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Electrical Conductivity Changes in α-FeOOH and β-FeOOH upon Surface Dehydration

Katsumi KANEKO and Katsuya INOUYE

Department of Chemistry, Faculty of Science, University of Chiba, Yayoi-cho, Chiba 280

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Synopsis. The electrical conductivity of α-FeOOH and β-FeOOH, preheated at 100—140 °C *in vacuo*, was determined over the temperature range from 0 to 140 °C. The conductivity increased considerably with a rise in the preheating temperature. The increase appears to be due to Fe^{2+} ions produced by surface dehydration in the preheating.

Among the polymorphs of iron(III) hydroxide oxide (the so-called ferric oxyhydroxide), α-FeOOH, β-FeOOH, and γ-FeOOH occur naturally as minerals and as major components of the corrosion product of iron-base alloys. Each iron(III) hydroxide oxide has the characteristic structure.[1-3] It has been known that iron(III) hydroxide oxides are transformed into iron oxides (α-Fe_2O_3 or γ-Fe_2O_3) at around 300 °C in air according to this formula:

$$2\,FeOOH \longrightarrow Fe_2O_3 + H_2O.$$

However, when FeOOH crystals are heated under 10^{-5} Torr, the decomposing dehydration begins at temperatures as low as 100 °C.[4] In the preceding papers,[5,6] the present authors reported that the electrical conductivity of γ-FeOOH increases remarkably with a rise in the preheating temperature in the range of 100—140 °C under 10^{-5} Torr, and that this behavior can be explained by the formation of excess d-electrons due to dehydration. It was proposed that excess d-electrons migrate in γ-FeOOH crystals by means of the small-polaron hopping mechanism.[6]

In this work, the effect of the preheating temperature (100—140 °C) on the electrical conductivity will be examined for α-FeOOH and β-FeOOH in order to discuss the mechanism of carrier formation in comparison with the case of γ-FeOOH.

The α-FeOOH and β-FeOOH used in this study were the same samples as those examined earlier.[7] The pretreatment of the samples was also identical to that carried out for γ-FeOOH.[6] The conductivity of the compressed specimens, formed by applying a pressure of 150 kg/cm², was measured over the temperature range from 0 to 140 °C and at various frequencies (d.c., 200 Hz—10 MHz) by a method described previously.[8] The current-voltage characteristics for d.c. indicated that the contact between the specimen and an electrode was nearly ohmic.

The effect of oxygen on the dc conductivity was examined for α-FeOOH and β-FeOOH, evacuated at 10^{-5} Torr and 140 °C, by supplying oxygen of 0.1 Torr at 30 °C.

The total iron and Fe^{2+} contents were determined by conventional titration methods.[6,7]

The electrical conductivity at d.c. and in the lower-frequency range increased with the preheating temperature in the range from 100 to 140 °C. The variation in the conductivity, σ_{dc}, at 30 °C with the preheating temperature is shown in Fig. 1 (a). The Fe^{2+} concentration also increased with the preheating temperature (Fig. 1 (c)).

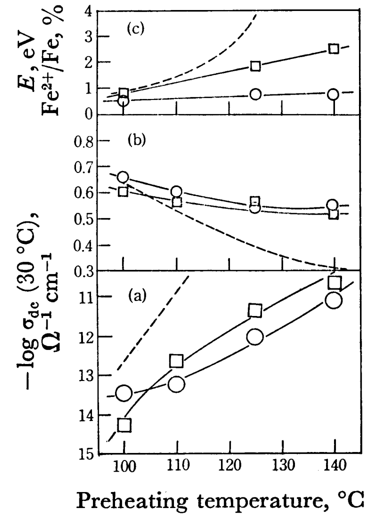

Fig. 1. Variations of (a) the logarithm of d.c. electrical conductivity at 30 °C, (b) activation energy of conductivity at d.c., and (c) Fe^{2+} concentration, with the preheating temperature for α-FeOOH (○) and β-FeOOH (□). The broken lines show the results on γ-FeOOH.[6]

It was found that logarithm of σ_{dc} is proportional to the reciprocal of the measuring temperature (0—140 °C), as is shown in Figs. 2 and 3 for α-FeOOH and β-FeOOH respectively. The notations α(β)-100, α(β)-110, α(β)-125, and α(β)-140 denote α-FeOOH or β-FeOOH samples preheated at 100, 110, 125, and 140 °C respectively. These linear relations have previously been found for γ-FeOOH.[6] The activation energy at

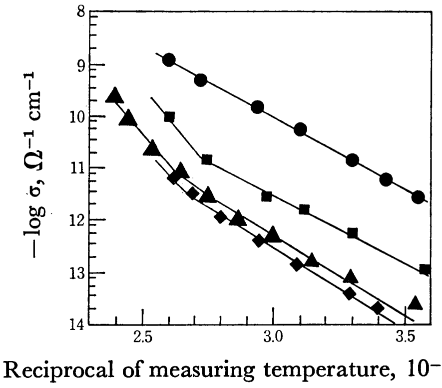

Fig. 2. The temperature dependence of electrical conductivity at d.c. for α-100 (◆), α-110 (▲), α-125 (■), and α-140 (●).

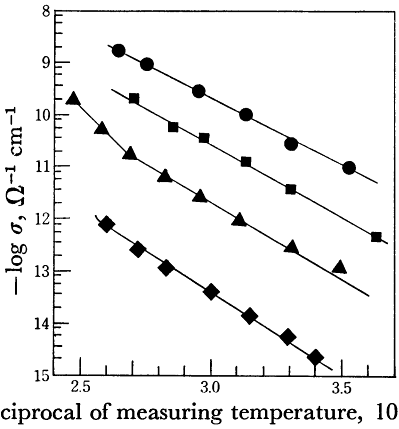

Fig. 3. The temperature dependence of electrical conductivity at d.c. for β-100 (◆), β-110 (▲), β-125 (■), and β-140 (●).

d.c., calculated from the linear relation below 100 °C, was less than 1 eV and decreased slightly with the preheating temperature, as is shown in Fig. 1 (b). The activation energy above 100 °C was 1—1.5 eV. The activation energy generally decreased with an increase in the frequency. The conductivity at higher frequencies varied slightly with the measuring temperature.

It was confirmed that the a.c. conductivity σ_{ac} $(=\sigma-\sigma_{dc})$ was proportional to f^s $(0.5<s<1)$ in the frequency range of 200 Hz—1 MHz. The constant s, representing the frequency dependence of the conductivity, decreased with an increase in the measuring temperature.

The exposure to oxygen of α-FeOOH and β-FeOOH preheated at 140 °C resulted in a lowering of the electrical conductivity at d.c. to less than a half of the initial value within 2 h.

The surface property of α-FeOOH and β-FeOOH crystals is characterized by their predominant surfaces, namely, the (100) planes for both α-FeOOH and β-FeOOH. The structures of these predominant surfaces were discussed in a previous paper.[9] The OH groups aligned in the c direction on surfaces are connected with each other by hydrogen bonding. The dehydration of an OH^- pair below 150 °C *in vacuo* appears to proceed through the formation of a quasi-molecular water by means of the following mechanism:

$$2\,OH^- \longrightarrow H_2O + V_o^- + O^-,$$

where V_o^- denotes the mono-charged oxygen vacancy. The dehydration causes an increase in the Fe^{2+} concentration by providing electrons from V_o^- to Fe^{3+}, which results in an increase in the conductivity.

α-FeOOH has OH^- pairs only at the surface, whereas β-FeOOH has the pairs not only on the surface, but also in pores in parallel to the c-axis (see Ref. 9). For γ-FeOOH, on the other hand, the dehydration occurs on the surface as well as in the bulk of the crystal.[6] The increase in the Fe^{2+} concentration with the pretreating temperature, in the order γ-FeOOH>β-FeOOH>α-FeOOH (Fig. 1 (c)), is pertinent to both the ability to dehydrate by the mechanism mentioned above and the difference in the surface area for each crystal form. The BET surface areas are in the following decreasing order[7]: γ-FeOOH: 124 m^2/g, α-FeOOH: 65 m^2/g, and β-FeOOH: 34 m^2/g.

The conductivity is assumed to follow the small-polaron hopping mechanism of excess d-electrons formed by the same surface dehydration for α-FeOOH and β-FeOOH as for γ-FeOOH. This assumption is supported by the frequency-dependence of the conductivity and the small activation energy of the conduction, and further by the fact that the mobility calculated from the conductivity and the Fe^{2+} concentration is less than 10^{-7} cm^2 V^{-1} s^{-1} at 30 °C. It was explained in the case of γ-FeOOH[6] that a decrease in the activation energy is due to an increase in the Fe^{2+} concentration and that the conductivity increase with the preheating temperature is caused by the increase in the interaction between Fe^{2+} ions. The same mechanism may also be applied to α-FeOOH and β-FeOOH. However, the decrease in activation energy with the preheating temperature for α-FeOOH and β-FeOOH is smaller than that for γ-FeOOH (Fig. 1 (b)). A lower interaction between Fe^{2+} ions in α-FeOOH and β-FeOOH than γ-FeOOH is presumed, because the Fe^{2+} concentration is considerably lower in α-FeOOH and β-FeOOH than in γ-FeOOH. It is noteworthy that the conductivity increase with the preheating temperature is less marked for α-FeOOH and β-FeOOH than for γ-FeOOH.

The decrease in the d.c. conductivity observed when oxygen was introduced into the evacuated sample indicates that electrons once formed by the dehydration are consumed by chemisorbed oxygen molecules at surface defects.

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