

Sintering of yttrias with addition of divalent metal oxide and water vapour pressure dependence of their electrical conductivity

K. KATAYAMA, H. ŌSAWA, T. AKIBA

Research and Development Division, Chichibu Cement Co. Ltd, 5310 Mikajiri, Kumagaya 360, Japan

K. URABE

Institute for Science and Technology, Ryukoku University, Fukakusa, Kyoto 612, Japan

H. YANAGIDA

Department of Industrial Chemistry, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

The sinterability of divalent metal oxide (MO)-doped yttrias and their electrical conductivity have been studied. The density measurement and SEM observation revealed that the addition of a small amount of MO greatly improves the sinterability of yttria. Yttrias with densities more than 97% could be obtained with the addition of CaO, SrO or MgO by sintering in air at 1600°C. The electrical conductivity of yttria ceramics was found to increase by such addition. The highest electrical conductivity was attained in a CaO-doped yttria. The water vapour pressure sensitivity of yttrias has been confirmed in air at temperatures of 500 to 800°C. As the water vapour pressure increases, the overall electrical conductivity decreases. The electromotive force for the water vapour cell using CaO-doped yttrias was measured and the proton conductivity was calculated. It was found that the decrease in the overall electrical conductivity with increasing water vapour pressure is primarily attributed to the decrease of electron hole conductivity even though proton conductivity increases.

1. Introduction

Yttria is a promising material for high-temperature refractories, high-temperature envelopes, or other applications because of its high melting point. The high melting point, however, makes yttria difficult to sinter in air and several sintering methods have been used to obtain dense yttria ceramics. Sintering in reduced atmospheres or hot-press sintering [1-6] has commonly been performed and almost fully dense yttria ceramics could be prepared. On the other hand, efforts have been made to obtain dense yttria ceramics by sintering in air. Furlong and Domingues [7] prepared yttria ceramics with densities exceeding 97% by sintering at 1600°C with carefully prepared yttria powders. Ciftcioglu *et al.* [8] studied the effect of the degree of agglomeration of yttria powder on sintering and prepared yttria ceramics with 98% density.

Many papers have been published concerning the electrical conductivities of yttria [6, 9, 10]. Most papers agree that at higher temperatures in air, pure or doped yttria is predominantly a p-type conductor and little ionic conduction can be observed. The interpretation of p-type conductivity, however, was inconsistent with whether oxygen or yttrium defects predominate. Tallan and Vest [9] mentioned that point defects are responsible for the electrical conductivity in fully ionized yttria, whereas Bratton [11] concluded that

oxygen defects dominate in yttria. Norby and Kofstad [5] successfully explained their results by employing Bratton's idea.

In this paper, the effects of addition of divalent metal oxide (MO) on sintering of yttria and the electrical conductivities of these yttrias are presented, and the water vapour pressure dependence on the electrical conductivities of CaO-doped yttrias is briefly described.

2. Experimental procedure

Starting materials were commercially available 99.99% pure yttria powder and alkaline earth nitrates (analytical grade). These nitrates were dissolved in distilled water and 0.05 mol l⁻¹ solutions of each nitrate were prepared. Required amounts of each nitrate solution and yttria powder were mixed in ethyl alcohol in an agate mortar and pestle for 30 min and dried at 125°C. The amount of each nitrate was fixed at 1 mol%. The dried products were calcined at 1000°C for 1 h and pulverized in an agate mortar and pestle to prepare fine powders. These powders were pressed into pellets 20 mm diameter and 2 mm thick at 50 MPa. The pressed pellets were then sintered in air at temperatures of 1300 to 1700°C and ground to a thickness of 1 mm. The ceramics sintered at various temperatures were confirmed to be only a single-phase yttria by X-ray diffraction (XRD) and it was found

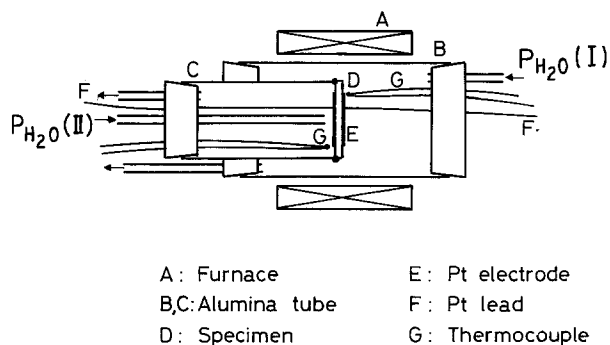


Figure 1 Illustration of the experimental arrangement for EMF measurement.

that additives are doped into the yttria lattice and the solid solutions are formed by adding each additive.

Densities were measured by a water-immersion technique and weight-and-size calculation. These densities are referred to as the apparent density and the bulk density, respectively. The microstructures of the ceramics were observed by SEM. The electrical conductivity (σ) was measured at a frequency of 10 kHz at 600 to 1200°C. Platinum porous electrodes were fired to both sides of the pellets. The frequency of 10 kHz was employed because the phase angle of impedance at this frequency in a cole-cole plot measured at frequencies of 5 to 13 MHz was nearly zero. The water vapour pressure (P_{H_2O}) dependence was also measured at temperatures of 600 to 800°C by changing P_{H_2O} from 0 to 1600 Pa. All measurements were performed in air and the water vapour pressure was controlled by a commercial humidity generator (SRH-1R, Shinei Co. Ltd, Kobe).

The electromotive force was measured in air by changing $P_{H_2O}(I)$ while keeping $P_{H_2O}(II)$ constant using the arrangement shown in Fig. 1. The theoretical electromotive force, E_{theor} , of this cell is given as

$$E_{theor} = (RT/2F) \ln [P_{H_2O}(I)/P_{H_2O}(II)]$$

where R , T and F are gas constant, absolute temperature and Faraday constant, respectively. However, when some electronic conduction, such as hole conduction, exists, the measured electromotive force, E , is lowered and the proton transference number, t_p , can be calculated as

$$t_p = E/E_{theor}$$

if there is no oxygen ion conduction. Moreover, it can be thought that E/E_{theor} represents the ratio of proton conductivity to the sum of proton and electron hole conductivities if oxygen ion conduction definitely exists but does not vary with changing ambient water vapour pressures.

3. Results and discussion

3.1. Effect of MO addition on sintering and electrical conductivity

Apparent densities of sintered pellets are shown in Fig. 2. Because pure yttrias sintered at 1300 or 1400°C were fragile, densities could not be measured. All additives exhibit a positive effect on the densification of yttria. Apparent densities of CaO-, SrO- and MgO-

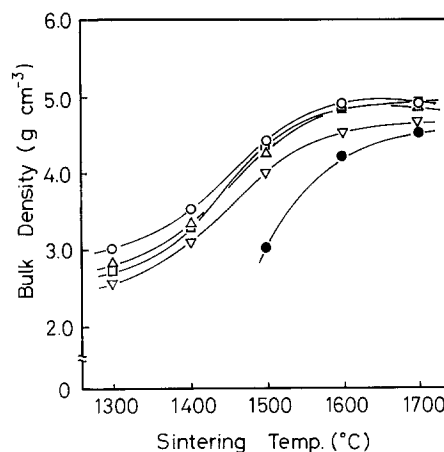


Figure 2 Bulk densities of yttrias with or without additives. Amount of each additive: 1 mol %. Duration of sintering: 5 h. (●) Y₂O₃, (□) Y₂O₃ + MgO, (○) Y₂O₃ + CaO, (△) Y₂O₃ + SrO, (▽) Y₂O₃ + BaO.

doped yttrias sintered at 1600° or above exceed 97% theoretical. In MgO-added yttrias, the density of yttria sintered at 1700°C increases more than that sintered at 1600°C, while in yttrias with other additives, the densities sintered at 1700°C do not change or decrease, compared with those sintered at 1600°C. The microstructures of these yttrias are shown in Fig. 4. The sintering degree of yttrias with additives at 1600°C proceeds more significantly than that at 1500°C and many pores can be seen in yttrias sintered at 1500°C. The restriction of grain growth can be observed in an MgO-doped yttria sintered at 1700°C [12], while in other yttrias, the acceleration of grain growth can be observed. In particular, in CaO-doped yttria especially, the exaggerated grain growth with intra-grain pores can clearly be observed. The lower densities of BaO-doped yttrias shown in Fig. 2, can be understood, due to the many pores in BaO-doped yttrias. The bulk densities of CaO- or MgO-doped yttrias are shown in Fig. 3. In MgO-doped yttrias, the apparent density, d_{appar} , and the bulk density, d_{bulk} , are almost the same, while in CaO-doped yttrias, a small difference can be detected. It is thought that the difference between d_{appar} and d_{bulk} results from the existence of open and closed pores. In this paper, an open pore is one in which water molecules can move in and out and, on the other hand, a closed pore is one which is

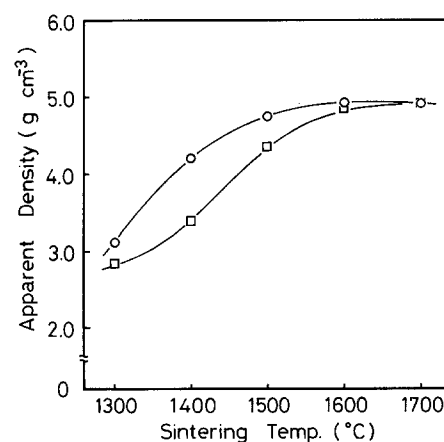


Figure 3 Apparent densities of (□) MgO- and (○) CaO-doped yttrias. Duration of sintering: 5 h.

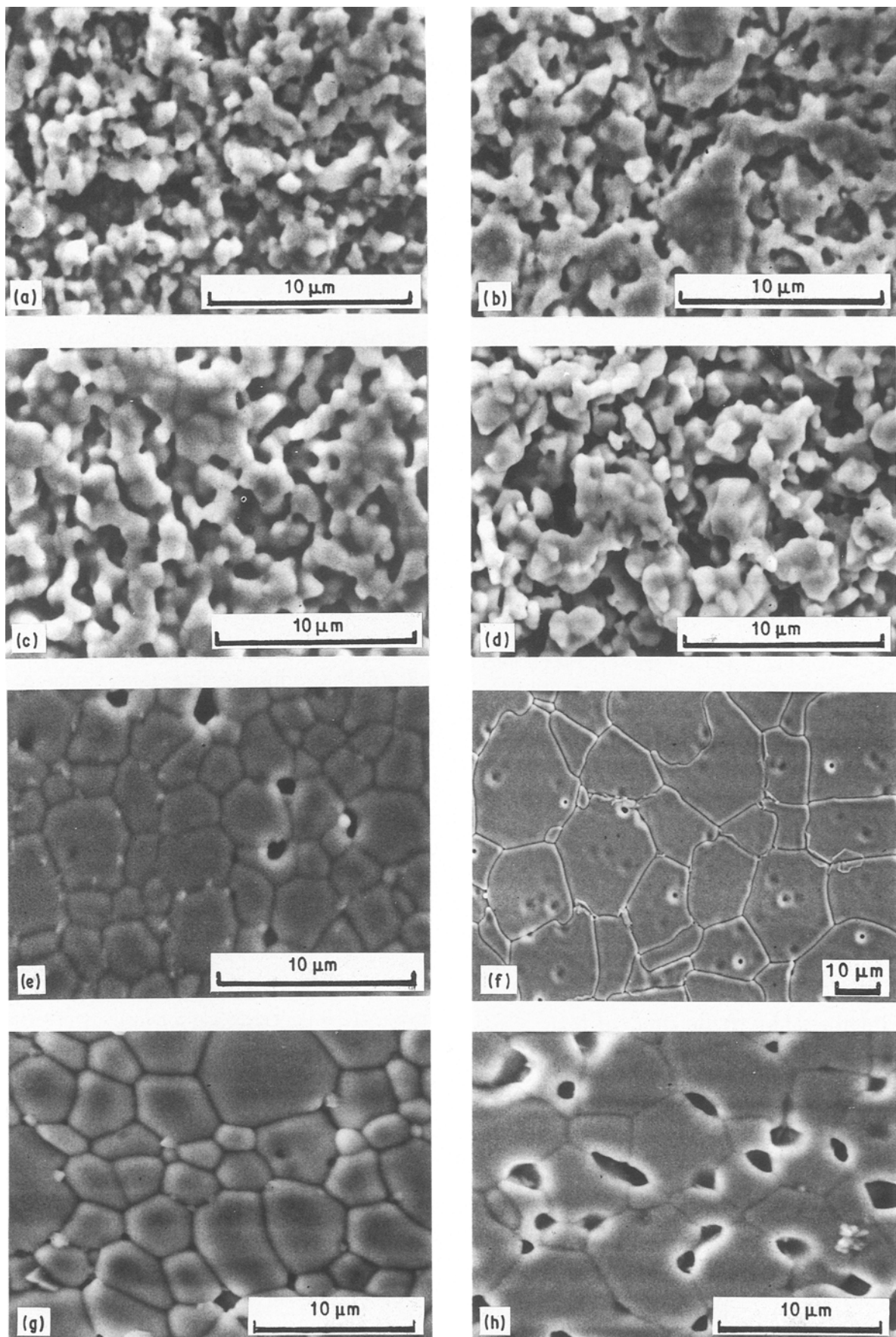


Figure 4 Scanning electron micrographs of yttrias sintered at 1500° C for 5 h, (a) without additive, (b) with MgO, (c) with CaO and sintered at 1600° C for 5 h, (d) without additive, (e) with MgO, (f) with CaO, (g) with SrO, (h) with BaO. (e) to (h) are thermally etched.

too small for water molecules to migrate freely. If only closed pores exist in the ceramics, d_{appa} is quite large compared to d_{bulk} . According to the definition above, although the microstructures of MgO- and CaO-doped yttrias sintered at 1500° C do not vary signifi-

cantly as shown in Fig. 4, it is understood that open pores dominate in MgO-doped yttria, while closed pores dominate in CaO-doped yttria. These considerations proved that open pores may play an important role in the densification of yttria as shown in MgO-

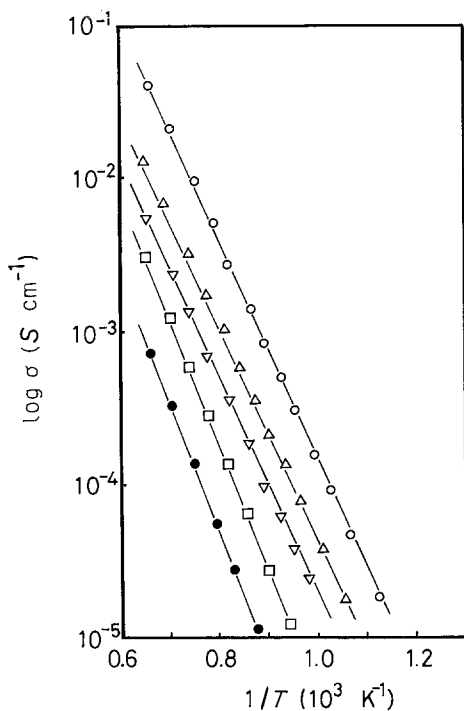


Figure 5 $\sigma-1/T$ in dry air. (●) Y_2O_3 , (□) $Y_2O_3 + MgO$, (▽) $Y_2O_3 + BaO$, (Δ) $Y_2O_3 + SrO$, (○) $Y_2O_3 + CaO$.

doped yttrias in Fig. 2, and that the existence of closed pores, including intra-pores, retards further densification as shown in CaO-, SrO- or BaO-doped yttrias.

The effect of MO addition on electrical conductivity of yttria was studied at temperatures of 600 to 1200°C using yttrias sintered at 1600°C for 5 h. The measurement was performed in dry air. The linearity of $\log \sigma-1/T$ is found to be maintained in all yttrias in this temperature range, as shown in Fig. 5). The electrical conductivity increases with the addition of MO to yttria. It can be found from Fig. 5 that the highest conductivity is observed with CaO addition and the σ of CaO-doped yttria is 100 times higher than that of pure yttria.

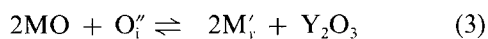
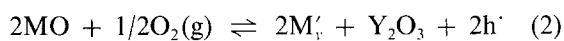
3.2. Interpretation of the effect of MO addition

As stated in Section 1, Norby and Kofstad [5] satisfactorily explained their results using Bratton's idea. In the following, only oxygen or oxygen-related defects will be treated and the notations proposed by Kröger and Vink are used here.

In air, oxygen gas migrates into the pure yttria lattice to create oxygen interstitials, O_i'' , and electron holes, h' , by Equation 1



Divalent metal oxide, MO is added to pure yttria and the solid solution is formed. In this case, two equations (2 and 3) may possibly be considered



In Equation 2, with the addition of MO, oxygen gas in the air migrates into the yttria lattice and a divalent metal ion substitutes an yttrium ion and two electron

holes are produced. With increased concentration of electron holes, the electrical conductivity would increase. On the other hand, in Equation 3, an oxygen interstitial is consumed and a divalent metal ion substitutes for an yttrium ion. No electron holes are produced, which results in no variation of the electrical conductivity. The increase in electrical conductivities in yttrias with addition of MO shown in Fig. 5, suggests that Equation 2 occurs more predominantly than Equation 3.

Equation 1 may be important when electrical properties are considered as well as when the sintering proceeds. This means that oxygen interstitials play an important role when yttria is sintered and that concentration of oxygen interstitials appreciably affects the sintering. Many workers have found that yttria cannot be sintered well in air but can be in a reduced atmosphere. These considerations lead to the speculation that the concentration of oxygen interstitials must be reduced in order to obtain well-densified yttrias. When MO is added to yttria, the concentration of electron holes increases according to Equation 2. The increased concentration of electron holes leads to a decreased concentration of oxygen interstitials, according to Equation 1, which results in better densification of yttria as shown in Figs 2 and 4.

3.3. Water vapour pressure dependence of electrical conductivity of yttria

The variation of electrical conductivity of yttrias was measured in air as a function of the water vapour pressure. In Fig. 6, the measuring temperature dependence of electrical conductivity of CaO-doped yttrias is shown; Fig. 7 shows the sintering temperature dependence. Both sintering temperature and measuring temperature affect the electrical conductivity but the water vapour pressure dependence is similar. As the water vapour pressure increases, the electrical conductivity decreases. The water vapour pressure dependence on electrical conductivity is also observed in other yttrias, which is similar to that of CaO-doped yttrias. The overall electrical conductivity of yttria in

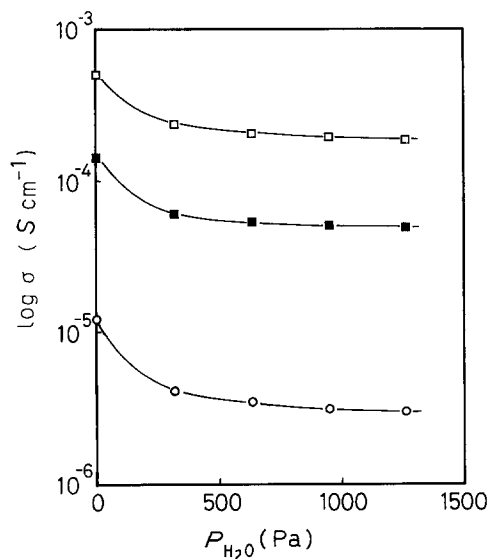


Figure 6 $\sigma-P_{H_2O}$ of CaO-doped yttria sintered at 1600°C. Measurement temperatures: (□) 800°C, (■) 700°C, (○) 600°C.

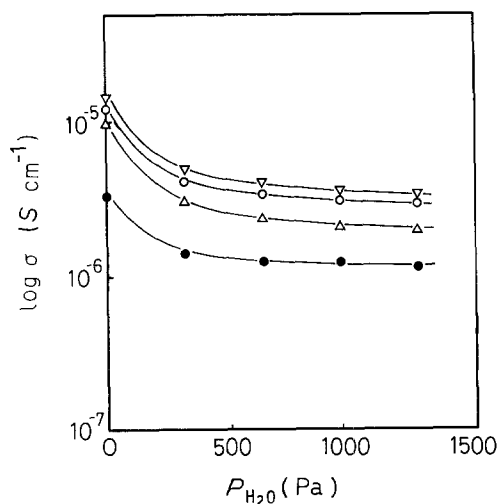


Figure 7 σ - $P_{\text{H}_2\text{O}}$ of CaO-doped yttrias measured at 600°C. Sintering temperatures: (∇) 1700°C, (\circ) 1600°C, (Δ) 1500°C, (\bullet) 1400°C.

air can be divided into contributions from electron holes, oxygen ionic defects and protons [14]. The proton contributions can only be observed when there is water vapour in the ambient atmosphere. Therefore, the decrease in electrical conductivity with increasing water vapour pressure as shown in Figs 6 and 7, might be responsible for the appearance of proton conductivity of yttria, σ_{all} , may be expressed as

$$\sigma_{\text{all}} = \sigma_{\text{h}} + \sigma_{\text{i}} + \sigma_{\text{p}}$$

where σ_{h} , σ_{i} , and σ_{p} are the electrical conductivities of electron holes, oxygen ions and protons, respectively, and the respective transference numbers are expressed, respectively, as

$$t_{\text{h}} = \sigma_{\text{h}}/\sigma_{\text{all}}$$

$$t_{\text{p}} = \sigma_{\text{p}}/\sigma_{\text{all}}$$

$$t_{\text{i}} = \sigma_{\text{i}}/\sigma_{\text{all}}$$

In order to measure the proton contribution to overall conductivity, the electromotive force (EMF) measurement was performed using the arrangement shown in Fig. 1. Glass O-rings were used for sealing and the permeability of water molecules was confirmed to be absent.

The variation of EMF was observed when the flow rate of air was varied. The faster the flow rate, the higher the EMF. This variation was found to be caused by the lowering of measuring temperatures because of fast flow rates. Therefore, the appropriate flow rate must be chosen and was determined to be $100 \text{ cm}^3 \text{ min}^{-1}$ in this study. The EMFs measured at 500°C in Fig. 8 are higher than the theoretical ones and rather stable. The EMFs measured at 600 to 800°C using other yttrias showed the same tendency. The reason for these higher EMFs is not known clearly yet but lower conductivities might be responsible for the abnormal values. These phenomena suggest that because the EMF measurement might be largely influenced by its own electrical conductivity, higher conductivities are required in order to measure EMF precisely.

Figure 8 shows the EMF of CaO-doped yttria sintered at 1600°C for 5 h which possesses a higher conductivity than other yttrias. The linearity of EMF as

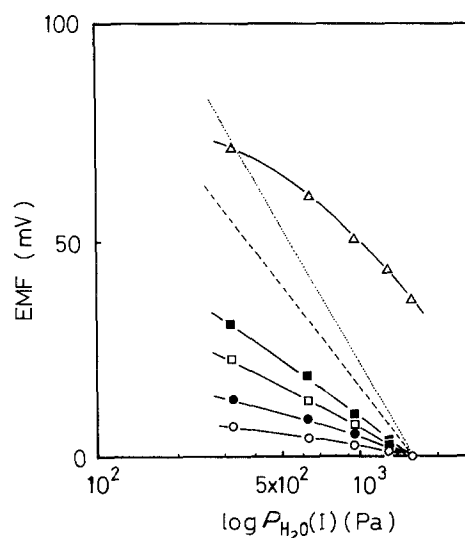


Figure 8 EMF of CaO-doped yttria sintered at 1600°C for 5 h. Measurements are performed with changing $P_{\text{H}_2\text{O}}(\text{I})$ and keeping $P_{\text{H}_2\text{O}}(\text{II})$ constants ($1.59 \times 10^3 \text{ Pa}$) at (\circ) 800°C, (\bullet) 700°C, (\square) 600°C, (\square) 550°C, (Δ) 500°C. Flow rate: $100 \text{ cm}^3 \text{ min}^{-1}$.

a function of $\log P_{\text{H}_2\text{O}}(\text{I})$ is almost preserved except in measurements of 500°C, but as measuring temperatures increase, the departure of the measured EMF from the theoretical values become remarkable. Iwahara *et al.* [14] observed similar deviations in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$ ceramics and concluded that it is ascribed to electronic conduction.

This might also be the case for our measurements, but in our case, besides electronic conduction, oxygen ion conduction must be considered because, as stated above, Norby and Kofstad [13] showed that oxygen conduction inherently exists in yttrias and that with increasing the water vapour pressure in air, the oxygen conductivity increases and the overall conductivity decreases. As the overall conductivity decreases and the oxygen conductivity increases, the contribution of oxygen ion conduction to overall conductivity becomes relatively large. If these speculations are true, the departures from the theoretical EMF become small with decreasing $P_{\text{H}_2\text{O}}(\text{I})$. All measurements performed here are not the case. The reasons for them not being applicable to the speculations above are not clear but one is thought to be that the variation of oxygen ion conductivity is fairly small, compared with the variation of the electrical conductivities of electron holes and protons.

Schieltz *et al.* [6] have measured oxygen ion transference numbers, t_{i} , of yttria at 700 to 1000°C. They found that t_{i} decreases with increasing measuring temperatures. The oxygen transference number at 700°C can be read off as 0.2 from Fig. 5 in their paper. Employing 0.2 for t_{i} and assuming that the variation of t_{i} is quite small, other contributions of protons and electron holes to overall conductivity at 700°C were calculated and are shown in Fig. 9. For the water vapour pressure, the mean water vapour pressure [15], $\{P_{\text{H}_2\text{O}}(\text{av}) = [P_{\text{H}_2\text{O}}(\text{I}) P_{\text{H}_2\text{O}}(\text{II})]^{1/2}\}$, is used. It can be seen from Fig. 9 that the decrease in hole conductivity is mainly responsible for the decrease in overall conductivity with increasing water vapour pressure even though proton conductivity increases.

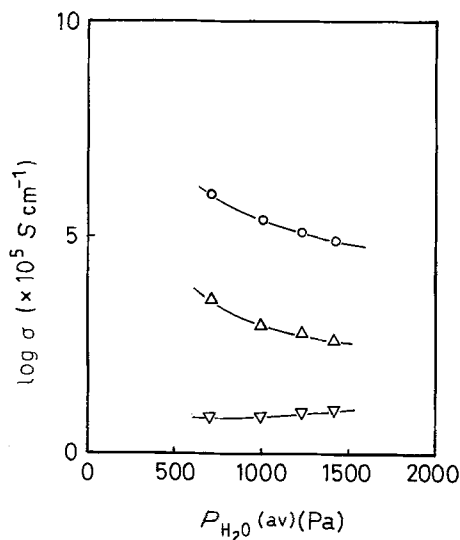


Figure 9 Contribution of (∇) proton and (Δ) hole conductivities to (\circ) overall conductivity of CaO-doped yttrias sintered at 1600°C for 5 h. Oxygen ion transference number is assumed unchanged.

4. Conclusions

The effect of MO addition on the sintering and electrical conductivity of yttria has been studied. MO addition remarkably improves the sinterability of yttria, and yttrias with densities exceeding 97% theoretical could be obtained by sintering in air at 1600°C for 5 h. With these MO additions, the electrical conductivity of yttrias increases and the highest conductivity could be attained in CaO-doped yttria.

The proton and hole conductivities of CaO-doped yttria were investigated using EMF measurements. It

was found that the decrease of overall conductivity with increasing water vapour pressure was mainly caused by the decrease of hole conductivity while proton conductivity increases.

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