

# Modeling of Electrical Conductivity from $\sigma_{\text{tot}}$ vs. $p_{\text{O}_2}^{1/4}$ Plot in Wet Atmosphere for High-Temperature Proton-Conducting Oxides

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This work demonstrates a method for modeling of electrical conductivity in high-temperature proton-conducting oxides. Total conductivity was calculated assuming that it comprises partial conductivities contributed by protons, oxygen ions and electron holes. From the plot  $\sigma_{\text{tot}}$  vs.  $p_{\text{O}_2}^{1/4}$  in wet atmosphere, thermodynamic and kinetic parameters were obtained representing transport properties such as concentration and mobility of the charge-carrying defects. The formulae for the calculation of partial conductivities were derived based on the defect structure of HTPCs. Illustrative calculations were made for  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$  system.

**Key words :** Modeling, HTPC, Water vapor pressure,  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$

## I. Introduction

High-temperature proton conductors (HTPCs) are most often acceptor-doped rare earth oxides or perovskites, which exhibit mixed p-type electronic and oxygen ion conduction under oxidizing conditions.<sup>1,2</sup> The proton conduction stems from the hydrogen ions incorporated from water vapor. In these mixed conductors, more than two carriers participate simultaneously in the transport of electrical charges; thus the characterization of electrical properties is not simple.<sup>3-5</sup> The concentrations of charge carriers are functions water and oxygen content in the gas phase, and consequently the nature of electrical conduction depends on the external atmosphere.<sup>1,2,4,6,7</sup> A materials investigation resorting solely to an experimental method is, however, limited by measuring conditions. To cover the whole spectrum of different gaseous environments, the conductivity was modeled. Thermodynamic and kinetic parameters representing charge transport properties of the material must be determined from experiments; the problem is, how to obtain them in a simple and reliable way.

In the present study, defect equations describing the effects of water vapor and oxygen pressure on electrical conductivity were reviewed.<sup>3</sup> For the plot  $\sigma_{\text{tot}}$  vs.  $p_{\text{O}_2}^{1/4}$ , the slopes and intercepts of the curve yielded some important parameters for defect equilibria, such as proton concentration, and charge mobilities. These parameters, in turn, were used in the calculation of partial and total conductivities. Thus this paper presents a method for obtaining parameters for the modeling of electrical conductivity in HTPCs, using data reported in the literature

for  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$  system. The modeling was performed in a more manual, stepwise manner than a computer fit of the entire data set.<sup>5,9</sup>

## II. Theory

The defect equilibria concerning the effects of the gas phase on HTPCs have been discussed by many authors.<sup>2,4,6,7</sup> The expressions hereinafter stem mainly from Ref. 4

Oxygen and water vapor competitively dissolve into the crystal according to the following equations. On assuming relatively small concentrations of defects, the mass action law can be applied:



where the Kröger-Vink notation is used.  $\text{OH}_\text{O}$  represents incorporated proton bound to oxygen ions.  $p$ ,  $[\text{OH}_\text{O}^{\bullet}]$ , and  $[\text{V}_\text{O}^{\bullet\bullet}]$  are the concentrations of electron holes, protons, and oxygen vacancies.  $p_{\text{O}_2}$  and  $p_w$  denote partial pressures of oxygen and water vapor, respectively. Oxygen ion vacancies are generated by doping acceptor-oxides. Denoting the concentrations of dopant ions and electron as  $[\text{M}'_\text{B}]$  and  $n$ , respectively, the electro-neutrality condition requires that

$$2[\text{V}_\text{O}^{\bullet\bullet}] + p + [\text{OH}_\text{O}^{\bullet}] = [\text{M}'_\text{B}] + n \quad (3)$$

where it is assumed that all of the dopant cations substitute the host cations having a higher valency. If the

concentrations of electronic defects  $n$  and  $p$  can be neglected, the electro-neutrality condition is frequently approximated as

$$2[V_O^-] + [OH_b^*] \approx [M_B'] \quad (4)$$

Combining Equations (2') and (4) gives defect concentrations:

$$[OH_b^*] = (K_2 p_w / 4) \{ [1 + 8y / (K_2 p_w)]^{1/2} - 1 \} \quad (5)$$

$$[V_O^-] = (K_2 p_w / 16) \{ [1 + 8y / (K_2 p_w)]^{1/2} - 1 \}^2 \quad (6)$$

where  $y = [M_B']$ . Under oxidizing conditions the electron hole is the most important electronic defect, and its concentration is obtained from Equations (1') and (6):

$$p = (K_1 K_2 / 2)^{1/2} (p_{O_2})^{1/4} p_w^{1/2} \{ [1 + 8y / (K_2 p_w)]^{1/2} - 1 \} \quad (7)$$

The respective conductivity contributions of protons, oxygen ions, and electron holes,  $\sigma_H$ ,  $\sigma_V$ , and  $\sigma_h$ , are expressed as follows.

$$\sigma_H / \sigma_H^* = \{ [1 + \alpha / p_w]^{1/2} - 1 \} p_w / \{ (1 + \alpha)^{1/2} - 1 \} \quad (8)$$

$$\sigma_V / \sigma_V^* = \{ [1 + \alpha / p_w]^{1/2} - 1 \} p_w / \alpha \quad (9)$$

$$\sigma_h / \sigma_h^* = \{ [1 + \alpha / p_w]^{1/2} - 1 \} (p_w / \alpha)^{1/2} p_{O_2}^{1/4} \quad (10)$$

where the conductivity at the standard partial pressures was adopted;  $\sigma_H^*$  is protonic conductivity at  $p_w = 1$  atm and  $\sigma_h^*$  is hole conductivity at  $p_{O_2} = 1$  atm and  $p_w = 0$  atm.  $\sigma_V^*$  is oxygen ion conductivity when  $p_w = 0$ . The parameter  $\alpha$  equals  $8y / K_2$ . A partial conductivity is given as the product of charge, mobility, and concentration of the defect. The division of the two conductivities in the above equations allows the mobility and charge terms to be canceled out, on the assumption that the mobilities of defects are independent of gas composition. In consequence, standard conductivities are parameters including charges and mobilities of the defects.

Equations (8), (9), and (10) are reduced as the following equations, setting  $P = p_w / \alpha$ ,  $f(P) = (1 + P)^{1/2} - P^{1/2}$ , and  $f(\alpha) = \alpha / \{ (1 + \alpha)^{1/2} - 1 \}$ .

$$\sigma_H = \sigma_H^* f(P) P^{1/2} f(\alpha) \quad (11)$$

$$\sigma_V = \sigma_V^* f^2(P) \quad (12)$$

$$\sigma_h = \sigma_h^* p_{O_2}^{1/4} f(P) \quad (13)$$

Total electrical conductivity is the sum of partial conductivities:

$$\sigma_{tot} = \sigma_H + \sigma_V + \sigma_h \quad (14)$$

The equilibrium constant  $K_2$  and thus  $\alpha$ , which are the most important thermodynamic parameters relating the equilibrium proton concentration and water vapor pressure, can be determined from  $\sigma_{tot}$  vs.  $p_{O_2}^{1/4}$  plot at a constant water vapor pressure. Partial conductivities  $\sigma_H$  and  $\sigma_V$  are not functions of oxygen partial pressure; thus the intercept with the vertical axis (a) is given as Eq. (15).

$$a = \sigma_H + \sigma_V \quad (15)$$

The slope of the plot from Eq. (13);

$$b = \sigma_h^* f(P) \quad (16)$$

Eq. (15) allows the separation of ionic conductivity from hole conductivity at a given oxygen partial pressure. The schematic plot for  $\sigma_{tot}$  vs.  $p_{O_2}^{1/4}$  is given in Fig. 1. If the slope  $b$  values can be determined at different water pressures  $p_{w1}$  and  $p_{w2}$ , then from Eq. (16)  $\sigma_h^* f(P_1) = b_1$ , and  $\sigma_h^* f(P_2) = b_2$ , which gives Eq. (17).

$$\frac{f(P_1)}{f(P_2)} = \frac{b_1}{b_2} \quad (17)$$

Here  $f(P_1)$  and  $f(P_2)$  are expressed as functions only of  $\alpha$ , of which value can be calculated with known  $b_1$  and  $b_2$ . Then  $\sigma_h^*$  is also to be obtained from  $\alpha$  or  $f(P)$ . As shown in Fig. 2,  $f(P)$  falls very slowly at high water pressures, it is recommended to choose low water pressures to reduce error in the application of Eq. (17).

For a water partial pressure  $p_{w1}$ , from Equations (11), (12) and (15),

$$\sigma_H^* f(P_1) P_1^{1/2} f(\alpha) + \sigma_V^* f^2(P_1) = a_1 \quad (18)$$

For a given water pressure, the values of  $P$ ,  $f(P)$ , and  $f(\alpha)$  are known because  $\alpha$  was obtained previously. For a water partial pressure  $p_{w2}$ , we can write a similar equation. From these two equations, the two parameters  $\sigma_H^*$  and  $\sigma_V^*$  can be determined. Now we have all the parameters, i.e.,  $\sigma_H^*$ ,  $\sigma_V^*$ ,  $\sigma_h^*$  and  $\alpha$  and thus partial conductivities and total conductivity can be calculated.

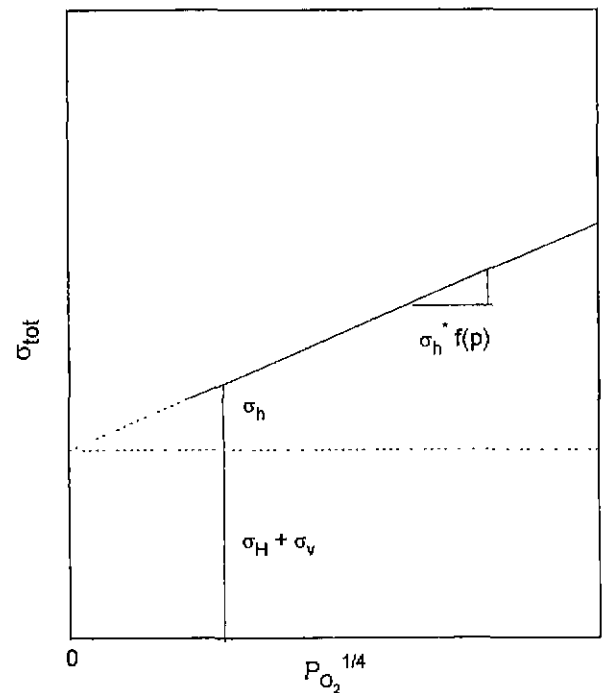


Fig. 1. Schematic plot for  $\sigma_{tot}$  vs.  $p_{O_2}^{1/4}$ .

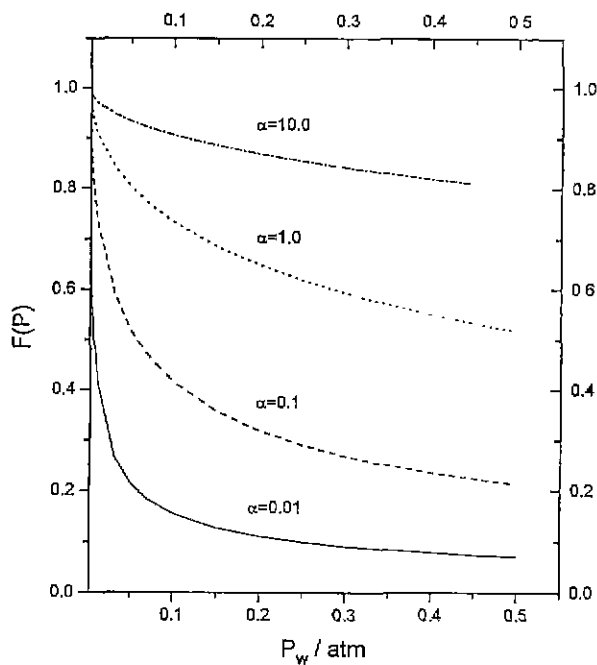


Fig. 2.  $R(P)$  against water vapor pressure for varying  $\alpha$ .

### III. Illustrative Calculation for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ system

$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$  ceramic has been one of the widely studied HPTC oxides since Iwahara and coworkers found proton conduction at elevated temperatures. The dependence of electrical conductivity on oxygen and water pressure was investigated most extensively by Uchida and coworkers.<sup>2)</sup> Using their data, the proposed modeling concept was demonstrated. From some of their conductivity data at various oxygen and water pressures, required thermodynamic and kinetic parameters were determined. The starting data used are given in Table 1, which are read from Fig. 9 in Ref. 2. Because the number of data points was not sufficient, a careful consideration was given in the selection of the starting data. The water pressures chosen were 0.0121, 0.0204, 0.0470 atm because they gave better linear fit, i.e. regression coefficient larger than 0.998 in the  $\sigma_{\text{tot}}$  vs.  $p_{\text{O}_2}^{1/4}$  plot, than the others. The conductivity data when  $P_{\text{O}_2}=1$  atm was not included because of consistent negative deviation in the  $\sigma_{\text{tot}}$  vs.  $p_{\text{O}_2}^{1/4}$  plot (See Fig. 10 in Ref. 2)

Table 1. The Intercept and the Slope of  $\sigma_{\text{tot}}$  vs.  $P_{\text{O}_2}^{1/4}$  at Different Water Pressures.

water pressure /atm	intercept(a)/ $10^{-3} \text{ Scm}^{-1}$	slope(b)/ $10^{-3} \text{ Scm}^{-1} \text{ atm}^{-1/4}$	Reg. Coeff.
0.0121	2.613	10.53	0.9991
0.0204	2.468	9.78	0.9982
0.0470	1.816	8.66	0.9988

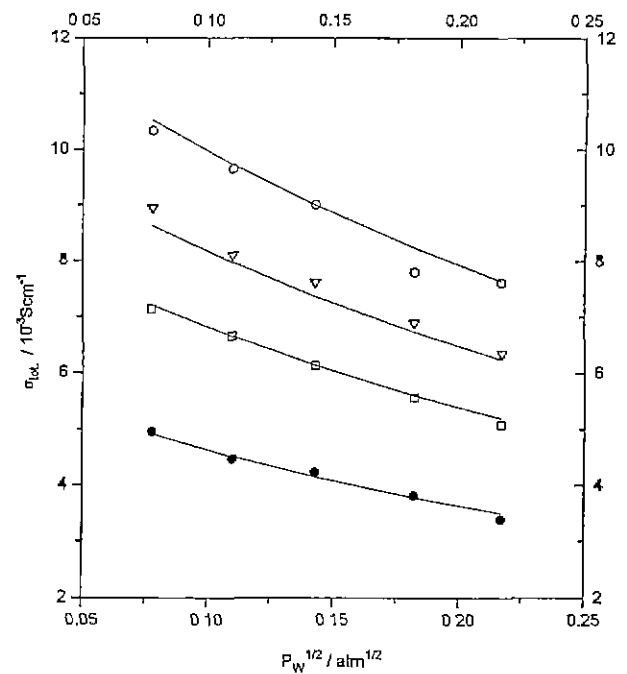


Fig. 3. Total conductivity against  $p_w^{1/2}$  at 950°C.  $P_{\text{O}_2}(\text{atm})$ ;  $\circ$  : 0.21,  $\triangle$  :  $6.73 \times 10^{-2}$ ,  $\square$  :  $2.18 \times 10^{-2}$ ,  $\bullet$  :  $1.07 \times 10^{-3}$ . Data from Ref. [2].

#### 1. The prediction of total conductivity at various water and oxygen pressures.

1) Determination of  $\sigma_{\text{H}}^*$  and  $\alpha$ : The  $\alpha$  value was calculated using Eq. (17) from the slopes of the  $\sigma_{\text{tot}}$  vs.  $p_{\text{O}_2}^{1/4}$  plots at the two water pressures of 0.0121 and 0.0204 atm. The calculation gave  $\alpha=0.1834$  at 950°C. This value was compared with the one reported in the literature;  $\alpha=8\gamma/K_2$  and  $K_2$  was determined from the measurement of water uptake in the temperature range from 700 to 1100°C by Krug *et al.*<sup>10)</sup> It was given as:

$$\log K_2(\text{L/Pa})=8.188 \times 103/T-11.706 \quad (19)$$

Y, the saturation limit for the water absorption, was given as 0.0233 and thus  $\alpha$  is 0.1890 at 950°C. These two values are very close, so 0.1890 will be used hereafter. With  $\alpha$  and Eq. (16),  $\sigma_{\text{H}}^*$  can be obtained. For  $p_w=0.0121$  atm,  $\sigma_{\text{H}}^*$  was  $0.01352 \text{ Scm}^{-1}$ .  $\sigma_{\text{H}}^*$  must have the same value for different water pressures. Actually it turned out to be  $0.01351$  and  $0.0139 \text{ Scm}^{-1}$  for  $p_w$  of 0.0204 and 0.0470 atm, respectively. Thus it can be said that Eq. (16) showed a reasonable consistency with the measured data at three different partial pressures of water vapor.

2) Determination of  $\sigma_{\text{H}}^*$  and  $\sigma_{\text{V}}^*$ : From the intercept of the  $\sigma_{\text{tot}}$  vs.  $p_{\text{O}_2}^{1/4}$  plot, the sum of  $\sigma_{\text{H}}^*$  and  $\sigma_{\text{V}}^*$  was separated from total conductivity. If Eq. (18) is applied for any two water pressures of 0.0121, 0.0204 and 0.0470 atm, the values of  $\sigma_{\text{H}}^*$  and  $\sigma_{\text{V}}^*$  can be determined. The intercept 'a' values are given in Table 1 for each  $p_w$ . For the three pairs of  $p_w$ , different values of  $\sigma_{\text{V}}^*$  and  $\sigma_{\text{H}}^*$  were obtained.

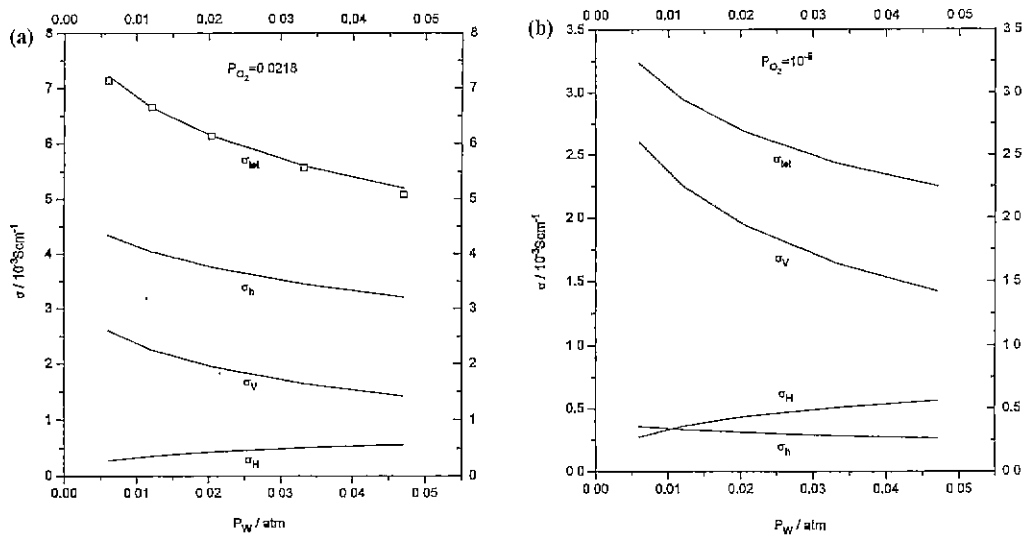


Fig. 4. Partial conductivities at two different oxygen pressures (a)  $P_{O_2}=0.0218$  atm. Data from Ref. [2]. (b)  $P_{O_2}=10^{-6}$  atm.

They could be given as  $\sigma_v^* = 3.7(\pm 0.4) \times 10^{-2} \text{ Scm}^{-1}$  and  $\sigma_H^* = 1.05(\pm 0.4) \times 10^{-3} \text{ Scm}^{-1}$  at  $950^\circ\text{C}$ .

3) Calculation of total and partial conductivities: Now that all the unknown parameters were obtained, partial conductivities and thus the total conductivity were calculated at various oxygen and water pressures. Using Equations (11) through (14), conductivities are calculated and compared with data reported in the reference. The parameters used were slightly adjusted;  $\sigma_h^* = 1.35 \times 10^{-2} \text{ Scm}^{-1}$  and  $\sigma_v^* = 3.71 \times 10^{-3} \text{ Scm}^{-1}$  and  $\sigma_H^* = 0.87 \times 10^{-3} \text{ Scm}^{-1}$ . Total conductivity variation with water pressure at several oxygen pressures is shown in Fig. 3. The apparent linearity of total conductivity in  $\sigma_{tot}$  vs.  $p_w^{1/2}$  plot is dis-

cussed elsewhere.<sup>11</sup> Generally the prediction showed a good agreement. Partial conductivities contributed by holes, oxygen ions and protons are shown in Fig. 4 at two different oxygen pressures. It shows quantitatively that the nature of electrical conduction changes with the surrounding gas phase. From Fig. 4(b) it is obvious that the electrical conductivity is dominated by oxygen ion conduction at the given condition, i.e.  $950^\circ\text{C}$  and  $p_{O_2}=10^{-6}$  atm. Uchida *et al.* measured protonic transport number from steam concentration cell. They obtained two or three times higher values than ours calculated from Fig. 4. Recently K.J. de Vries<sup>12</sup> reported a protonic conductivity significantly lower than that observed by his previous workers. Because of difficulties connected with attaining equilibrium conductivity and with measurement of transport numbers for this mixed conductor, few data may report true proton conductivity.

2. The determination of the activation energy of hole conductivity ( $\sigma_h^*$ )

From  $\sigma_{tot}$  vs.  $p_{O_2}^{1/4}$  plot at a given water pressure, we can calculate  $\sigma_h^*$ , or the hole conductivity at  $p_{O_2}=1$  atm and  $p_w=0$  atm, if  $\alpha$  or  $f(P)$  values are available. The slope, i.e.  $f(p)\sigma_h^*$  values are from the Fig. 10 in Ref. 10 and is given in Table 2 in the temperature range from 800 to  $1000^\circ\text{C}$ . As  $K_2$  values are reported as a function of temperature as given by Eq. (19),  $f(P)$  values and thus  $\sigma_h^*$  can be obtained at various temperatures.  $\ln \sigma_h^*$  is plott-

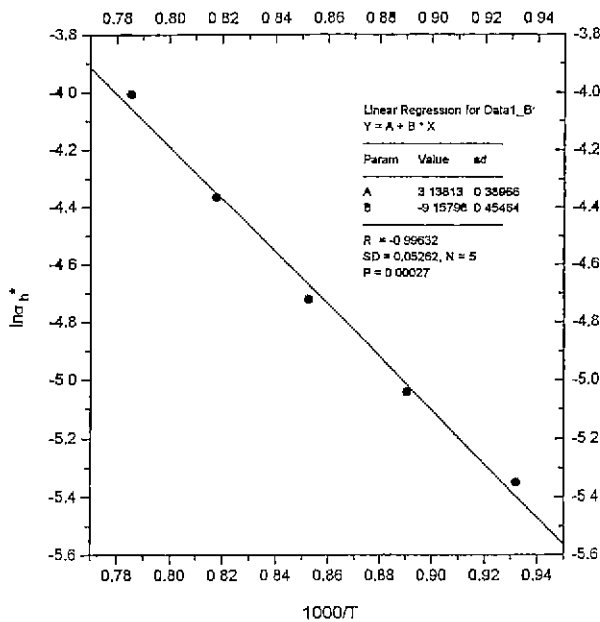


Fig. 5.  $\ln \sigma_h^*$  against  $1000/T$ .

Table 2. Calculation of  $\sigma_h^*$

Temp. ( $^\circ\text{C}$ )	$f(p)\sigma_h^*/10^{-3}$	$\alpha$	P	$f(p)$	$\sigma_h^*/10^{-3} \text{ Scm}^{-1}$
1000	15.79	0.346	0.0174	0.8676	18.20
950	10.64	0.189	0.0319	0.8372	12.71
900	6.97	0.098	0.0615	0.7823	8.91
850	4.56	0.048	0.1259	0.7063	6.46
800	2.87	0.022	0.2753	0.6046	4.75

ed against  $1000/T$  as shown in Fig. 5. The activation energy from the plot was 0.79 eV, which is compared with 0.77 eV reported in the literature.<sup>13)</sup> Published data were not sufficient to calculate the activation energies for conduction by protons and oxygen ions

#### IV. Summary

Graphical analysis of the plot  $\sigma_{tot}$  vs.  $p_{O_2}^{1/4}$  in wet atmosphere was performed in terms of the defect structure in HTPCs. It allowed to extract important parameters representing the concentration and the mobility of the defects, and thus to calculate partial conductivities contributed by each charge carrier. The parameters were determined for the  $SrCe_{0.95}Yb_{0.05}O_{0.2975}$  system based on the work of Uchida *et al.*<sup>2)</sup> and calculated total conductivity showed a reasonable agreement with their data measured in different partial pressures of water vapor and oxygen. Partial conductivities were also calculated. Calculated activation energy of electron hole conductivity at  $p_{O_2}=1$  atm and  $p_w=0$  atm, or  $\sigma_h^*$  was checked with that in the literature.

#### V. Acknowledgment

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