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Redox Reactions on α-Ferric Oxide Electrode

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The redox reactions of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, Fe^{2+}/Fe^{3+}, and Ce^{3+}/Ce^{4+} systems on α-Fe_2O_3 electrodes containing different amounts of titanium were studied. The anodic current showed a tendency to be saturated in the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems. The forward direction of the current flow in these systems was the reverse of the case with the lithiated NiO electrode. On the other hand, the cathodic current flow was negligible and the redox potential was not observed for the Ce^{3+}/Ce^{4+} system. It was concluded that the reaction proceeds through electron transfer and that *I–V* curves are determined by the influence of the potential barrier formed on the electrode surface over which an electron transfers from the electrode into the electrolyte or in the reverse direction.

In a previous paper,[1)] it was reported that redox reactions in the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, Fe^{2+}/Fe^{3+}, and Ce^{3+}/Ce^{4+} systems on a lithiated NiO electrode which had a P-type conduction were affected by the electrical properties of the electrode and the electrode potential of the redox system. The *I-V* characteristics of these redox systems show directly how charge carriers in the electrode relate with the reaction system, for at least the reactions of the Fe^{2+}/Fe^{3+} and Ce^{3+}/Ce^{4+} systems proceed *via* only a solvent-reorganization process[2)] without any formation of the adsorbed intermediate to cause a change in the surface property of the electrode. In this paper, we will study the redox reactions of these systems on a Ti-doped α-Fe_2O_3 electrode in order to clarify the relation between the charge carrier in the N-type 3*d* transition metal oxide electrode and the reaction systems. These studies will provide some information on the role of the oxide film on the electrode reaction; this film is often formed on the electrode during electrolysis.

Experimental

Electrode. The electrode was prepared and the effective area of the electrode was estimated by a method described previously.[3)] The material in contact with α-Fe_2O_3 was platinum, for this material act as an ohmic contact and platinum is electrochemically inert even if the electrolyte penetrates into the electrode. The α-Fe_2O_3's used as electrodes had specific resistivities of 15, 30, 280, and 7500 Ω-cm.

Cell Equipment and Chemicals. The cell equipment and chemicals were the same as those reported previously.[1)] The redox systems used in this study are also the same; they are shown in Table 1. All of the measurements were carried out at 25±1°C.

TABLE 1. REDOX SYSTEM STUDIED

System	Medium
10 mM Ce^{3+} 10 mM Ce^{4+}	1 N H_2SO_4
5 mM Fe^{2+}, 5 mM Fe^{3+}	0.1 N H_2SO_4
5 mM $Fe(CN)_6^{4-}$, 5 mM $Fe(CN)_6^{3-}$	0.1 N H_2SO_4

Results

The polarization curves of the α-Fe_2O_3 electrode in electrolytes containing the redox systems are

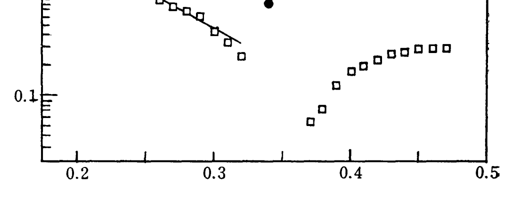

Fig. 1. *I-V* curves of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ on α-Fe_2O_3 electrodes.
—■— 15 Ω-cm, —●— 280 Ω-cm,
—□— 7500 Ω-cm

[*1] Previous name: Chemical Technology.

1) H. Yoneyama and H. Tamura, This Bulletin, **43**, 1603 (1970).

2) E. Sacher and K. J. Laidler, "Modern Aspects of Electrochemistry," Vol. 3, ed. by J.O'M. Bockris and B. E. Conway, Butterworth, London (1964), p. 7.

3) H. Yoneyama and H. Tamura, This Bulletin, **43**, 350 (1970).

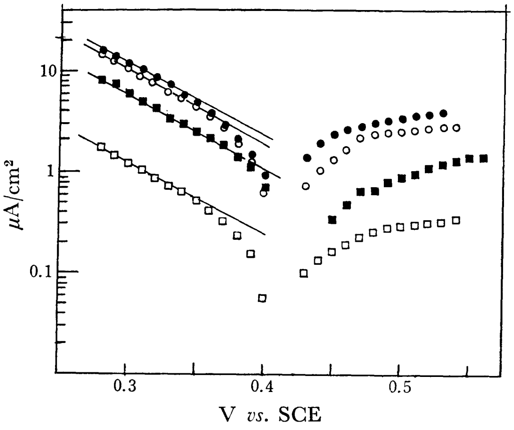

Fig. 2. *I-V* curves of Fe^{2+}/Fe^{3+} system on α-Fe_2O_3 electrodes.
—■— 15 Ω-cm, —○— 30 Ω-cm,
—●— 280 Ω-cm, —□— 7500 Ω-cm

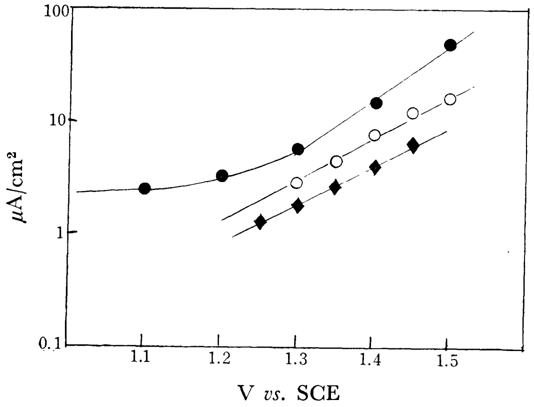

Fig. 3. *I-V* curves of α-Fe_2O_3 electrodes in 0.01 M Ce^{3+}/Ce^{4+} system.
—●— 15 Ω-cm, —○— 30 Ω-cm,
—◆— 280 Ω-cm

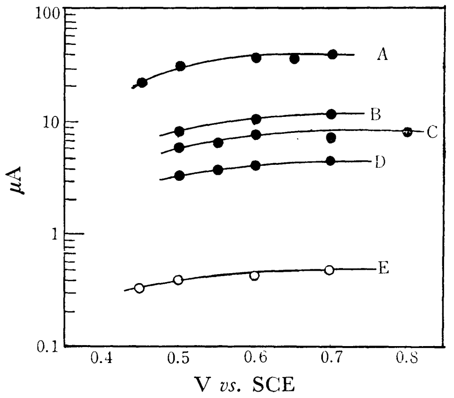

Fig. 4. *I-V* curves of α-Fe_2O_3 electrode in 1 N H_2SO_4 solution containing different amount of Fe^{2+}.
A: 1 M B: 0.2 M C: 0.1 M D: 0.05 M E: 0 M
Electrode area 0.2 cm².

presented in Figs. 1, 2, and 3 for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, Fe^{2+}/Fe^{3+}, and Ce^{3+}/Ce^{4+} systems respectively. The cathodic reaction seems to proceed under an "activation controlled condition" in the former two redox systems, which have relatively low redox potentials,[4] while in the Ce^{3+}/Ce^{4+} system, which has a higher redox potential, a distinct reaction seems to occur in the case of the anodic polarization and the measured open circuit potential was below 0.6V *vs.* SCE.

To clarify the nature of the anodic current hindrance in the Fe^{2+}/Fe^{3+} system, the dependence of the concentration of Fe^{2+} on the anodic portion of the current was measured. An approximate proportionality was observed between the concentration of Fe^{2+} and its oxidation current, as Fig. 4 shows. Likewise, the effect of the concentrations of Ce^{3+} and Ce^{4+} on the anodic current was investigated. The *I-V* curves of the α-Fe_2O_3 obtained in 1 N H_2SO_4 were not changed by the addition of these ions, as Fig. 5 shows. This result caused us to doubt whether the anodic current shown in Fig. 3 directly showed the reaction current of the redox system itself. In order to elucidate this question, the quantity of Fe which had been produced by the anodic dissolution of the α-Fe_2O_3 electrode into the electrolyte during polarization for a known period and at fixed potential was analytically determined for the

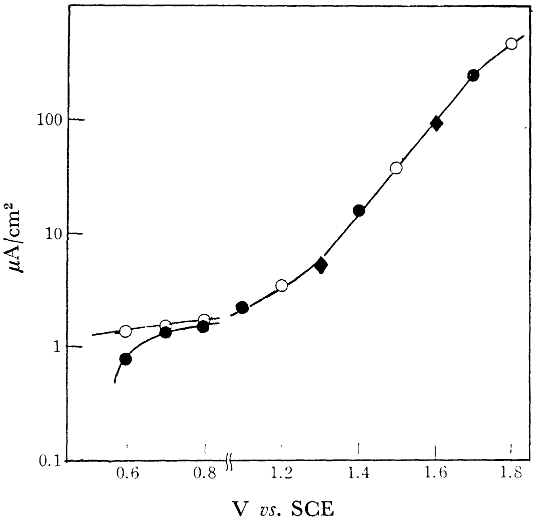

Fig. 5. *I-V* curves of α-Fe_2O_3 electrode in 1 N H_2SO_4, 0.01 M Ce^{3+}/1 N H_2SO_4 and 0.01 M Ce^{4+}/1 N H_2SO_4. Data was obtained with 0.1 v step in each electrolyte, but only some of them are plotted in this figure. Noticeable difference was not detected for the above three electrolytes except for especially figured.
—○— 1 N H_2SO_4, —◆— 0.01 M Ce^{3+}/1 N H_2SO_4,
—●— 0.01 M Ce^{4+}/1 N H_2SO_4

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[4] W. M. Latimer, "Oxidation Potential," 2nd ed. Prentice-Hall, Englewood Cliffs, N. J. (1961), p. 340.

TABLE 2. QUANTITY OF Fe IN THE ELECTROLYTE AFTER POLARIZATION OF ELECTRODE

Electrolyte	Potential V	Time of electrolysis hr	Quantity of electricity Q (coulomb)	Quantity of Fe g	Fe produced per unit coulomb g/Q
1 N H_2SO_4	1.3	3	2.7×10^{-3}	4.5×10^{-4}	1.7×10^{-1}
	1.3	8.2	1.1×10^{-2}	2.2×10^{-4}	2.0×10^{-2}
5 mM Ce^{3+}, 5 mM Ce^{4+}/1 N H_2SO_4	1.5	25.1	3.2×10^{-1}	9.3×10^{-5}	2.9×10^{-4}
	1.5	25.8	1.2×10^{-1}	19.7×10^{-4}	1.6×10^{-4}

case of 1 N H_2SO_4 containing Ce^{3+}/Ce^{4+} and of 1 N H_2SO_4 only. Table 2 indicates that the dissolution of the electrode was distinctly suppressed when the Ce^{3+}/Ce^{4+} was present. The current in Fig. 3, therefore, exhibits the reaction current of the redox system itself.

The apparent exchange current density, i_0, was obtained from the extrapolation of the Tafel region of the I-V curves on various electrodes to an open-circuit potential of each redox system, as measured with a Pt electrode, and was plotted against the conductivity of the electrodes for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems. Figure 6 shows a linear relationship between i_0 and the conductivity of the electrode for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$. Such a relation has already been observed with the redox reactions on the lithiated NiO electrode,[2] though i_0 had its maximum value at the specified conductivity of the α-Fe_2O_3 electrode in the Fe^{2+}/Fe^{3+} system.

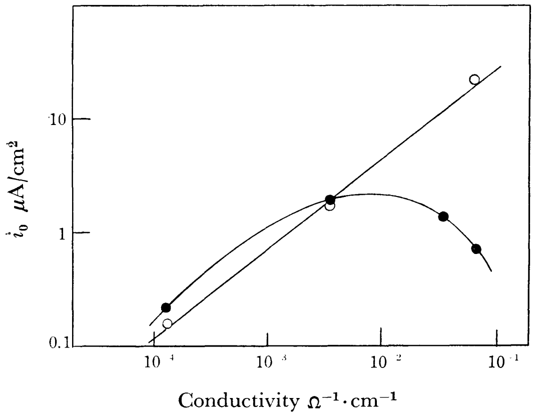
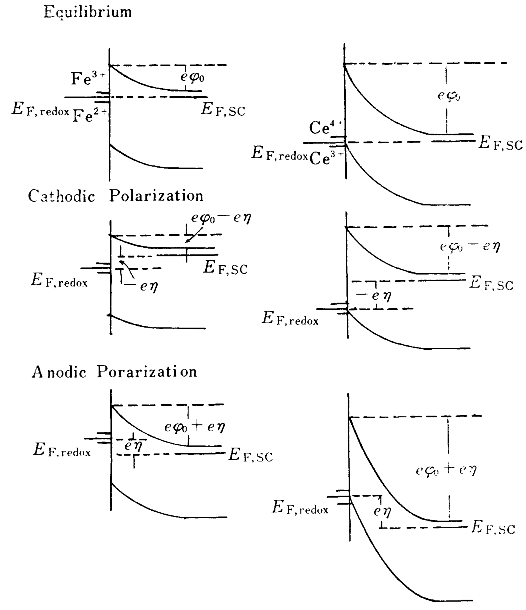


Fig. 6. Exchange current densities of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems as a function of the electrical conductivity of the electrodes.
—○— $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, —●— Fe^{2+}/Fe^{3+}

Discussion

The I-V curves of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and Fe^{2+}/Fe^{3+} systems were quite different from those on the lithiated NiO electrode,[1] where the cathodic current flow was hindered and where the anodic reaction proceeded under activation-controlled conditions. The suppression of the anodic current flow in these systems must occur as a result of either the delay of the supply of the charge carrier in the electrode[5-7] or the hindrance of the flow of the change carriers by the rectifying portion present in the electrolytic system. The former possibility is, however, obviated by the fact that the anodic current was proportional to the concentration of Fe^{2+}, as Fig. 4 shows. Therefore, the anodic current must be suppressed by the potential barrier.

The role of the potential barrier which might



(a) Fe^{2+}/Fe^{3+} system (b) Ce^{3+}/Ce^{4+} system

Fig. 7. Schematic energy level diagram of α-Fe_2O_3/redox electrolyte interface. (a) Fe^{2+}/Fe^{3+} system-electrode, (b) Ce^{3+}/Ce^{4+}-electrode. Each energy state in this diagram means the state of the maximum distribution probability of each species

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[5] D.R. Turner, *J. Electrochem. Soc.*, **103**, 252 (1956).
[6] R. Greth and M. E. Cowler, *J. Electrochem. Soc.*, **115**, 645 (1968).
[7] H. Gerischer, *Z. Elektrochem.*, **63**, 500 (1959).

exists at the Pt-α-Fe_2O_3 interface can be ignored, as was discussed previously.[3] Another possible potential barrier is the one formed on the electrode surface.[8] The electron density on the surface of the electrode must be poor in the potential shown in Fig. 4, since the flat-band potential is by far the lower.[3] Thus, the energy profile of the electrode/electrolyte interface can be pictured as is shown in Fig. 7(a), although the application of the band model to the energy structure of the 3*d* transition metal oxide may not necessarily be adequate.[9] In Fig. 7, the energy state of the redox electrolyte is also presented using a concept of the electron state which is fully anologous to that of the solid state.[10] In this figure, $E_{\mathrm{F,redox}}$ and $E_{\mathrm{E,sc}}$ represent the Fermi level of the redox electrolyte[10] and that of the semiconductor respectively. ψ_0 is the potential drop in the space-charge layer formed on the semiconductor electrode when it is in equilibrium with the redox electrolyte, and η is the overpotential.

According to Fig. 7(a), no potential barrier exists to the hole transfer from the electrode into the electrolyte. The hole transfer in this direction is equivalent to the anodic current. Therefore, if the positive holes were abundant in the electrode, the anodic current would not be saturated at such a small value as 10—100 $\mu A/cm^2$. By combining this fact with the fact that there is no possibility of a delay in the supply of a charge carrier in the electrode, the possibility of the hole transfer mechanism in these reactions can be denied.

On the other hand, there will be a potential barrier for electron transfer in the electrode/electrolyte interface, as Fig. 7(a) shows. However, the height of the potential barrier for the electron transfer from the electrode into the electrolyte will decrease in proportion to the cathodic polarization, because much of the polarization potential will be applied to the surface of the electrode. Thus, the cathodic current resulting from the electron transfer from the electrode into the electrolyte will not be suffered to pass through this potential barrier. In the case of the reverse direction of the current flow, the electron must flow from the electrolyte into the electrode, and during this process the electron should jump over the potential barrier. The height of the potential barrier in this case would not be changed distinctly with the polarization[11] if the polarization voltage is almost entirely applied in the electrode surface region. Then the situation could resemble the rectifying junction formed on the metal *N*-type semiconductor interface. The anodic current would, therefore, be saturated with the anodic polarization.[12] Almost the same interpretations is applicable to the reaction of the $Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$ system, because the redox potential of this system is near to that of the Fe^{2+}/Fe^{3+} system and the *I-V* curves of these two system resemble each other.

The situation is quite different in the Ce^{3+}/Ce^{4+} system (Fig. 7(b)). The charge carriers in the redox electrolyte will have a chance to come in contact with the unoccupied state of the electrode because of their high redox potentials. If the electron-transfer mechanism is also acceptable under these circumstances, the electron should jump over by far the higher potential barrier in the electrode surface and then flow into the electrolyte, although the height of this potential barrier decreases with an increase in the cathodic polarization.

Therefore, the reduction current necessarily decreases in this system compared with those in the Fe^{2+}/Fe^{3+} or the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ systems. The distinct reduction current which was observed below 0.6V may indicate that a distinct electron transfer over this barrier is possible below 0.6V (see Fig. 5). On the contrary, a distinct cathodic current would have been observed if the hole density had been rich enough in the electrodes. The almost negligible reduction current in the potential near the redox potential, that is, 1.3 —1.0V *vs.* SCE, suggests, however, that positive hole were scarce, if any existed at all. As has already been described, the distinct anodic current above 1.2V was not affected by the addition of Ce^{4+} or Ce^{3+}, although the dissolution of the electrode was suppressed by these ions. This finding suggests that

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[8] H. Gerischer, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, ed. by P. Delahey and C. W. Tobias, Interscience Publishers, New York, N.Y. (1961), p. 151.

[9] F. J. Morin, *Phys. Rev.*, **93**, 1195 (1954).

[10] H. Gerischer, *Z. Physik. Chem. N.F.*, **26**, 223 (1960).

[11] In the energy profile for the lithiated NiO/redox electrolyte interface presented previously (Ref. 1), a bending of the energy band of the electrode surface with the polarization was shown, but the energy difference between the electrode and the redox electrolyte during a steady-state polarization was not taken into consideration. However, an energy difference equivalent to the overvoltage will eventually exist between the redox electrolyte and the electrode. In this respect, the energy profile represented in the previous paper should be modified in such a manner that the Fermi level of the electrode is different from that of the redox electrolyte by an energy equivalent to the overvoltage. Accordingly, it should be possible to understand similarily the cathodic current of the redox system on the lithiated NiO electrode, presented previously, assuming that an almost constant potential difference is preserved between the redox electrolyte and the upper, or the lower energy state at the band edge of the electrode whether the electrode is polarized or not.

[12] According to the Mott-Schottoky theory, the current, J, is related to applied voltage, V, as in the following formula when there is a rectifying junction between a metal and a semiconductor:

$$J=J_0[\exp(eV/kT)-1]$$

the current was restricted by a factor other than the concentration of ions in the electrolyte.

The hole transfer mechanism may, then be considered to be inadequate. Therefore, an electron transfer mechanism should be considered. The distinct current increase above 1.2V might be brought by the electron tunneling[13] through the barrier layer. Under a high anodic polarization, the redox electrolyte will meet the electron in the electrode through the narrower part of the potential barrier, though the width of the potential barrier increases with an increase in the potential.[14] Thus, the electron tunneling through the narrower part of the potential barrier becomes possible. The width of the barrier layer at the same polarization potential is narrower for a electrode with a low resistivity.[14] Therefore, the probability of the electron tunneling is larger for the electrode with a low resistivity at the same polarization potential.

According to the above discussion, i_0 is determined by the numbers of the charge carriers which jump over the potential barrier. Therefore, i_0 may be expected to be larger for the electrode with the lower resistivity. Nevertheless, the highest i_0 was observed in the Fe^{2+}/Fe^{3+} system. The Fe^{2+}/Fe^{3+} system is the simpler redox system and are not usually form the adsorbed intermediate. However, either the ferric of the ferrous ion, or the both, in the electrolyte might adsorb on the electrode surface, which has unshared electrons pointing into the electrolyte, since ferric and ferrous ions were also constituent ions of the electrode. The energy-barrier height formed in the electrode surface region is conceivably determined by the quantity of the adsorbed ions and the polarization potential. The electrode with a large Ti content is rich in nonstoichiometry. Therefore, if it is assumed that the adsorption of the ions in the electrolyte occurs most effectively on the nontoichiometric parts of the electrode surface,[15] the quantity of adsorbant will be large for the electrode with a large Ti content; then, the potential barrier height of this electrode will be changed distinctly. The i_0 in the Fe^{2+}/Fe^{3+} system was possibly determined by this effect as well as by the concentration of the charge carriers in the bulk of the electrode.

Among 3*d*-transition metal oxides, Ti-doped α-Fe_2O_3 and Li-doped NiO are usually accepted as typical "hopping-type" semiconductors, while TiO_2 shows a typical "drift-type" conduction. In the drift-type semiconductor electrodes, such as Ge, ZnO, and TiO_2, the electrochemical reaction is occasionally controlled by the behavior of the minority carriers.[16] As has been discussed above, however, it seems that only the majority carrier is conceivably concerned in the electrochemical reaction on the α-Fe_2O_3 electrode. This is also suggested in the case of the lithiated NiO electrode.[1] In this sense, the electrode of a hopping-type semiconductor may play a different role in the electrochemical reaction from a drift-type semiconductor.

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[13] R. Stratton, *J. Phys. Chem. Solid*, **23**, 1177 (1962).

[14] A. R. Plummer, "The Electrochemistry of Semiconductors," ed. by P. J. Holmes, Academic Press, New York (1962), p. 162.

[15] H. Yoneyama and H. Tamura, *Denki Kagaku*, **38**, 644 (1970).

[16] For example, F. Beck and H. Gerischer, *Z. Elektrochem.*, **63**, 943 (1959); W. P. Gomes, T. Freund and S. R. Morrison, *J. Electrochem. Soc.*, **115**, 818 (1968); A. Fujishima, K. Honda and S. Kikuchi, *Kogyo Kagaku Zasshi*, **72**, 108 (1969).