Properties of Electrical Conductivity in Y-Doped CaZrO₃

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To clarify the high temperature electrochemical properties of Y-doped CaZrO₃, the electrical conductivity of the poly-crystalline specimen was measured for various kinds of hydrogen and oxygen-containing atmospheres by employing the two-terminal AC method. The H/D isotope effect of the electrical conductivity was examined in detail in order to specify the conditions in which the proton conduction was dominant. In the temperature range from 973 to 1273 K, it was found that protons are the dominant charge carrier both in hydrogen-rich and oxygen-rich atmospheres. At higher temperatures of 1373 to 1673 K, the dominant charge carrier is estimated to be the positive hole in oxygen-rich atmospheres, whereas to be the oxide ion vacancy in hydrogen-rich atmospheres by the analysis of the atmospheric dependence of the electrical conductivity. These results were almost the same as those of Al-doped CaZrO₃ which were reported previously by the present authors.

Keywords: proton conductor, isotope effect, mobility, isotope diffusion, hydrogen sensor

1. Introduction

The perovskite-type proton conductor which was developed first by Iwahara et al.¹²) is a promising material for the electrolyte of the hydrogen concentration cell used as the insertion-type hydrogen sensor for detecting the hydrogen content in molten metals.³⁴) The demand of this type of application is has spread to the higher melting-point metals.⁵⁻⁷) Therefore, the development of the more chemically and mechanically stable proton conductors in such a high temperature region has been desired.

As stated in the previous work, some perovskite type proton conductors have the problems of decomposition with forming carbonates by the reaction with CO₂ in the atmosphere. Zirconate-base perovskites have superior stability on this respect and In-doped calcium zirconate has been already used for commercial hydrogen sensors. However, indium oxide is relatively easily reduced to the metal and its stability in very low oxygen activity conditions becomes a new problem.

In order to develop a high-temperature proton-conducting electrolyte with high chemical stability in the reduced atmosphere, an alternative dopant for CaZrO₃ other than In has been examined in our laboratory. In the previous report, we reported the electrochemical properties of the CaZrO₃ doped with Al.⁵) In the present work, the electric conductivity of CaZrO₃ doped with Y is examined as one of the series of our researches.

2. Experimental

2.1 Sample preparation

Samples were prepared by the solid reaction method using CaCO₃, ZrO₂ and Y₂O₃ powders with 99.99% purity as the starting materials. The powders were mixed in a ball mill and pressed into a pellet, then calcined at 1673 K for 10 h. The pellets were ground again and sieved into a uniform-sized powder. The powder was pressed into pellets using 10-mm diameter dies at a pressure of approximately 1.5 ton cm⁻², and then statically pressed at a pressure of approximately 2 ton cm⁻². The prepared pellets were sintered at 1873 K for 16 h in air. The obtained samples were disk-shaped pellets with a 5.54 mm diameter and 0.73 mm thickness. In this study, we used samples with a compact density of 96% or higher for the electrical conductivity measurements. The phases of the prepared samples were identified by XRD (X-ray powder diffraction).

2.2 Experimental method

Porous platinum electrodes were attached to both sides of the sample disk and the impedance of the sample was measured by the two-terminal ac method. The 2345LCZ impedance meter made by NF (measurement frequency: 40Hz to 100kHz) and the 3532-80 Chemical Impedance Meter made by HIOKI (measurement frequency: 4Hz to 1MHz) were used. The measurement atmosphere was composed of either a mixture of oxygen, water vapor, and argon or a mixture of hydrogen, water vapor, and argon. We call the former the “oxygen-rich” and the latter the “hydrogen-rich” atmosphere in this text. Measurement of the H/D isotope effect on the electrical conductivity was performed in an oxygen-rich atmosphere (by using Ar/O₂/ H₂O and Ar/O₂/D₂O) and a hydrogen-rich atmosphere (by using Ar/H₂/H₂O and Ar/D₂/D₂O). To control the atmosphere, the mixtures of O₂/Ar or H₂/Ar (or D₂/Ar) of a predetermined ratio were over-saturated with water vapor (or heavy water vapor) and then equilibrated in a heat bath held at a constant temperature to adjust the water vapor (or heavy water vapor) to the desired partial pressure.

3. Results

3.1 Phase identification by XRD

Figure 1 shows the results of the XRD patterns of the specimen. The peaks attributed to perovskite structure of
CaZrO₃ were observed in all the samples. In the samples doped with 1, 9), 4 and 5 mol% Y, only the peaks assigned to CaZrO₃ were observed, whereas in the samples doped with 6, 7.5 and 10 mol% of Y, the secondary phase peaks that were assigned to CaO were observed. It is believed that this occurs from the fact that the composition line on the CaO–ZrO₂–Y₂O₃ ternary diagram represented by the formula CaZrₓO₃-Yₓ/100O₃-x/100 is located at a CaO richer side than the point where three phase, CaZrO₂, CaO, and Y₂O₃ coexist. The lattice constant for a-axis and c-axis was affected by the increase of mixing ratio of yttrium as shown in Fig. 2. In the situation of phase diagram mentioned above, the amount of Ca in CaZrO₃ on the tie-line composition must decrease with the mixing ratio of yttrium. This fact may be the reason why the abrupt increase of lattice constant starts with the precipitation of the second phase of CaO. The solubility limits of Y to the phase CaZrO₃ were, therefore, determined as 4.5 ± 0.5 mol% Y.

3.2 Temperature dependence of electrical conductivity and H/D isotope effect

Figure 3 shows a typical example of the cole-cole plot of the complex impedance of the sample under an atmosphere of the indicated activities of H₂ and H₂O (or D₂ and D₂O). In the same way as was observed in the case of Al-doped CaZrO₃, two semi-circles corresponding to the sample impedance in the high frequency side and a small dispersion corresponding to the electrode reaction in the low frequency region were observed. As the resistance at the point of minimum reactance on the low frequency region was confirmed to be proportional to the thickness of the specimen, the value was then adopted as the bulk resistance of the specimen. As shown in the figure, the resistance increases when the surrounding atmosphere changes from hydrogen with light water vapor to deuterium with heavy water vapor, which was similarly observed for the Al doped CaZrO₃ system. The observation of the H/D isotope effect on the conductivity implies that the proton is the most dominant charge carrier under these measurement conditions.

In this experiment, we measured the electrical conductivity of CaZr₀.₉₉Y₀.₀₁O₃−ₓ and CaZr₀.₉₅Y₀.₀₅O₃−ₓ samples. Figures 4 and 5 show the Arrhenius plots of the electrical conductivity in the oxygen-rich and the hydrogen-rich atmospheres, respectively. The doping effect of Y on the increase of the total conductivity of CaZrO₃ is not so good as that of In but almost the same as that of Al which was previously reported. The bold solid, the dashed and the alternate long and short dashed lines in these figures represent calculated values based on the defect model that will be described later in the discussion section. It was found that the electrical conductivity of CaZr₀.₉₅Y₀.₀₅O₃−ₓ is higher than that of CaZr₀.₉₉Y₀.₀₁O₃−ₓ for both atmospheres. The increase of acceptor dopant generally leads to the increase of concentration of the charge carriers such as positive hole, proton and oxide ion vacancy. Therefore, this increasing tendency is reasonable. In oxygen-rich atmospheres, the H/D
isotope effect was confirmed at low temperatures (1273 K or lower); therefore, protons appear to be the dominant charge carrier under these conditions. Conversely, because the H/D isotope effect could not be confirmed at the higher temperatures (1373 K or higher), charge carriers other than protons must be predominant in this range. On the other hand, in the hydrogen-rich atmospheres, the H/D isotope effect was confirmed in almost the entire temperature range of the measurement; therefore, protons appear to be the dominant conducting species under these conditions. These atmospheric dependence of the electrical conductivities are almost the same as that observed for Al doped CaZrO₃ system.

Figure 6 shows the relaxation curve of electrical conductivity for evaluating the H/D isotope effect at 1073 K. This relaxation curve was determined from the resistance measured at constant frequency (528 Hz). As shown in the figure, the electrical conductivity clearly changes when the surrounding atmosphere was exchanged from 1% D₂O–1% O₂–Ar to 1% H₂O–1% O₂–Ar. The diffusion coefficient of the proton was determined by the relaxation time of the ohmic resistance upon exchanging the atmosphere from D₂O to H₂O. By using infinite plate approximation, the compositional change from deuteron to proton is calculated according to the theory of the unsteady chemical diffusion of H/D diffusion pair. The corresponding change in electrical conductivity was calculated and fitted to the measured relaxation curve with the diffusion coefficient as the fitting parameter. The detailed procedure is the same as reported in our previous work.⁸ As shown in Fig. 6, the calculated relaxation curve based on the appropriate value of chemical diffusion coefficient is in good agreement with the measured value. Table 1 shows the chemical diffusion coefficient thus determined.

The self-diffusion coefficient, \( D_{H} \), was evaluated from the determined chemical diffusion coefficient by the following relation:¹¹

\[
\tilde{D} \approx 0.83 D_{H}
\]  
(1)

The proton mobility was determined from the self-diffusion coefficient using the following Nernst–Einstein equation:

\[
m_{H} = \frac{ZF}{RT} D_{H}
\]  
(2)

where \( Z \) is the valency of the carrier, \( R \) is the gas constant, and \( T \) is the temperature. The determined proton mobility can be represented as a function of temperature by the following equation:

\[
m_{H} = \frac{ZF}{RT} D_{H}
\]  
(2)
The value of the mobility is almost one third smaller than that of Al doped CaZrO$_3$ but the activation energy of the proton transport is almost the same as that of Al doped CaZrO$_3$. This fact implies that the moving path of the proton is close to the dopant atom and is considerably affected by the dopant species.

### 3.3 Atmosphere dependence of electrical conductivity

Figure 7 shows a log-log plot of the measured conductivity as a function of the oxygen activity in an oxygen-rich atmosphere when the water vapor or the heavy water vapor activity was fixed at 0.01. From the figure, it can be seen that the electrical conductivity proportionally increases to approximately the 1/4 power of the oxygen activity at the higher temperatures. However, in a lower temperature range, where the H/D isotope effect was observed, namely where protons appear to be the dominant charge carrier, this tendency is no longer apparent. Figure 8 shows the measured electrical conductivity as a function of the water vapor or the heavy water activity when the oxygen activity was fixed at 0.01. From the figure, it can be seen that the electrical conductivity remains constant regardless of the water vapor activity at higher temperatures, whereas in the lower temperature range where the isotope effect is significant, namely where protons appear to be the dominant charge carrier, the electrical conductivity exhibits an increase proportional to the 1/2 power of the water vapor activity.

Figure 9 shows the dependence of the electrical conductivity on the hydrogen or deuterium activity in the hydrogen-rich atmosphere when the water vapor or the heavy water vapor activity was fixed at 0.01. From this figure, it was confirmed that the electrical conductivity does not depend on the hydrogen activity in the whole temperature range of 973 to 1673 K. Figure 10 shows the dependence of the electrical conductivity on the activity of the water vapor or the heavy water vapor when the hydrogen or deuterium activity was fixed at 0.01. From the figure, it can be seen that the electrical conductivity proportionally increases to approximately the 1/4 power of the water vapor activity at the higher temperatures.
fixed at 0.01. From this figure, it is confirmed that the electrical conductivity is proportional to the 1/2 power of the water vapor activity in the relatively low temperature range measured, whereas the tendency gradually weakens as the temperature increases.

These atmosphere dependences of the electrical conductivity are almost the same as those observed in the system Al-doped CaZrO₃.

4. Discussion

4.1 Conduction mechanism

The temperature and atmosphere dependence of the H/D isotope effect observed in the measurements of the conductivity of Y doped CaZrO₃ was almost the same as observed for Al doped CaZrO₃ which was reported in the previous work. Therefore, almost the same defect model and the limiting conditions for the charge balance used for the crystals of Al doped CaZrO₃ may be applied for the present system. The complete attainment of equilibrium between the sample and the atmosphere was supposed in the present case also.

In the previous consideration for defects in Al doped CaZrO₃, we found that not all of the dopant was active for the proton incorporation. Therefore, in addition to the negatively charged substitutional yttrium on Zr site, YZrO, we introduce a new neutral association defect, (YZrVOYZr)⁺. This defect is assumed to be composed from the neighboring two yttrium on the zirconium site and an oxide ion vacancy and to associate with some binding energy. Therefore, yttrium in this associate defect does not work as the active charge compensator for the proton incorporation.

The equilibrium defects in yttrium-doped CaZrO₃ then consists of three movable defects; oxide ion vacancy (V̅O), interstitial proton (H'), and positive hole (h') and two immovable defects; substitutional yttrium (YZr), and associate defect (YZrVOYZr)⁺. Judging from ionic radius, the possibility of yttrium ion occupying the calcium ion site, a defect Yca, could not be denied at all. The amount of the defect, however, must be negligible for the samples prepared by the present atomic ratio: Y : Zr : Ca = x : (1 − x) : 1. Therefore, in the following discussion, we disregard this type of defect to first approximation.

The equilibrium reaction between these defects and the surrounding atmosphere can be expressed by the following three independent equations:

\[
\frac{1}{2}H_2 + h' = H'_i
\]  
\[
O_\bar{\chi}^+ + 2h' = V_\bar{O}^+ + \frac{1}{2}O_2
\]  
\[
2YZr + V_\bar{O}^+ = (YZrVOYZr)^+
\]

where, O̅O denotes the normal oxide ions on the oxygen sub-lattice. Assuming that Henry’s law holds for each charge carrier and that the activity of the oxide ions on the oxygen sub-lattice is substantially constant, the mass-action laws for the above equilibrium reactions can be expressed as follows:

\[
\frac{[H'_i]}{p_{H'_i}} = K_1
\]  
\[
\frac{[V_\bar{O}^+]}{p_{[V_\bar{O}^+]}} = K_2
\]  
\[
\frac{[Y(ZrVOZr)^+]}{[YZr]^+ [V_\bar{O}^+]} = K_3
\]

where K₁, K₂ and K₃ are the equilibrium constants determined by the temperature alone, [i] indicates the concentration of defect i in mol/(mol CaZrO₃), and pᵢ represents the activity of gas species i whose standard state is taken as the pure gas at a pressure of 1 bar.

These positively charged defects competitively compensate for the negative charges introduced by active dopant. Therefore, the following electrical neutrality condition must hold.

\[
[H'_i] + [h'] + 2[V_\bar{O}^+] = [YZr]
\]  
\[
\text{Moreover, the amount of yttrium must be conserved in the crystal, therefore}
\]
\[
[Y'_Zr] + 2([Y(ZrVOZr)^+] = Y_{\text{doped}}
\]  
\[
\text{where} Y_{\text{doped}} \text{represents the concentration of total yttrium in mol/(mol CaZrO₃).}
\]

In the entire atmosphere, the following equilibrium is always established:

\[
H_2 + \frac{1}{2}O_2 = H_2O
\]  
\[
\text{Therefore, between the activities of the gas species, the following relation can be observed:}
\]
\[
\frac{p_{H_2O}}{p_{H_2}p_{O_2}} = K_4
\]  
\[
\text{For conditions of electrical neutrality [eq. (10)] and yttrium conservation [eq. (11)], we may use the next limiting case according to the consideration for Al doped CaZrO₃. For electrical neutrality, we supposed that [V̅O] ≫ [H'], [h'] also in the present system. Therefore, we get from eq. (10),}
\]
\[
[V_\bar{O}^+] ≈ 1/2[YZr]
\]  
\[
\text{For yttrium conservation, we supposed that \([Y(ZrVOZr)^+] \gg [YZr]\) in reference to the fact that only a part of the dopant is active for the proton incorporation.}^8
\]

\[
\text{Therefore, we get the following relation:}
\]
\[
([Y(ZrVOZr)^+] \approx 1/2Y_{\text{doped}}
\]

Substituting the relation (14) and (15) into the eq. (9), we get the next relation.

\[
[YZr] = \left(\frac{Y_{\text{doped}}}{K_3}\right)^{1/3}
\]

This means that, when the temperature is determined, [YZr] is constant and then [V̅O] is also constant from eq. (14).

If the negative excess charge caused by the acceptor dopant is assumed to be substantially counterbalanced by the oxide ion vacancies, the concentration of each charge carrier can be expressed based on eqs. (7), (8) and (13) as follows:

\[
[V_\bar{O}^+] = \text{constant}
\]
[H\textsuperscript{+}] \propto P_{H_{2}O}^{1/4} \propto P_{O_{2}}^{1/4} \propto P_{H_{2}O}^{1/2} \quad (18)\\
[H\textsuperscript{+}] \propto P_{H_{2}O}^{1/4} \propto P_{O_{2}}^{1/4} \propto P_{H_{2}O}^{1/2} \quad (19)

Assuming the mobility of each charge carrier to be independent of the concentration, the electrical conductivity can be expressed as follows:

\[ \sigma_{\text{cc}} = \text{constant} \quad (20) \]
\[ \sigma_{H} \propto P_{H_{2}O}^{1/4} \propto P_{O_{2}}^{1/4} \propto P_{H_{2}O}^{1/2} \quad (21) \]
\[ \sigma_{\text{H}} \propto P_{H_{2}O}^{1/4} \propto P_{O_{2}}^{1/4} \propto P_{H_{2}O}^{1/2} \quad (22) \]

The results from the measurements of the H/D isotope effect on the electrical conductivity indicate that the proton is the dominant charge carrier at low temperatures below 1373 K. In addition, in the low temperature range where the proton is the dominant charge carrier, the dependence of the electrical conductivity on the atmosphere shown in Figs. 7, 8, 9 and 10 indicate that the electrical conductivity depends on the half power of the activity of water vapor and exhibits no dependence on the oxygen activity or the hydrogen activity when the water vapor activity is kept constant. This coincides with eq. (21). The experimental evidence then clearly supports the model that almost all the yttrium exists as the associate defect and the charge compensation is mainly fulfilled by the double-positively charged oxide ion vacancy. Moreover, in the high temperature range and the oxygen-rich atmosphere where the dominant charge carrier is assumed to be other than the proton from the H/D isotope effect, the electrical conductivity exhibited no dependence on the activity of the water vapor but exhibited a dependence on the oxygen activity to the power of 1/4, as shown in Fig. 7. According to eq. (22), it appears that the positive hole is the dominant charge carrier in this case. This evidence also supports the fact that the present model of the charge compensation and yttrium conservation is valid for this oxide system.

As shown in Fig. 9, under hydrogen-rich atmospheric conditions with a constant water vapor environment, the electrical conductivity exhibited no dependence on the hydrogen activity, therefore also on the oxygen activity, even in the high temperature range in which the H/D isotope effect was no longer observed. If the positive hole was the dominant charge carrier under hydrogen-rich atmosphere as well, then, according to eq. (22), the conductivity must exhibit a dependence on the hydrogen activity to the power of −1/2 under the constant water vapor activity. The experimental results, however, clearly contradicted this dependency. The predominant defect under the hydrogen-rich atmosphere and the high temperature conditions thus appears to be the oxide ion vacancy.

Based on the above examination, it was suggested that the defect-model predictions that only a part of dopant was used as the active compensator for positive defects and the charge compensation was mainly taken by the oxide ion vacancy were valid for all experimental conditions for the present oxide system. Under an oxygen-rich atmosphere, the proton appears to be the dominant charge carrier at low temperatures, whereas the positive hole is the dominant charge carrier at the higher temperatures. On the contrary, under a hydrogen-rich atmosphere, the proton appears to be the dominant charge carrier in the low- to middle-temperature range, whereas the oxide ion vacancy is the dominant charge carrier at the higher temperatures.

### 4.2 Partial conductivities

To clarify the contribution of each charge carrier to the total conductivity, the temperature dependence was analyzed by assuming that the mobilities of all charge carriers follow the thermal activation processes with a single activation energy.

From eqs. (4) and (5), the equilibrium reaction for the hydrogen dissolution, also known as the exchange of the charge carrier from the oxide ion vacancy to the proton, can be written as follows:

\[ H_{2} + V_{0}^{\text{H}_{2}O} + \frac{1}{2} O_{2} = O_{0}^{\text{H}_{2}O} + 2H_{\text{+}} \quad (23) \]

The reference states of the species in eq. (23) are taken as those in the infinite dilute solution for both the gas and crystal, and the standard states are taken as the pure perfect gas of 1 bar for the gas species and as the virtual dissolved state of one mole per mole of oxide for the crystal imperfections. Therefore, the standard free energy change of this reaction \( \Delta G^{\circ} \) can be represented as follows:

\[ \Delta G^{\circ} = -RT \ln K_{5} \quad (24) \]
\[ K_{5} = \frac{[H_{\text{+}}^{2}]}{P_{H_{2}O}^{1/2}[V_{0}^{\text{H}_{2}O}]} \quad (25) \]

As the equilibrium reaction in gas phase (12) is always attained, eq. (25) can be written as follows:

\[ \frac{[H_{\text{+}}^{2}]}{[V_{0}^{\text{H}_{2}O}]} = \frac{K_{5}}{K_{4}}P_{H_{2}O} = K_{6}P_{H_{2}O} \quad (26) \]

where \( K_{6} \) coincides with the equilibrium constant for the apparent equation of the hydrogen dissolution that is represented as:

\[ H_{2}O + V_{O}^{\text{H}_{2}O} = O_{0}^{\text{H}_{2}O} + 2H_{\text{+}} \quad (27) \]

As the concentration of the positive hole \( [h^{+}] \) is much lower than \( [V_{0}^{\text{H}_{2}O}] \) and \( [H_{\text{+}}^{2}] \), the electrical neutrality (10) may be written as,

\[ [H_{\text{+}}^{2}] + 2[V_{0}^{\text{H}_{2}O}] = [Y_{Z_{2}}] \quad (28) \]

And, from the assumption that almost all the yttrium exists as associate defect, eq. (16) is valid.

\[ [Y_{Z_{2}}] = \left( \frac{Y_{\text{doped}}}{K_{3}} \right)^{1/3} \]

Therefore, \( [H_{\text{+}}^{2}] \) and \( [V_{0}^{\text{H}_{2}O}] \) may be calculated from eqs. (26) and (28) as follows:

\[ [H_{\text{+}}^{2}] = \frac{-K_{6}P_{H_{2}O}}{2} + \sqrt{\left( \frac{K_{6}P_{H_{2}O}}{2} \right)^{2} + 2K_{6}P_{H_{2}O}\left( \frac{Y_{\text{doped}}}{K_{3}} \right)^{1/3}} \]

(29)
Because the electrical conductivity is the sum of that of the proton and the oxide ion under hydrogen-rich conditions, we can write the total conductivity as follows:

$$\sigma_T = \sigma_{H^+} + \sigma_{V^/} = \frac{1}{V_{\text{oxide}}} (Fm_{H^+}[H^+] + 2Fm_{V^/}[V^/])$$ (31)

where, $m_{H^+}$ and $m_{V^/}$ are the mobilities of the proton and oxide ion vacancies, respectively, and $V_{\text{oxide}}$ represents the molar volume of CaZrO$_3$. To separate the total conductivity into the partial conductivities of the proton and the oxide ion vacancies, the calculated total conductivity was fitted by using eqs. (29), (30) and (31) to the measured value for CaZr$_{0.95}$Y$_{0.05}$O$_3$ with setting $K_3$, $m_{V^/}$ and $K_6$ as the fitting parameters. The value of $m_{H^+}$ determined in the present study [eq. (3)] was used for the calculations.

This result is shown by the solid line in Fig. 5. Each of the partial conductivities thus determined is also depicted in the figure by the dotted and the alternately long and short dashed line. As seen in the Fig. 5, a good agreement was obtained between the measured and calculated values. The best fit was obtained when the parameters had the following values:

$$\ln K_3 = \frac{2070}{T} + 18$$ (32)

$$m_{V^/}/\text{cm}^2 \text{s}^{-1} \text{V}^{-1} = \frac{0.00025}{T} \exp\left\{-\frac{2.6 \text{ eV}}{kT}\right\}$$ (33)

$$\ln K_6 = \frac{18040}{T} - 15$$ (34)

The concentration of active dopant [$Y_{2p}$] calculated from the above value of the equilibrium coefficient is only 1/40 of the total amount of dopant even at 1673 K, the highest temperature of this work. This ratio is smaller than that for the Al-doped CaZrO$_3$ system. Only a part of the dopant participates in the proton incorporation for the CaZrO$_3$ system. This phenomenon was also observed for SrZrO$_3$ by Kreuer and Müller.

For oxygen-rich atmosphere conditions, the partial conductivity of the proton was calculated using above estimated parameters and the measured mobility. The partial conductivity of the positive hole is then calculated by subtracting it from the measured total conductivity. Both partial conductivities thus determined were represented by the bold dotted and the alternately long and short dashed line in Fig. 4. The activation energy of the hole conductivity thus determined was 1.1 eV which was almost the same as that of Al-doped CaZrO$_3$.

5. Conclusion

In this study, the solubility limit of Y for yttrium-doped CaZrO$_3$ designated by the formula CaZr$_{1(100-x)/100}$Y$_{x/100}$O$_{3-\delta}$ was determined as $X = 4.5 \pm 0.5$. Based on the electrical conductivity measurements of CaZr$_{0.95}$Y$_{0.05}$O$_3$ it was confirmed that protons are the dominant charge carrier in both the oxygen-rich atmosphere and the hydrogen-rich atmosphere at temperatures ranging from 973 to 1373 K. Furthermore, it was demonstrated that at higher temperatures ranging from 1373 to 1673 K, the positive hole is the dominant charge carrier in an oxygen-rich atmosphere, whereas the oxide ion is the dominant charge carrier in hydrogen-rich atmospheres. The standard free energy change for the apparent hydrogen dissolution reaction, eqs. (27), can be represented as follows.

$$\Delta G^\circ / \text{J mol}^{-1} = -RT \ln(K_6) = 150,000 + 120T$$

These results suggest that CaZrO$_3$ doped with Y is also one of the candidates as a replacement material for the In-doped CaZrO$_3$ that is currently used as hydrogen sensor probes.

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9) The molar fraction of Y is represented relating atoms on the Zr site of CaZrO$_3$ crystal. Therefore the sample of $x$ mole% Y corresponds to the compound designated as CaZr$_{1(100-x)/100}$Y$_{x/100}$O$_{3-\delta}$.
10) All p’s in this paper represent activities of the denoted gas species whose standard state is taken as the respective pure gas at the pressure of 1 bar.