

tween hydride and cis phosphorus (3–20HZ). The small coupling constants of **1** indicate that the hydride is cis to the phosphorus. Therefore, the possible structure of **F** will be eliminated.

The <sup>31</sup>P{H} NMR spectrum (See Figure 2) provides additional information on the structure of **3**. It consists of one doublet and one triplet due to the spin coupling between the chemically equivalent two phosphine ligands and one phosphine ligand, corresponding to the AX<sub>2</sub> spin system. This pattern is very similar to that of the compound Os(PMe<sub>2</sub>Ph)<sub>3</sub>Cl<sub>2</sub>(MeCN)<sup>17</sup>, which has the mirror plane formed by one phosphine, MeCN and two chlorine. Accordingly, from our experimental observations, the correct structure of the compound **3** appears to favor the structure **E**. The complexes of **1**, **2**, and **4** can be similarly assigned as the complex **3**.

In further studies, we are investigating the possibility of carbon-carbon bond cleavage under the same condition.

**Acknowledgements.** We wish to thank the Korea Science and Engineering Foundation for the financial support.

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## Transport Mechanisms and Defect Structures of the System $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-CoO

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The electrical conductivity of the system  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-CoO was measured in the temperature range 200–1000°C and Po<sub>2</sub> range 10<sup>-7</sup>–2 × 10<sup>-1</sup> atm. Possible defect models were suggested on the basis of conductivity data, which were measured as a function of temperature and of oxygen partial pressure. The observed activation energies were 0.50 eV and 1.01 eV in the low- and high-temperature regions, respectively. The observed conductivity dependences on Po<sub>2</sub> were  $\sigma \propto Po_2^{-1/6}$  in the Po<sub>2</sub> range 10<sup>-7</sup>–10<sup>-4</sup> atm and  $\sigma \propto Po_2^{-1/4}$  at Po<sub>2</sub>'s of 10<sup>-4</sup>–2 × 10<sup>-1</sup> atm at temperatures from 300–1000°C. An extrinsic electron conduction due to an V<sub>o</sub> defect and an intrinsic electron conduction due to an Fe<sup>+</sup> defect were suggested at different temperature and oxygen partial pressure regions, respectively.

### Introduction

Fe<sub>2</sub>O<sub>3</sub> is known to be metal excess,<sup>1,2</sup> oxygen deficient<sup>3</sup>, and an intrinsic semiconductor,<sup>4,5</sup> while FeO and Fe<sub>3</sub>O<sub>4</sub> are metal deficient p-type semiconductors, represented as Fe<sub>1-x</sub>O<sup>6-8</sup> and Fe<sub>3-x</sub>O<sub>4</sub><sup>1,9</sup>, respectively. Salmon<sup>1</sup> suggested that predominant defects in Fe<sub>2</sub>O<sub>3</sub> are oxygen vacancies or interstitial iron ions.

Two surface sites, probably an Fe<sup>2+</sup> interstitial and an ox-

xygen vacancy were suggested by Kim *et al*<sup>10</sup> from the kinetic measurements of the oxidation of CO on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which was prepared by FeCl<sub>2</sub> and KOH according to the Balz method.<sup>11</sup> The oxygen vacancy was also found from the measurements of conductivities on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub><sup>12</sup>, Ni-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub><sup>13</sup>, and Cd-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub><sup>14,15</sup> at temperatures from 250 to 460°C under various P<sub>co</sub>, P<sub>so<sub>2</sub></sub>, and Po<sub>2</sub> conditions. The conductivity data showed that the adsorption of O<sub>2</sub> on pure and doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> withdraws the conduction electrons from an

oxygen vacancy, while CO and SO<sub>2</sub> donates electrons to the conduction band.<sup>12-14</sup>

The electrical conduction mechanism in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has been generally proposed as a wide band conduction or a hopping conduction of small polaron in a narrow band. The microwave and dc conductivity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> have been measured at temperatures from 925 to 1194°C in air, and a polaron below 925°C and free carriers above 925°C were suggested as the electrical conduction mechanisms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>16</sup> Mochizuki interpreted  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as an intrinsic semiconductor in the temperature range from 925 to 1194°C. Gardner *et al.*,<sup>3</sup> on the other hand, reported that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was an extrinsic semiconductor at temperatures below 800°C.

In this investigation, dc conductivities of the systems  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 0.53 mol % CoO,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 1.02 mol % CoO, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 1.51 mol % CoO were measured as a function of temperature and an oxygen partial pressure in the temperature range 200 to 1000°C and P<sub>O<sub>2</sub></sub> range 10<sup>-7</sup> to 2 × 10<sup>-1</sup> atm.

## Experimental

**Sample preparations: Pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.**<sup>17,18</sup> Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O solution in water was added to 6% aqueous ammonia with constant stirring. The precipitate was washed with distilled water until the washed liquor was free from nitrates and then dried at 50°C. The product was heated at 200°C for 10 hrs with a dry stream of air in order to remove the water. The phase of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was identified by x-ray powder technique. The x-ray pattern showed a fine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. The atomic absorption spectroscopy (A.A.S.) showed that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder contains less than 153 ppm of total impurities such as Ni, Cu, Mn, Ca, Mg, etc.

**The systems  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-CoO:** Fine powders of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CoO (obtained from Johnson Matthey Co. 99.99%) were uniformly dispersed in various mol ratios with chemically pure ethanol for 72 hrs and then dried at 200°C.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-CoO solid solutions were prepared by the direct solid-state reaction between the relatively high m.p. CoO and low m.p.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The fine powders of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CoO were sintered at 800°C for 10 hrs and annealed at 1350°C for 72 hrs in covered platinum crucible and cooled slowly to room temperature in order to minimize the defects produced by heating. The preheated

specimen was etched in dilute HNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The amount of CoO incorporated into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was determined by A.A.S. and found to be 0.53, 1.02, and 1.51 mol %, respectively. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples doped with 0.53, 1.02, and 1.51 mol % CoO were compressed into pellets under 196 MPa in vacuum and then heated at 1350°C for 10 hrs. The pellet density measured by the mercury immersion method showed 96% of the theoretical density, with an average grain size of approximately 6.13  $\mu$ m. The specimen had 4-5% porosity and the average pore size was approximately 0.72  $\mu$ m. The pellet was cut into a rectangular form, 1.2 × 0.65 × 0.20 cm<sup>3</sup> in size, by diamond cutter and polished flat using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder as an abrasive. Before the sample was introduced into the sample basket, it was always etched in (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and dilute HNO<sub>3</sub>, and washed with distilled water, dried, and then connected to the Pt probes.

**P<sub>O<sub>2</sub></sub> establishment.** The various oxygen partial pressures were established using pure oxygen or nitrogen, and or a mixture of 0.001% oxygen in nitrogen obtained from Matheson Gas Products. The quartz sample basket was evacuated to a pressure of 1 × 10<sup>-7</sup> torr by the diffusion pump<sup>19</sup> at room temperature, and then the temperature of the sample container was increased up to 200°C. A mixture of oxygen and nitrogen, or pure oxygen, was introduced into the sample basket, which was then evacuated again to a pressure of 1 × 10<sup>-6</sup> torr. The introduction and evacuation of gas at 200°C were performed two or three times, and then total pressure was controlled with 0.001% oxygen in nitrogen in order to establish the required P<sub>O<sub>2</sub></sub>. The pressures of the evacuated sample container and the O<sub>2</sub>-N<sub>2</sub> mixture were read on a McLeod gauge, a thermocouple gauge, Pirani gauge, and an ultra-high vacuum ionization gauge, respectively.

**Conductivity measurement.** Measurements of electrical conductivity were performed according to the Valdes' technique,<sup>20</sup> which was briefly described in the previous articles.<sup>21,22</sup> This technique has also been employed to measure the electrical conductivity of other oxide semiconductors; for example,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: Cd,<sup>10,12,14,15</sup> La<sub>2</sub>O<sub>3</sub>: Cd,<sup>23</sup> Sm<sub>2</sub>O<sub>3</sub>,<sup>24</sup> H<sub>2</sub>-Reduced Rutile,<sup>25</sup> SrTiO<sub>3</sub>: Ni/CO-Reduced SrTiO<sub>3</sub>: Ni,<sup>26</sup> and Tm<sub>2</sub>O<sub>3</sub>.<sup>27</sup> A schematic diagram of the conductivity cell, the cell geometry, electrical circuit, and four-probe was shown in Figure 1. Details have been described for the vacuum system,<sup>28</sup> instruments,<sup>29</sup> and the conductivity calculation procedure.<sup>21,22</sup> The current through the sample was maintained from 10<sup>-7</sup> to 10<sup>-2</sup> A by a rheostat and the potential across the inner two probes were maintained between 0.3 and 1.7 V. The potential difference was measured by a Keithley 642 digital multimeter, and the current through the sample was measured by a Keithley 616 digital electrometer. The measurements of electrical conductivity were performed over a cycle in the temperature range 200-1000°C under P<sub>O<sub>2</sub></sub>'s from 10<sup>-7</sup> - 2 × 10<sup>-1</sup> atm, starting from the low temperature end, proceeding toward the high temperature end, and then back again to the lower end. The sample was held at each temperature until equilibrium between the oxygen phase and sample was achieved, indicated by a constant conductivity.

## Results and Discussion

**Temperature dependence of electrical conductivity.** Electrical conductivities were investigated as a function of temperature and an oxygen partial pressure(P<sub>O<sub>2</sub></sub>). Figure 2

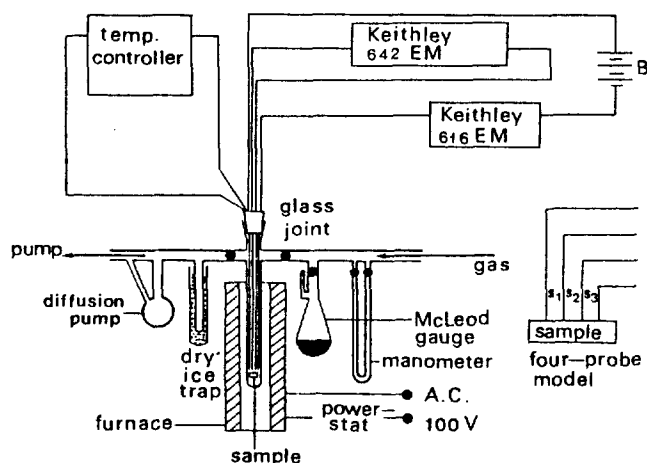
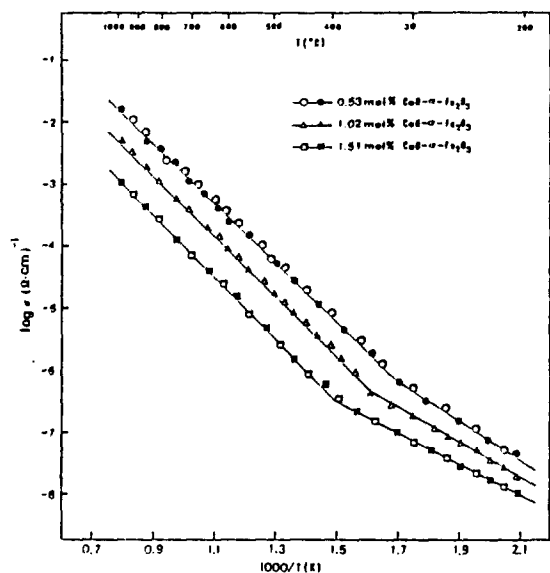
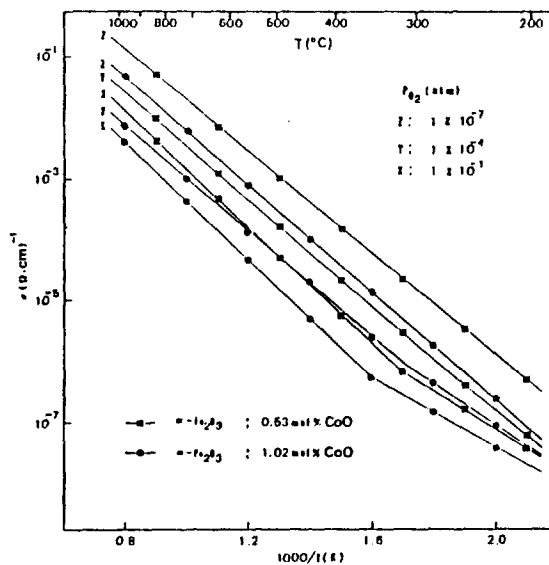


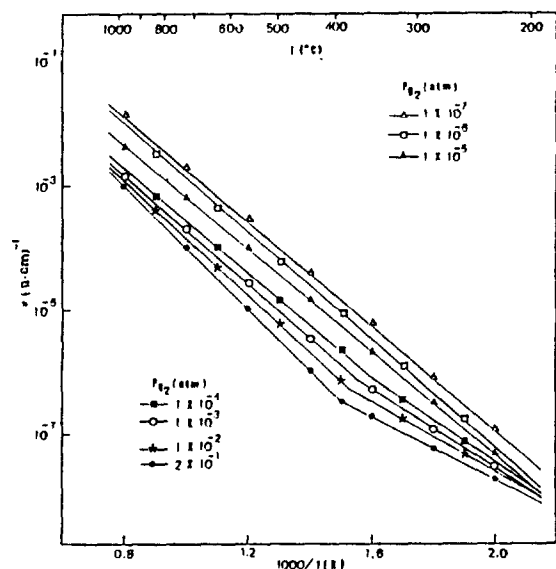
Figure 1. Schematic drawing of the conductivity measurement circuitry and the four-probe model.



**Figure 2.** Electrical conductivities of  $\alpha\text{-Fe}_2\text{O}_3\text{:CoO}$  as a function of reciprocal absolute temperature at constant oxygen partial pressure of  $2 \times 10^{-1}$  atm.  $\circ\text{-}\Delta\text{-}\square\text{-}$ : data measured at increasing temperature;  $\bullet\text{-}\blacktriangle\text{-}\blacksquare\text{-}$ : data measured at decreasing temperature.



**Figure 4.** Conductivity isobars of  $\alpha\text{-Fe}_2\text{O}_3\text{:1.02}$  and  $\alpha\text{-Fe}_2\text{O}_3\text{:0.53}$  mol % CoO at three typical oxygen partial pressures.



**Figure 3.** Temperature dependence of electrical conductivity of  $\alpha\text{-Fe}_2\text{O}_3\text{:1.51}$  mol % CoO at constant oxygen partial pressures.

shows the  $\log \sigma$  vs.  $1/T$  for 0.53, 1.02, and 1.51 mol % CoO-doped  $\alpha\text{-Fe}_2\text{O}_3$  at temperatures from 200 to 1000°C and  $P_{O_2}$  of  $2 \times 10^{-1}$  atm. The electrical conductivity data measured at increasing temperature are in good agreement with the data measured at decreasing temperature for all CoO-doped  $\alpha\text{-Fe}_2\text{O}_3$  samples. From the electrical conductivity dependences on temperature in Figure 2, two regions are possibly assumed: The low- and high- temperature portions of the  $\log \sigma$  vs.  $1/T$  plots are the extrinsic and intrinsic regions, respectively. At  $P_{O_2}$  of  $2 \times 10^{-1}$  atm all samples show the distinct extrinsic

**Table 1.** Observed Activation Energies(eV) for the Conductivity of Pure and Doped  $\alpha\text{-Fe}_2\text{O}_3$

Gardner <i>et al.</i> <sup>3</sup>	Tannhauser <sup>30</sup>	Geiger & Wagner <sup>31</sup>	Chang & Wagner <sup>32</sup>	This work	
				high temp.	low temp.
1.00	1.07	1.15	1.18	1.01	0.50

regions and inflection points appear in the temperature range 300–400°C, indicating all the experimental curves of  $\log \sigma$  vs.  $1/T$  plots to be linear at the low- and high-temperature regions away from the inflection points.

Activation energy obtained by the least-square method from the conductivity-temperature data for 1.51 mol % CoO-doped  $\alpha\text{-Fe}_2\text{O}_3$  is 0.50 eV for the extrinsic region and 1.01 eV for the intrinsic region. Table 1 shows the activation energies for the conductivity of pure and doped  $\alpha\text{-Fe}_2\text{O}_3$  observed by several workers.<sup>3, 30-32</sup> As shown in Table 1, the activation energy(1.01 eV) for the high temperature region is in good agreement with the values of Gardner *et al.*<sup>3</sup> and Tannhauser<sup>30</sup> and is in reasonable accordance with those of Geiger and Wagner<sup>31</sup> and Chang and Wagner.<sup>32</sup> From good or reasonable agreement of an activation energy in the high temperature region, the intrinsic conductivity of the CoO-doped  $\alpha\text{-Fe}_2\text{O}_3$  is confirmed at  $P_{O_2}$  of  $2 \times 10^{-1}$  atm.

Figure 3 shows the temperature dependence of electrical conductivity for 1.51 mol % CoO doped  $\alpha\text{-Fe}_2\text{O}_3$  at  $P_{O_2}$ 's of  $10^{-7}$  to  $2 \times 10^{-1}$  atm. As shown in this figure, the extrinsic conductivities disappear at  $P_{O_2}$ 's lower than  $1 \times 10^{-4}$  atm. As can be seen in Figure 4, the extrinsic conductivity vanishes even at  $P_{O_2}$  of  $1 \times 10^{-4}$  atm for 0.53 mol % CoO-doped  $\alpha\text{-Fe}_2\text{O}_3$ . This extension of the extrinsic region to the lower  $P_{O_2}$  with increasing doping level indicates that some parts of the intrinsic region in n-type  $\alpha\text{-Fe}_2\text{O}_3$  change to the extrinsic region due to impurity doping. This change of the intrinsic to the extrinsic appears at the temperature lower than 300–400°C,

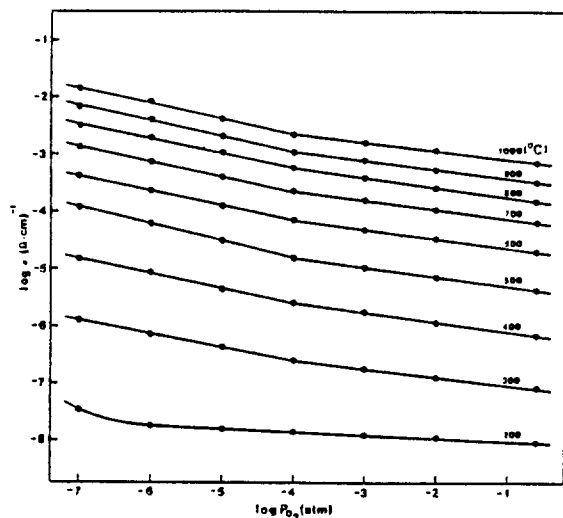


Figure 5. Conductivity isotherms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 1.51 mol % CoO as a function of oxygen partial pressure.

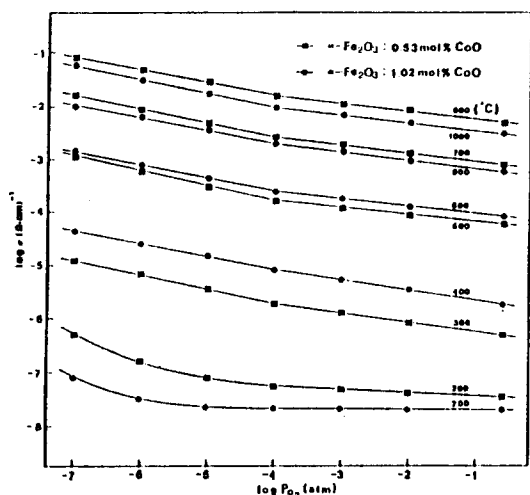


Figure 6. Conductivity isotherms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 1.02 and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 0.53 mol % CoO as a function of oxygen partial pressure.

regardless of the doping level.

**Po<sub>2</sub> dependence of Electrical Conductivity.** Figure 5 shows the conductivity isotherms of 1.51 mol % CoO-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as a function of Po<sub>2</sub>. The conductivity increases with decreasing Po<sub>2</sub> at constant temperature. A similar increase in conductivity with decreasing Po<sub>2</sub> is seen in 1.02 and 0.53 mol % CoO-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, as shown in Figure 6. In Figures 5 and 6, the conductivity dependences on Po<sub>2</sub> are approximately fixed, regardless of the dopant level of CoO in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. However, at 200°C it is difficult to evaluate the slope in log  $\sigma$  vs. log Po<sub>2</sub> plot for three samples. In the temperature range 300–1000°C, log  $\sigma$  vs. log Po<sub>2</sub> shows a discontinuity at Po<sub>2</sub> of  $1 \times 10^{-4}$  atm for all samples, as shown in Figures 5 and 6. This indicates that the conduction mechanism is the same for the three different samples. The  $-1/n$  values in  $\sigma \propto Po_2^{-1/n}$  are listed in Table 2 at the various temperatures investigated. As shown in Table 2,  $-1/n$  values are approximately 1/4 and 1/6 at low ( $<10^{-4}$  atm) and high ( $>10^{-4}$  atm) pressure regions, respectively. Because two different defect structures may

Table 2. Electrical Conductivity Dependence on PO for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Doped with Various CoO Contents (mol %) at Measured Temperatures

Temperature(°C)	$-1/n$ (average values)	
	Low Pressure Region ( $<10^{-4}$ atm)	High Pressure Region ( $\geq 10^{-4}$ atm)
200	—	—
300	1/4.3	1/6.5
400	1/4.0	1/5.8
500	1/4.3	1/6.0
600	1/4.1	1/6.0
700	1/4.2	1/6.0
800	1/3.9	1/6.0
900	1/3.8	1/6.3
1000	1/4.0	1/6.5

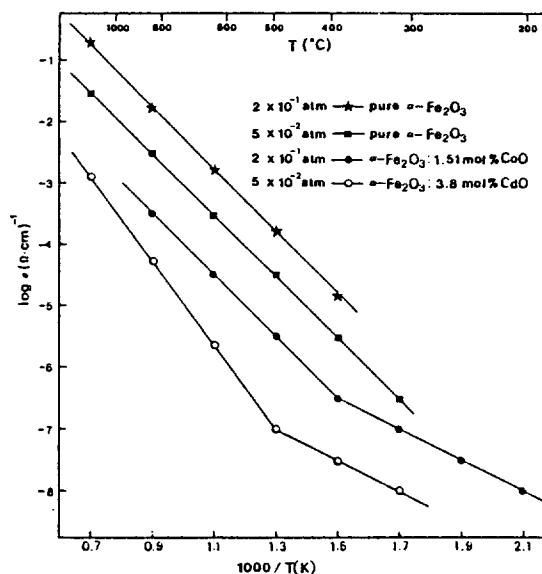


Figure 7. Comparative electrical conductivities of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CdO, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CoO at constant oxygen partial pressures. —★—: data from ref.(3); —○—: data from ref.(15); —●—: present work.

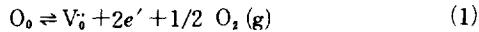
originate from 1/4 and 1/6, the error in the slope measurement is critical. It is generally believed that this log  $\sigma$  vs. log Po<sub>2</sub> plot is insensitive to a small change of slope. However, our test plots of  $\sigma$  vs.  $Po_2^{-1/n}$  at several measured temperatures give the same slope as those in the log  $\sigma$  vs. log Po<sub>2</sub> plots, showing a straight lines away from Po<sub>2</sub> of  $1 \times 10^{-4}$  atm.

Figure 7 shows the comparative electrical conductivities of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CdO, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CoO at constant Po<sub>2</sub>'s. As shown in this figure, the slope of the intrinsic region in Arrhenius plot for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 1.51 mol % CoO is in good agreement with the slopes of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at Po<sub>2</sub>'s of  $2 \times 10^{-1}$  atm<sup>3</sup> and  $5 \times 10^{-2}$  atm,<sup>15</sup> however it is somewhat different from the slope of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: 3.8 mol % CdO. The activation energy for 3.8 mol % CdO-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is 1.34 eV and inflection point appears at about 500°C. These large activation energy and high-temperature inflection point in comparison with 1.01 eV and 400°C for 1.51 mol % CoO-doped

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> indicate that the conduction mechanism may be different in the intrinsic region, and the extrinsic region extends to the high temperature side. However, the activation energy (0.51 eV) in the extrinsic region is exactly same for CdO- and CoO-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples. This indicates that the conduction mechanism in extrinsic region may be unique for two samples.

### Electrical Conduction Mechanisms

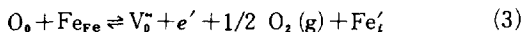
**Intrinsic region ( $P_{O_2} < 10^{-4}$  atm).** The activation energy and  $P_{O_2}$  dependence of electrical conductivity are 1.01 eV and  $\sigma \propto P_{O_2}^{-1/4}$ , respectively. At  $P_{O_2}$  lower than  $10^{-4}$  atm, the electrical conductivity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CoO shows the typical intrinsic conductivity.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CoO was already annealed at 1350°C, and in addition to heating,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was readily doped with impurity. By heating  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at high temperature, oxygen vacancy can be produced.<sup>1, 33-35</sup> The diffusion of lattice oxygen may supply electrons for the conduction band by the following disorder



where  $V_o^{\bullet}$  and  $e'$  are effectively doubly and singly charged oxygen vacancy and electron, respectively. In Eq.(1) the carrier concentration<sup>3</sup> will increase with increasing concentration of oxygen vacancy produced by the diffusion of lattice oxygen. However, the activation energy for migration of the electron localized at donor level has been known to be 0.1-0.3 eV.<sup>30,36,37</sup> Therefore, it is believed that the observed activation energy (1.01 eV) in the intrinsic region consists of the total energy for migration of carrier, for diffusion of Fe ion, and for the formation of oxygen vacancy. The energy for the formation of an oxygen vacancy is small in comparison with that for the diffusion of Fe ion, since oxygen vacancies are easily produced in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> when the diffusion of lattice Fe ions occurs.<sup>1,3,16,34</sup> Furthermore, according to the diffusion data reported by Salmon<sup>1</sup>, Gardner *et al.*,<sup>3</sup> and Kingery *et al.*,<sup>34</sup> the diffusion of lattice Fe ion supports this fact, since the self-diffusion rate of Fe ion nearly equals to that of lattice oxygen. The diffusion of lattice Fe may be presented by the following



where  $Fe_{Fe}$  and  $Fe'_i$  represent neutral Fe in lattice site and effectively singly charged Fe interstitial, respectively. If reactions(1) and (2) occur simultaneously in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: CoO, the summation of two disorders is the form.



The equilibrium constant(K) in disorder(3) is

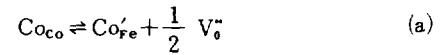
$$K = \frac{(Fe'_i)}{(Fe_{Fe})} (V_o^{\bullet}) (e') P_{O_2}^{1/2} \quad (4)$$

where  $(Fe'_i)/(Fe_{Fe})$  is constant, and in disorder(1) electroneutrality condition is  $2(V_o^{\bullet}) = (e')$ . Substituting  $C = (Fe'_i)/(Fe_{Fe})$  and  $2(V_o^{\bullet}) = (e')$  into eq.(4), and rearranging Eq.(4) for  $(e')$ ,  $(e') = \left(\frac{K}{C}\right)^{1/2} P_{O_2}^{-1/4}$ . Since  $\sigma \propto (e')$ , the electrical conductivity dependence on  $P_{O_2}$  is

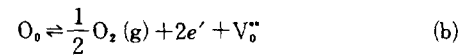
$$\sigma \propto P_{O_2}^{-1/4} \quad (5)$$

$\sigma \propto P_{O_2}^{-1/4}$  is consistent with the experimentally observed dependence in the intrinsic region at  $P_{O_2} < 10^{-4}$  atm, as shown in Table 2. Therefore, the transport mechanism is possibly explained by the disorders(1) and (2), and this mechanism can be conserved only when the two disorders(1) and (2) proceed simultaneously to reach equilibria.

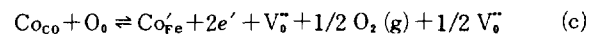
**Extrinsic region ( $P_{O_2} > 10^{-4}$  atm).** The activation energy and  $\sigma \propto P_{O_2}^{-1/6}$  are 0.50 eV and  $\sigma \propto P_{O_2}^{-1/6}$ , respectively. The ratio of the number of regular cation and anion sites in CoO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is constant, respectively. Thus in CoO the ratio of regular Co and oxygen sites is 1:1 regardless of whether the actual composition is stoichiometric or nonstoichiometric. Correspondingly, in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> the ratio of regular Fe to oxygen sites equals to 1:1.5. Through a defect reaction, 1/2  $V_o^{\bullet}$  is created when CoO incorporates with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This formation of an oxygen vacancy is presented by the reaction where  $Co'_{Fe}$



is singly charged cobalt at Fe site. According to the principle of controlled valency, the doped Co may act as an electron acceptor, and equilibrium(a) proceeds to the right as the mol % of CoO increases. As shown in Figures (2), (4), and (7), the conductivities decrease with increasing doping level. This indicates that another disorder may occur in this extrinsic region at  $P_{O_2} > 10^{-4}$  atm. This disorder reaction can be assumed as follows.



The increasing concentration with increasing doping in equilibrium(a) decreases oxygen vacancy concentration in equilibrium(b). The activation energy (0.50 eV) supports this fact: In the extrinsic region, Fe in regular Fe sites does not reduce, and the activation energy for the formation of oxygen vacancy is 0.4-0.3 eV, while the activation energy for the diffusion of Fe ion is estimated 0.51 eV. When the equilibrium(b) proceeds to the left due to the increasing doping level, the electron concentration in disorder (b) decreases. This decreasing electron concentration decreases the electrical conductivity, as shown in Figures (2), (4), and (7). The sum of the two disorders (a) and (b) is as follows.



In reaction (c),  $(Co'_{Fe})$  and  $1/2 (V_o^{\bullet})$  are determined by the doping level of CoO, and therefore, the equilibrium constant ( $K_c$ ) is

$$K_c = K(V_o^{\bullet}) n^2 P_{O_2}^{1/2} \quad (d)$$

where  $(V_o^{\bullet})$  can be replaced by  $1/2 n$ , and rearranging Eq.(d) for  $n$ ,  $n = \left(\frac{2K_c}{K}\right)^{1/3} P_{O_2}^{-1/6}$ . Since  $\sigma \propto n$ , the electrical conductivity dependence on  $P_{O_2}$  is

$$\sigma \propto P_{O_2}^{-1/6} \quad (e)$$

$\sigma \propto P_{O_2}^{-1/6}$  is consistent with experimentally observed

dependency in the extrinsic region at  $P_{O_2} > 10^{-4}$  atm. Therefore, it is possibly suggested that the transport mechanism is the reaction (c).

**Intrinsic region ( $P_{O_2} > 10^{-4}$  atm).** The activation energy and  $\sigma \propto P_{O_2}^{-1/6}$  are 1.01 eV and  $\sigma \propto P_{O_2}^{-1/6}$ , respectively.  $\sigma \propto P_{O_2}^{-1/6}$  indicates that even at high temperatures above 400°C the reduction process (1) does not easily take place at  $P_{O_2}$ 's higher than  $10^{-4}$  atm.  $\sigma \propto P_{O_2}^{-1/6}$  supports that the disorder reaction (2) occurs predominately, since the  $P_{O_2}$  dependence of electrical conductivity can be theoretically derived with the disorder reaction (2). With a view to an activation energy, however, this disorder reaction (2) requires more energy to proceed at  $P_{O_2}$ 's above  $10^{-4}$  atm.

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