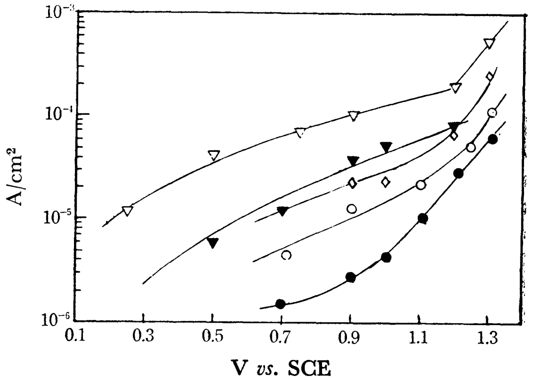

Fig. 1. *I*-*V* curves for lithiated NiO electrodes in 0.1N H_2SO_4.
—▽— 1.9Ω-cm, —▼— 5.0Ω-cm, —◇— 13.3Ω-cm, —○— 44Ω-cm, —●— 192Ω-cm

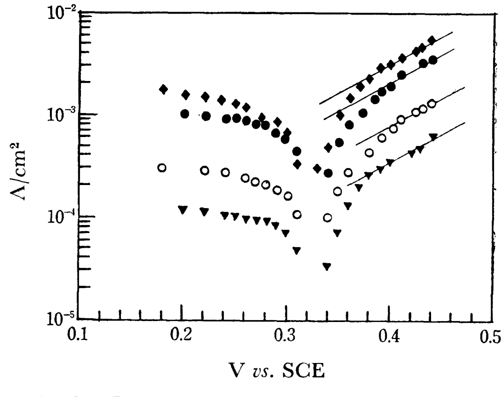

Fig. 2. *I*-*V* curves in the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system.
—◆— 1.9 Ω-cm, —●— 5.0 Ω-cm, —○— 13.3 Ω-cm, —▼— 44 Ω-cm

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[11] H. Yoneyama and H. Tamura, This Bulletin, **42**, 1795 (1969).

[12] L. B. Valdes, *Proc. IRE*, **42**, 420 (1954).

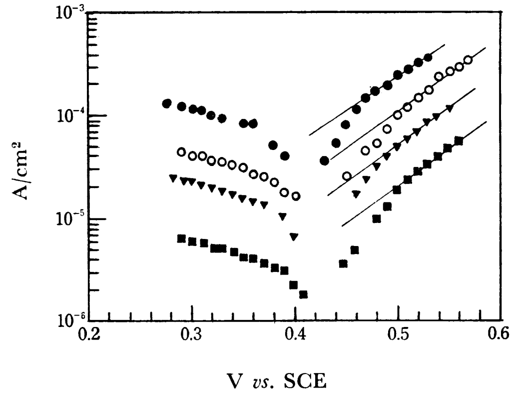

Fig. 3. *I-V* curves in the Fe^{2+}/Fe^{3+} system.
—●— 5.0 Ω-cm —○— 13.3 Ω-cm
—▼— 44 Ω-cm —■— 192 Ω-cm

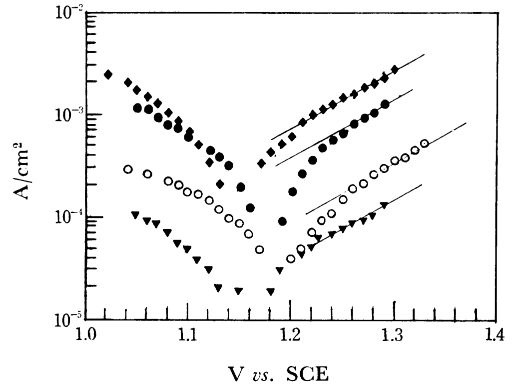

Fig. 4. *I-V* curves in the Ce^{3+}/Ce^{4+} system.
—◆— 1.9 Ω-cm, —●— 5.0 Ω-cm,
—○— 13.3 Ω-cm, —▼— 44 Ω-cm

polarization was increased to about 1.5 V, and with a further increase in polarization beyond 1.6 V the current increased again, supposedly because of commencement of the oxygen-evolution reaction. In these figures, the following facts can be noticed: (a) In a cathodic polarization the current tends to become saturated in the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems, this phenomena appearing more distinctly in the former. (b) In the anodic polarization, the electrode reaction seems to proceed by an activation process. (c) The current in Figs. 2—4 is considered to be related to the reaction of the redox system itself, since this current is over 10 times that in Fig. 1. (d) The reactivity of the redox system was much influenced by the resistivity of the electrode. To make clear the nature of the cathodic current for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems, which showed a tendency toward saturation, the dependence of this current on the concentration of the oxidant was obtained. One typical result is shown in Fig. 5 for the reduction of Fe^{3+}.

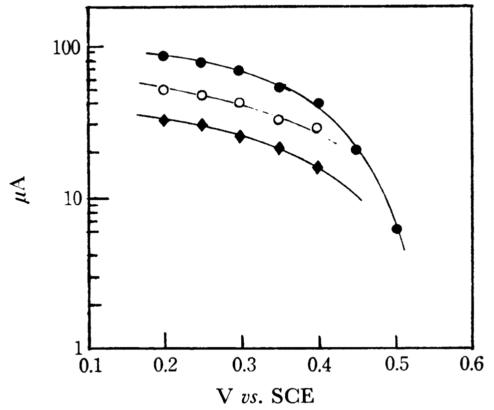

Fig. 5. *I-V* curves for the 192 Ω-cm electrode in Fe^{3+} solutions
Electrode area: 0.65 cm^2
—●— 0.1M Fe^{3+} —○— 0.05M Fe^{3+}
—◆— 0.025M Fe^{3+}

Discussion

When a metal comes in contact with a P-type semiconductor, a barrier layer may be formed on the contact surface between them. If this layer exists, the current is hindered by this layer when a metal is biased positively against the P-type semiconductor. As is shown above, however, the current flowed more easily in the anodic polarization and a Tafel slope was observed. Therefore, the contact between the Pt and the lithiated NiO can be considered not to have caused any serious problem if it existed at all.

The (a) fact in the previous section conceivably does not indicate the character of the redox system itself, but that of the redox reaction restricted by the behavior of the charge carrier participating in the reaction, because the *I-V* curves of the same redox system were quite different on an N-type semiconductor electrode of αFe_2O_3 doped with titanium.[13] Therefore, the *I-V* curves of the various redox systems can be reasonably explained if it is assumed that the flow of the cathodic current was hindered by the potential barrier formed on the electrode surface as a result of the polarization. As the flat-band potential of the lithiated NiO is 0.65 V *vs.* SCE in 0.1N H_2SO_4 and 0.76 V in 0.17N H_2SO_4,[14] the energy levels of the electron and positive hole of the electrode were lowered in the electrode surface region for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems because the redox potentials of these systems are lower than the flat-band potential; hence, the Fermi level of the

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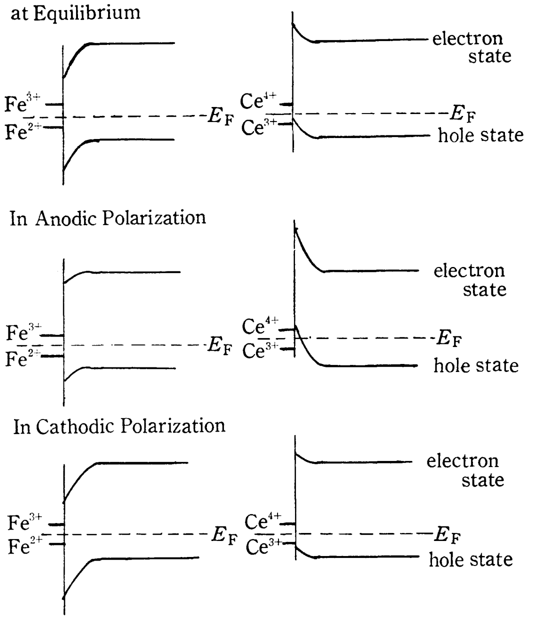
[13] H. Yoneyama, S. Hamamatsu and H. Tamura, This Bulletin, to be published.

[14] T. O. Rouse and J. L. Weininger, *J. Electrochem. Soc.*, **113**, 184 (1966).



Fe^{3+}/Fe^{2+} system Ce^{3+}/Ce^{4+} system

Fig. 6. Schematic representation of energy profile at the interface of electrode and redox electrolyte.

electrode surface is apparently shifted toward a higher energy state compared to the inside of the electrode. The hole concentration in the surface region of the electrode will then decrease, while electron density will increase if it is present at all. This situation is strengthened by the cathodic polarization. Such a energy scheme of the electrode and the electrolyte is represented in Fig. 6 using a band model, though it may not precisely represent the energy structure of 3*d* transition metal oxide.[15] In Fig. 6, each energy state pictured by a solid line in the electrode part indicate the localized energy level at which a positive hole and a localized free electron exist. According to Fig. 6, the electron exchange may occur in the cathodic polarization if the energy state of the electron in the electrode is higher than that of the oxidant of the redox system, that is, $Fe(CN)_6^{3-}$ or Fe^{3+}. However, if electron transfer had occurred, the tendency of the current toward saturation with an increase in the cathodic polarization would not have been observed because the electron transfer from the electrode into the electrolyte could not possibly have been hindered. The only exceptional case is when the current had been hindered by the deficiency of the electron on the electrode surface, but if this were true in this case, no dependence of the cathodic current on the Fe^{3+} concentration would have been observed. The electron transfer mechanism can be eliminated from such a consideration, though Bosman and Crevecouer[16] reported the existence of an electron in the lithiated NiO. On the contrary, the hole-transfer mechanism is reasonable for the following reasons. The height of the potential barrier over which the hole should jump into the electrode under the reaction increases with an increase in the cathodic polarization. The cathodic current would then show a tendency toward saturation. The dependence of the cathodic current on the concentration of Fe^{3+} shown in Fig. 5 means that the probability function of the electron state in the electrolyte[17] was almost proportional to the concentration of Fe^{3+}. In the anodic polarization of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems, hole transfer would more easily occur, since the barrier height for the hole transfer into the electrode decreases with a rise in the anodic potential; thus the Tafel slope was observed. One possible explanation[18] for the mechanism in which the reaction proceeds only through hole transfer is that the energy state of the electron is separate from that of the hole state even if free electron exists in the lithiated NiO.[16] According to Houten's calculation,[19] the energy level of the electron denoted as Ni^+ is located about 5.4 eV above the acceptor level of Ni^{3+} next to a substitutional Li^+.

The situation is very different for the Ce^{3+}/Ce^{4+} system, which has a higher redox potential, that is, 1.36 V *vs.* SCE.[20] The energy levels occupied by charge carriers are raised; this causes the hole concentration in the electrode surface to increase. Such a situation is also represented in Fig. 6. The potential barrier for hole transfer into the electrode will decrease with polarization in the cathodic direction. Thus, the cathodic current would apparently not be suppressed by this potential barrier. On the other hand, hole transfer from the electrode into the electrolyte would occur in the anodic polarization, and no potential barrier would exist in this pathway. The Tafel relation conceivably appears because of such a condition. The *I-V* curves of the Ce^{3+}/Ce^{4+} system possibly indicate

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[15] F. J. Morin, *Phys. Rev.*, **93**, 1195 (1954); *ibid.*, **93**, 1204 (1954). Bosman *et al.* claimed that application of band model is larther erasonable (see Ref. 16). Yu. M. Ksendzov and I. A. Darbkin also support existence of a band for the energy state of Ni^+ (*Soviet Physics-Solid State*, **7**, 1519 (1965)).

[16] A. Bosman and C. Crevecouer, *Phys. Rev.*, **144**, 763 (1966). If N_D and N_A denote concentration of donors and acceptors $(N_A-N_D)/N_D\sim10$ and density of states at 300°K is about 3.5×10^{20}.

[17] H. Gerisher, "Advance in Electorchemistry and Electrochemical Engineering," Vol. 1, ed. by P. Delahey and C. W. Tobias, Interscience Publishers, New York (1961), p. 193.

[18] H. Gerisher, *ibid.*, p. 201.

[19] S. van Houten, *J. Phys. Chem. Solid*, **17**, 7 (1960).

[20] W. M. Latimer, "Oxidation Potential," 2nd ed. Prentice-Hall, Inc., Englewood Cliffs, N. J. (1952), p. 339.

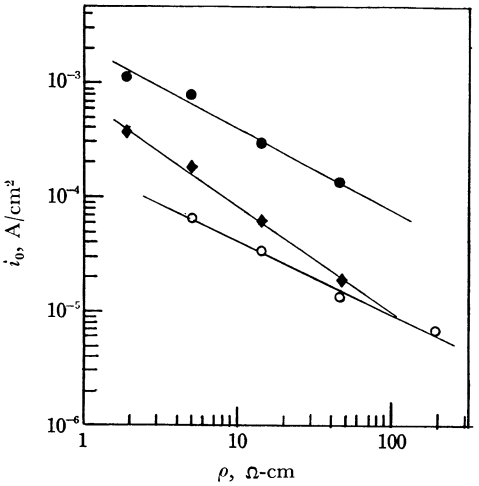

Fig. 7. Relationship between i_0 and resistivity of electrodes.

—●— $Fe(CN)_6{}^{4-}/Fe(CN)_6{}^{3-}$
—○— Fe^{2+}/Fe^{3+}
—◆— Ce^{3+}/Ce^{4+}

the reaction patterns of this redox system itself.

The apparent exchange current density, i_0, was estimated by extraporation of the anodic Tafel slope to the measured open-circuited potential of each redox system; it is plotted against the resistivity of the electrode in Fig. 7. The i_0 value increases with a lowering of the resistivity of the electrode, and nearly a linear relationship exists between these two values. From this result, it is obvious that i_0, and, accordingly, the rate of the electrochemical reaction is determined by the charge carrier density in the electrode. This is a reasonable result, since the charge carrier density on the surface of the electrode is larger for the electrode with the lower resistivity.

In conclusion, we can state that the charge carrier density in the lithiated NiO is the most important factor in determining the reaction rate for the electrochemical reaction which proceeds on this electrode. The reaction potential is another important factor in controlling the reaction rate in either oxidation or reduction. The present studies may give instructive information on the rate of some electrochemical reactions on the Ni electrode, since the Ni electrode in solution usually forms a passivated or oxide film in the specified potential region and the flat-band potential of this film coincides with that of the lithiated NiO.[21]

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[21] S. Toshima, *Denki Kagaku*, **34**, 564 (1966).