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Mixed Conduction in Stabilized Zirconia at a Low Oxygen Partial Pressure*[1]

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The electromotive force of the oxygen concentration cell, O_2 gas|stabilized zirconia|Fe(+C)-melt+COgas, was measured at 1900°K as a function of the carbon concentration in iron melt, and the transference number of the stabilized zirconia was calculated. The transference number of the ions in the stabilized zirconia partition is less than unity over the whole range of carbon concentration. When the results are compared with the equations derived from plausible models, a reasonable coincidence is obtained.

In the stabilized zirconia crystals, the mobility or the diffusion coefficient of the oxygen ion is exceptionally large at temperatures far from the melting point,[1,2] while those of the metal ions are negligibly small.[3] The stabilized zirconia, therefore, has practically only one kind of charge carrier at an elevated temperature.[4,5]

This ideal character as an ionic conductor disappears at very low oxygen partial pressures due to the partial reduction of zirconia. Kiukkola and Wagner[4] first showed that the electronic conduction is negligible in comparison with the oxygen ion conduction at oxygen partial pressures as low as $10^{-21.5}$ atm at 870°C.

Vest and Tallan[6] have since reported on the transference number of the oxygen ion in calcia-stabilized zirconia, determined by their polarization method, as a function of the oxygen partial pressure at 1000°C, and have reported a transference number of less than 0.5 at 10^{-16} atm, for example.

Schmalzried[7] has measured the electromotive force of the cell, air|ZrO_2(+CaO)|Ca+CaO, at temperatures from 700 to 1000°C and has shown that, at 1000°C for example, the average transference number of oxygen ions in the zirconia electrolyte is about 0.5 when the oxygen partial pressure is 10^{-35} atm at one side of the electrolyte, while the other side is air.

Baker and West[8] have measured the electromotive force of the cell, H_2+H_2O|solid electrolyte|H_2+H_2O, over the range of temperatures from 1000 to 1600°C. They thought that their results for calcia-stabilized zirconia were consistent with those of Schmalzried. However, the numerical coincidence in their transference number for the zirconia electrolyte is only apparent, because the difference in oxygen partial pressure between air and a hydrogen-steam mixture at the reference electrodes must result in a difference in the transference number in the zirconia for the same oxygen partial pressures at the other side of the electrodes.

Tretyakov[9] has measured the electromotive force of the cell, air|ZrO_2(+CaO)|Cr+Cr_2O_3, or Mn+MnO, at temperatures from 600 to 1600°C and has given the relation;

$$\log P_{O_2}{}^* = -60.5\cdot 10^3/T + 19.5$$

where $P_{O_2}{}^*$ (in atm) is the partial pressure of oxygen gas at which the transference number of the ion in the zirconia becomes 0.5.

As one can see, these findings on the transference number cited above do not coincide with each other.

In these investigations, the measurements were done at several fixed oxygen partial pressures, or under several sets of limited conditions; the results were then extended to more general expressions by

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*1 Presented at the 73rd I. S. I. J. Meeting, Tokyo, April, 1967.

1) L. A. Simpson and R. E. Carter, *J. Am. Ceram. Soc.*, **49**, 139 (1967).

2) W. D. Kingery, J. Pappis, M. E. Doty and D. C. Hill, *ibid.*, **42**, 393 (1959).

3) W. H. Rhodes and R. E. Carter, *ibid.*, **49**, 244 (1966).

4) K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, **104**, 379 (1959).

5) The literature was cited in detail by M. F. Lasker and R. A. Rapp, *Z. phys. Chem. Neue Folge*, **49**, 198 (1966).

6) R. W. Vest and V. M. Tallan, *J. Appl. Phys.*, **36**, 543 (1965); *cf.* also R. W. Vest and V. M. Tallan, *J. Am. Ceram. Soc.*, **48**, 472 (1965).

7) H. Schmalzried, *Z. Elektrochem., Ber. Bunsenges. physik. Chem.*, **66**, 572 (1962).

8) R. Baker and J. M. West, *J. Iron Steel Inst.*, **1966**, 212.

9) Yu. D. Tret'yakov, *Izv. Akad. Nauk SSSR Neorgan. Materialy*, **2**, 501 (1966) [*Chem. Abstr.*, **65**, 1759c (1966)]; *cf.* also A. A. Vecher and D. A. Vecher, *Zh. Fiz. Khim.*, **41**, 1288 (1967).

adopting plausible, but not decisive, models for mixed conduction.

For the use of zirconia as a solid electrolyte, it is necessary to establish facts on the transference number over a wide range of oxygen partial pressure; such facts will make it possible to calculate the region of oxygen partial pressure in which the electronic conduction can be neglected.

Richardson and Dennis[10] and Rist and Chipman[11] have given a reliable value for the activity coefficient of carbon in liquid iron. In this system, the equilibrium:

$$\text{C(in Fe melt)} + \text{O(in Fe melt)} = \text{CO(in gas phase)} \quad (1)$$

can be expected. Therefore, one may calculate the activity of oxygen from the carbon concentration in the iron melt and the partial pressure of CO in the gas phase in equilibrium with the iron melt. This system can cover a wide range of oxygen partial pressures at low oxygen partial pressures, and has a relatively large buffer action in reaction to the leak of oxygen. Therefore, this system was used in the following experiment.

Similar cells, iron melt|stabilized zirconia|reference oxygen activity, have been reported by many investigators. They have given the relation between the electromotive force of their cells and the $\underline{O}$ in the iron melt, in the region where the average transference number of the stabilized zirconia was assumed to be unity.[12] In their measurments, the iron melts were in contact with such inert gases as argon gas; this may result in the serious scattering of the observed values.

Experimental

The electromotive force of the cell; O_2 gas|stabilized zirconia|Fe(+C), CO gas, was measured at 1900±2°K. Commercial zirconia tubes, Zr-23 of the Degussa Co., Ltd., were used in the cell as the stabilized zirconia partition. The results of the wet analysis of the tubes used are listed in Table 1, together with their change in chemical composition with use in the measurements. The arrangement of the cell is shown in Fig. 1. The cell was hung in a vertical-tube furnace, and then CO gas, mixed with from 0% to 3% of CO_2 gas, was made to flow upwards through the furnace at the flow rate of 2 cm/sec.

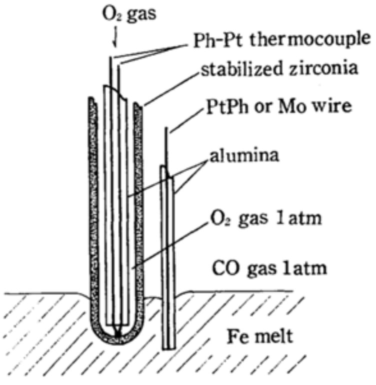

Fig. 1. Schematic illustration of cell arrangement.

The furnace used was a resistance-type furnace. A wire of 60%Pt-40%Rh alloy was wound round an alumina tube (40 mm in diameter, Al-23, of the Degussa Co., Ltd.), coated with fine powder of pure alumina (99.9% pure, Alcoa Co., Ltd.) and surrounded with the same powder about 15 cm thick for thermal insulation. The thermocouple for temperature control was fixed close to the wire. The temperature controllers used were the EC-51 type of the Ohkura Electric Co., Ltd. The center of the furnace, about 18 cm wide, was kept at 1900±2°K during operation.

The electromotive force was measured between a Pt-Rh wire of the thermocouple at the inside of the zirconia tube and a Pt-Rh wire or Mo wire immersed in the iron melt outside the zirconia tube. Because of the use of molybdenum wire, a correction of the electromotive force of the cell, corresponding to the thermoelectromotive force, was made. The dissolution rates of these wires in the iron melt were so high that the time available for the measurement of the electromotive force was about ten seconds for each measurement. The contamination of the iron melts from these wires was about 0.3% in atm ratio; this contamination was assumed to be negligible.

The 6%Rh94%Pt-30%Rh70%Pt thermocouple used in the cell was checked with the gold point, the diopside point, and the palladium point both before and after the experiment. No change in electromotive force was found.

TABLE 1. CHEMICAL COMPOSITIONS OF STABILIZED ZIRCONIA TUBES USED IN THE MEASUREMENT

Tube No.		ZrO_2(in wt%)	MgO	Fe_2O_3	TiO_2	Al_2O_3, CaO
Tube 1	before use	94.7 (±0.3)	5.0 (±0.1)	0.18 (±0.02)	0.20 (±0.1)	<0.1
	after use*	—	5.0	0.46	0.25	—
Tube 2	before use	94.5	5.0	0.16	0.20	<0.1
	after use**	—	5.1	0.32	0.20	—

* The part immersed in iron melt at the measurement condition for about 30 hr.
** For about 10 hr.

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10) F. D. Richardson and V. E. Dennis, *Trans. Faraday Soc.*, **49**, 171 (1953).

11) A. Rist and J. Chipman, "The Physical Chemistry of Steelmaking," ed. by J. F. Elliott, John Wiley and Sons, New York (1958), p. 3.

12) For example, W. A. Fischer and W. Ackermann, *Arch. Eisenhüttenwes.*, **36**, 643 (1965); Y. Matsushita and K. Gotō, *Transactions, I. S. I. J.*, **6**, 131 (1966).

Each iron sample was prepared by mixing 99.9% pure iron powder with graphite powder of a spectroscopic grade. The iron sample was placed in an alumina crucible, and was elevated slowly in the furnace. Then, the zirconia tube was immersed in the iron melt thus obtained and kept at 1900±2°K for ten minutes or more, after which the electromotive force was measured.

After the measurement, the sample was quenched immediately by lowering the crucible in the gas flow. A half of each sample pellet (about 30 g in weight) thus obtained was made into chips by a shaper or a diamond cutter and a hammer. The carbon concentration was measured by the method prescribed in JIS G-1211-2.3 (1963), *i. e.* the volume metric method. A standard sample of U. S. National Bureau of Standards, Cat. No. 12h (0.41 wt% carbon) was analyzed to check the carbon analysis; the value of 0.43 wt% carbon was thus obtained.

The immersion of the zirconia tube in a high-carbon iron melt results in numerous fine cracks on the zirconia surface. The cracks enlarge upon repeated exposure to the heating, immersing, and cooling cycle. Thus, the gas-tightness of the zirconia tube was lost in the work on high-carbon specinens. The effect of cracks on electromotive force was also examined; it was found that immediately after the stirring of the iron melt, the electromotive force of the cell was independent of the cracks, even if the cracks were not small.

The exposure of zirconia tubes to air at a high temperature results in a reaction between the zirconia and the iron drops retained on the surface of the zirconia tube; it also results in a decrease in the electromotive force. When this reaction is avoided, no detectable change in the appearance of the zirconia tube results from repeated coolings, heatings, and immersions in low-carbon iron.

Results and Discussion

1) Average Transference Number in Zirconia Partition. The relation between the carbon concentration of the iron melt and the electromotive force of the cell is plotted in Fig. 2. The values scatter about ±5 mV in electromotive force and about 10% in carbon concentration from the calculated line, shown as a solid line in Fig. 2.

The important part of this scattering, perhaps, results from the fact that the iron melt is not homogeneous, a condition which itself results partly from the transfer of carbon from or to gas phase, and partly from the permeation of oxygen through the zirconia partition. It was found that the stirring of the iron melt produced, sometimes, a fluctuation in the magnitude of the electromotive force. The contamination of the zirconia by the iron oxide during the measurements was negligible in comparison with the iron oxide originally present. The error resulting from the presence of iron oxide may be smaller than the other errors, since the correlation between the iron concentration and the electromotive force was not observable in contamination of this magnitude.

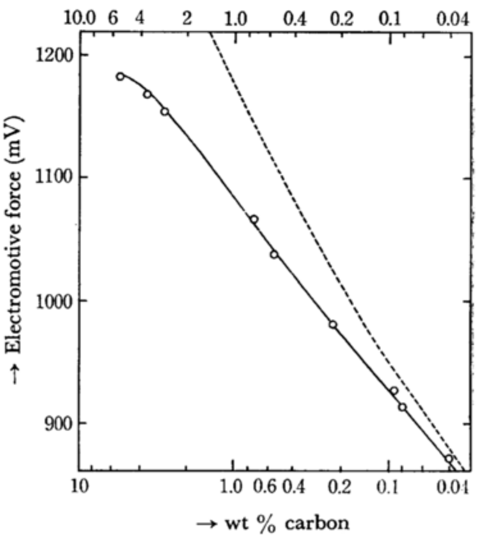

Fig. 2. Electromotive force of the cell as a function of carbon concentration in iron melt at 1900 ±2°K.

------ calculated from Eq. (6) when $\bar{t}_{\text{ion}}=1$,

○○ measured electromotive force,

—— calculated from Eqs. (6), and (10) or (11) giving $A=1$ and $B=1.7\cdot 10^3$.

From the results shown in Fig. 2, the average transference number of the oxygen ion in the zirconia partition, $\bar{t}_{\text{ion}}$, was calculated as follows. The electromotive force of the cell, E, may be expressed by the use of $\bar{t}_{\text{ion}}$:

$$E = \bar{t}_{\text{ion}}\cdot E_{\text{cal}},$$

$$E_{\text{cal}} = -\,(\boldsymbol{R}T/4\boldsymbol{F})\int_0^{\ln P} \mathrm{d}(\ln f_{O_2}) \tag{2}$$

where P is the fugacity of molecular oxygen, which is in equilibrium with the oxygen in the iron melt, where $\boldsymbol{R}, T$, and $\boldsymbol{F}$ are the gas constant, the absolute temperature, and the Faraday constant respectively, and where f_{O_2} is the fugacity of O_2.

Rist and Chipman[11)] have given the carbon concentration in the carbon-iron system as a function of the partial pressures of CO and CO_2, P_{CO} and P_{CO_2} as follows;

$$\begin{aligned}\log \gamma_c &= 4450(1-N_{Fe}^2)/T\\ \log K &= -\,7280/T + 7.98\\ \log K' &= \log K + \log \gamma_c\\ K' &= P_{CO}^2/P_{CO_2}\cdot N_C,\end{aligned} \tag{3}$$

where N_C and N_{Fe} are the mole fractions of carbon and iron in the iron melt and where γ_C is the activity coefficient of carbon.

The standard free energy change of the reaction,

$$CO + (1/2)O_2 = CO_2 \tag{4}$$

has previously been given as −28220 cal/mol at

1900°K.[13] The fugacity of molecular oxygen can, then, be given as a function of P_{CO} and P_{CO_2} when the system is in equilibrium.

$$-\ln P = 2\cdot\ln(P_{CO}/P_{CO_2}) + 14.95 \qquad (5)$$

From Eqs. (2), (3), and (5) and from the fact that $P_{CO}=1$, one may give the electromotive force of the cell as a function of the carbon concentration in the iron melt:

$$E = \bar{t}_{ion}[(\log N_C - 2.34\,N_{Fe}^2)/5.305 + 1.835] \qquad (6)$$

When $\bar{t}_{ion}=1$, Eq. (6) gives the broken line shown in Fig. 2. The average transference number, $\bar{t}_{ion}$, was calculated on the basis of Eq. (6) from the measured electromotive force of the cell; it is given in Fig. 3 as a function of the carbon concentration.

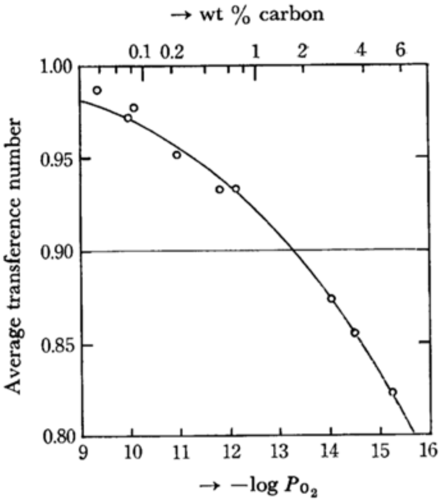

Fig. 3. Average transference number, $\bar{t}_{ion}$, of zirconia partition at 1900°K.

○○ measured values,
—— calculated with Eq. (10) or (11) giving $A=1$ and $B=1.7\cdot10^3$.

2) Oxygen Permeation Resulting from Electronic Conduction. In Fig. 3 the depression in the transference number of the oxygen ion is shown over the whole range of carbon concentration. Such a depression in transference number must, theoretically, restrict the application of Eq. (6). In the experiment, the electromotive force is measured when the external current of the cell is zero. However, this does not mean that the ionic current in the zirconia partition is zero. The electronic current and the ionic current might be equal in absolute value and opposite in current direction. The consequent leakage or permeation of oxygen may result in the disturbance of the equilibrium of the system. Therefore, Eq. (6) can be applied only when the equilibration rate within the iron melt is sufficiently large in comparison with the transport of oxygen through the zirconia partition.

The electrical resistance of the stabilized zirconia partition per square centimeter was about 10 ohm. Therefore, the leakage rate, corresponding to the carbon concentration from 10^{-4} to 10^{-2} mol/cm^3, may be from 10^{-8} to 10^{-7} mol/sec·cm^2. The temperature of the system is so high that the distrubance of this magnitude was ignored in these measurements.

3) Transference Number of the Oxygen Ion in the Zirconia Electrolyte. It is well recognized that, in a sufficiently low oxygen partial pressure region, the zirconia becomes dark in color, diminishes in weight, and changes in volume as the partial reduction proceeds. It is reasonable, therefore, to doubt whether the partial reduction of zirconia has any effect on the ionic conductivity under the present experimental conditions. Two models, as examples, were compared with the experimental results from this point of view:

$$\text{Model 1:}\quad \sigma_I = C_1 + C_2 f_{O_2}^{-1/4}$$
$$\sigma_e = C_3 f_{O_2}^{-1/4}$$
$$\text{Model 2:}\quad \sigma_I = C_1 + C_2 f_{O_2}^{-1/4}$$
$$\sigma_e = C_3 f_{O_2}^{-1/4}$$

where C_1, C_2, and C_3 are the constants and where σ_I and σ_e are the ionic and electronic conductances respectively. Model 1 corresponds to the case where the loss of an oxygen ion results in two additional defects in the electrolyte; *i. e.*, each electron remained needs to be trapped in the defect of the crystal lattice near the oxygen-deficient zirconium ion. Model 2 means that the loss of an oxygen ion results in one additional defect in the crystal lattice.

From the relation:

$$E = \int[\sigma_I/(\sigma_I + \sigma_e)]\mathrm{d}E_{cal} \qquad (9)$$

one may obtain the following relations for these models:

Model 1:

$$(1 - \bar{t}_{ion}) = A_1\ln[(P^{-1/4} + B_1)/(1 + B_1)]/\ln P^{-1/4},$$
$$A_1 = C_3/(C_3 + C_2),\ B_1 = C_1/(C_3 + C_2) \qquad (10)$$

Model 2:

$$(1-\bar{t}_{ion}) = A_2\ln[(P^{-1/4}+B_2)(1+D)/(P^{-1/4}+D)$$
$$\times(1+B_2)]/\ln P^{-1/4},$$
$$A_2 = (C_3/2C_2)/[(C_3/2C_2)^2 - C_1/C_2]^{1/2},$$
$$B_2 = C_3/2C_2 - [(C_3/2C_2)^2 - C_1/C_2]^{1/2},$$
$$D = C_3/2C_2 + [(C_3/2C_2)^2 - C_1/C_2]^{1/2} \qquad (11')$$

or, in a good approximation:

$$(1 - \bar{t}_{ion}) = A_2\ln[(P^{-1/4} + B_2)/(1 + B_2)]/\ln P^{-1/4} \qquad (11)$$

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[13] Natl. Bur. Standards Series. III. March, 1949, and June, 1948 or "Thermochemistry for Steelmaking," Vol. 1, ed. by J. F. Elliott and M. Gleiser, Addison-Wesley Pub. Co., Reading, Mass. (1960).

Equation (10) or (11) may be rewritten in this form:

$$\frac{(1-\bar{t}_{\text{ion},1})\log P_1^{-1/4}}{(1-\bar{t}_{\text{ion},2})\log P_2^{-1/4}}=\frac{\log[(P_1^{-1/4}+B)/(1+B)]}{\log[(P_2^{-1/4}+B)/(1+B)]} \tag{12}$$

where B is B_1 or B_2, corresponding to Model 1 or 2, and where $\bar{t}_{\text{ion},1}$ and $\bar{t}_{\text{ion},2}$ are the transference numbers when $P=P_1$ and $P=P_2$ respectively. The left side of Eq. (12) is an observable quantity; it is plotted against $\log P_1$ in Fig. 4, where P_2 is the fugacity of oxygen in carbon-saturated iron. The right side of Eq. (12) gives the lines in Fig. 4, corresponding to the values of B. Judging from Fig. 4, B must be about 2.10^3, perhaps in the range:

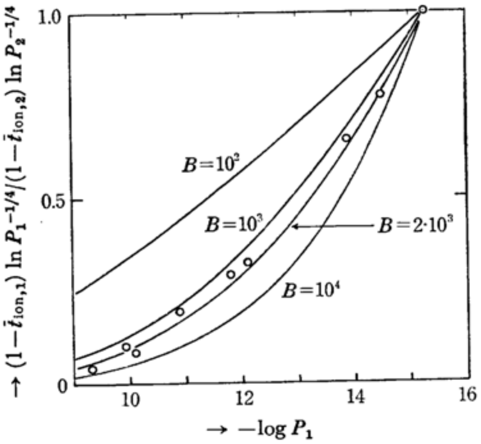

Fig. 4. Evaluation of B in Eq. (12).
○○ calculated with left side of Eq. (12)
—— calculated with right side of Eq. (12)

$$1.7\cdot10^3 \leqq B \leqq 2\cdot10^3 \tag{13}$$

One may, then, estimate the probable value of A:

$$1.0 \leqq A \leqq 1.1 \tag{14}$$

It is obvious from their definitions that $A_1 \leqq 1 \leqq A_2$. If A_1, $A_2=1$, then $C_2/C_1=0$. Since A is very close to unity, C_2/C_1 is not larger than $1.3\cdot10^{-8}$ when Model 2 holds true, which means that the ionic conductivity, σ_I, is constant within the range of experimental error under the present experimental conditions. Therefore, we cannot choose between Models 1 and 2 on the basis of only the present results. This means that the concentration of additional defects resulting from the loss of oxygen is rather negligible in comparison with the concentration of magnesium oxide. This finding may consistent with the fact that the stabilized zirconia is doped deeply and has a large concentration of lattice defects.

The transference number was reproduced from these constants when $B=1.7\cdot10^3$ and $A=1$, for example; it is given by a solid line in Fig. 3. The electromotive force of the cell, E, was calculated from the same constants; it is given by a solid line in Fig. 2. The coincidence between the calculated and measured values seems to be satisfactory.

From these constants, the "true" transference number, $\sigma_I/(\sigma_I+\sigma_e)$, can also be calculated as a function of the oxygen fugacity; it is shown in Fig. 5. According to Tretyakov's empirical equation, which is the only finding available at this temperature, $-\log P^*_{O_2}$ is 12.3 for calcia-stabilized zirconia at 1900°K. The corresponding value, $-\log f_{O_2}$ at $\sigma_I/(\sigma_I+\sigma_e)=0.5$, is about 12.8 for magnesia-stabilized zirconia in Fig. 5. It seems that these two values coincide very well with each other in spite of the difference in the chemical composition of the electrolytes.

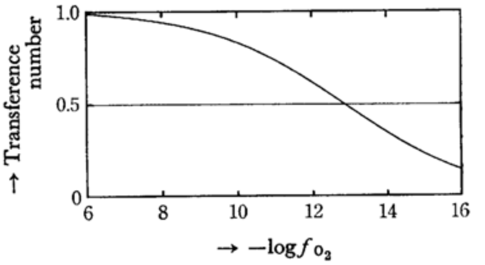

Fig. 5. Transference number, $\sigma_I/(\sigma_I+\sigma_e)$, of stabilized zirconia as a function of oxygen fugacity at 1900°K, when $C_2/C_1=0$ and $C_1/C_3=1.7\cdot10^3$, *i. e.* $B=1.7\cdot10^3$ and $A=1$.

The partial reduction of zirconia may result not only in electronic conduction but also in a volume change or in a response-time increase in electromotive force. The penetration of partial reduction in the zirconia partition can be calculated as follows. It is obvious that:

$$\mathrm{d}E=(1/\sigma_e)\,i\,\mathrm{d}\,l, \tag{15}$$

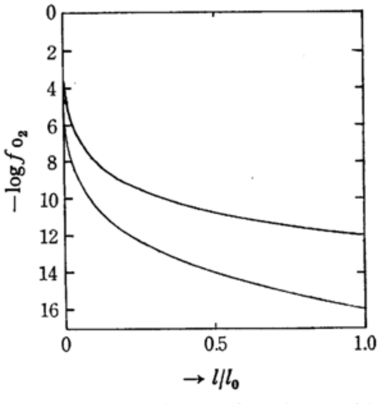

Fig. 6. Oxygen fugacity in zirconia partition calculated with $C_1/C_3=1.7\cdot10^3$ and $C_2/C_1=0$. l_0 is the thickness of the partition, and l is the length vertical to the partition.

where i is the electronic current in zirconia and where l is the length parallel with the electronic current. At the steady state, i is independent of l. From Eqs. (2), (9), and (15), the following equation can be derived:

$$-i\mathrm{d}l = \frac{\sigma_{\mathrm{I}}\sigma_{\mathrm{e}}}{\sigma_{\mathrm{I}}+\sigma_{\mathrm{e}}}\cdot\frac{\boldsymbol{RT}}{4\boldsymbol{F}}\cdot\mathrm{d}(\ln f_{\mathrm{O}_2}) \qquad (16)$$

The result calculated from Eq. (16) is shown in Fig. 6. The result shows that the partial reduction penetrates deeply into the partition.

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