On the Chemical Diffusion Coefficient of H_2O in $AB_{(1-\chi)}B'_\chi O_{(3-\chi/2)}$-type Perovskites

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ABSTRACT

In proton-conducting perovskites, oxygen ions and protons make a diffusion pair for a chemical diffusion and thus lead to the transport of H_2O under its chemical potential gradient. The present manuscript develops relationships between the chemical diffusion coefficient of H_2O and the diffusion coefficients of protons and oxygen vacancies with an emphasis on the thermodynamic behavior of the oxygen vacancies. Depending on the degree of hydration X, two different expressions of the chemical diffusion coefficient were obtained : $\tilde{D}_{H_2O} = \dfrac{2(1-X)D_{H_i^{\cdot}}D_{V_O^{\cdot\cdot}}}{XD_{H_i^{\cdot}}+2(1-X)D_{V_O^{\cdot\cdot}}}$ as $X \to 0$, and $\tilde{D}_{H_2O} = \dfrac{(2-X)D_{H_i^{\cdot}}D_{V_O^{\cdot\cdot}}}{XD_{H_i^{\cdot}}+2(1-X)D_{V_O^{\cdot\cdot}}}$ as $X \to 1$.

Key words : Chemical diffusion coefficient, Degree of hydration, Thermodynamic factor, Perovskite

1. Introduction

Many oxide perovskites when doped on the B-site with a lower valent ion become proton conductors in water-containing atmospheres.[1-4] Doping with a lower valent ion creates oxygen vacancies. When heated in a moist environment, water is absorbed filling up oxygen vacancies thereby introducing quasi-free protons into the structure. Absorption of water requires the transport of both protons and oxygen ions. As the water content increases, the concentration of protons increases at the expense of oxygen vacancies. This results in an increase in proton conductivity and a simultaneous decrease in oxygen ion conductivity. It is readily understood that the chemical diffusion coefficient of H_2O into the structure must depend upon the concentrations of oxygen vacancies and protons. An equation describing the chemical diffusion coefficient of water in perovskites, $\tilde{D}_{H_2O}$, has been given by Kreuer et al.[5] as follows.

$$\tilde{D}_{H_2O} = \frac{(2-X)D_{H_i^{\cdot}}D_{V_O^{\cdot\cdot}}}{XD_{H_i^{\cdot}}+2(1-X)D_{V_O^{\cdot\cdot}}} \tag{1}$$

where $D_{H_i^{\cdot}}$ and $D_{V_O^{\cdot\cdot}}$ are respectively diffusion coefficients of protons and oxygen vacancies, and X is the degree of hydration given by

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$$X = \frac{X_{H_2O}}{X_{V_O^{\cdot\cdot}}^0} \tag{2}$$

where $X_{V_O^{\cdot\cdot}}^0$ is the initial (in a dry atmosphere) oxygen vacancy concentration, and X_{H_2O} is the fractional water concentration. Eq. (1) was based on the assumption of ideal behavior for both defects, protons and oxygen vacancies and negligible concentrations of electronic defects. Water vapor dissolves into the perovskites through the oxygen vacancies. The reaction is given, using Kröger-Vink notation, as

$$H_2O(g)+V_O^{\cdot\cdot} = 2H_i^{\cdot}+O_O^x \tag{3}$$

Note that $C_{H_i^{\cdot}} = 2C_{H_2O}$, assuming the solved water is fully ionized. The equilibrium constant for the hydration reaction is given by

$$K = \frac{a_{H_i^{\cdot}}^2 a_{O_O^x}}{a_{V_O^{\cdot\cdot}} a_{H_2O}} = \frac{4\gamma_{H_i^{\cdot}}^2 C_{H_2O}^2 a_{O_O^x}}{a_{V_O^{\cdot\cdot}} p_{H_2O}} \tag{4}$$

where a, γ, and C denote activity, activity coefficient and concentration of the subscripted species, respectively. The dependence of C_{H_2O} on p_{H_2O} is given by

$$C_{H_2O} = \frac{\sqrt{Ka_{V_O^{\cdot\cdot}}}}{2\gamma_{H_i^{\cdot}}\sqrt{a_{O_O^x}}}\sqrt{p_{H_2O}} \tag{5}$$

Square root dependence of water solubility on p_{H_2O} has been reported up to a substantial degree of hydration for the various proton-conducting perovskite oxides at medium-to-high temperatures.[6-11] This implies the values of the $a_{V_O^{\cdot\cdot}}$, $a_{O_O^x}$, $\gamma_{H_i^{\cdot}}$, and are constant in Eq. (5). The constancy of $a_{V_O^{\cdot\cdot}}$ contradicts the assumption of Henrian ideal behav-

ior for oxygen vacancies employed in Eq. (1). Considering the chemical diffusion coefficient is a function of the activity or chemical potential of the defects, Eq. (1) may not be a valid expression for the chemical diffusion coefficient of water in all conditions. In this respect, reexamination of Eq. (1) may be required and an attempt was made to develop an appropriate equation (or equations) to represent chemical diffusion coefficient of water in proton conducting- perovskites.

2. Chemical Diffusion of H_2O in Oxygen-deficient Perovskites

H_2O can transport into a perovskite under a chemical potential gradient. It is assumed that the concentration of electronic defects, i.e., electrons and holes, are negligible. Electroneutrality dictates that the fluxes of H^+ and O^{2-} must be coupled. Thus,

$$j_{H^+} = 2j_{O^{2-}} = 2j_{H_2O} \tag{6}$$

Assuming that a flux of a charged species occurs down its electrochemical potential gradient, the transport equations can be readily written in terms of electrochemical potential gradients, mobilities and concentrations as follows:[12]

$$j_{H^+} = -C_{H^+}B_{H^+}\nabla\eta_{H^+} = -\frac{C_{H^+}D_{H^+}}{RT}\nabla(\mu_{H^+} + F\Phi) \tag{7}$$

and

$$j_{O^{2-}} = -C_{O^{2-}}B_{O^{2-}}\nabla\eta_{O^{2-}} = -\frac{C_{O^{2-}}D_{O^{2-}}}{RT}\nabla(\mu_{O^{2-}} - 2F\Phi) \tag{8}$$

where C's concentrations, B's are mobilities, η's are electrochemical potentials, μ's are chemical potentials, T is the temperature, F is the Faraday constant, R is the gas constant, and Φ is the electrostatic potential. The electroneutrality condition and the condition of local equilibrium, allow one to replace electrochemical potential gradients in terms of gradients in chemical potentials of neutral species. It can be readily shown that

$$j_{H_2O} = -\frac{C_{H^+}B_{H^+}C_{O^{2-}}B_{O^{2-}}}{C_{H^+}B_{H^+} + 4C_{O^{2-}}B_{O^{2-}}}\nabla\mu_{H_2O}$$

$$= -\frac{C_{H^+}D_{H^+}C_{O^{2-}}D_{O^{2-}}}{RT(C_{H^+}D_{H^+} + 4C_{O^{2-}}D_{O^{2-}})}\nabla\mu_{H_2O} \tag{9}$$

The chemical potential of H_2O, μ_{H_2O}, in the perovskite may be given by

$$\mu_{H_2O} = \mu_{H_2O}^o + RT\ln(\gamma_{H_2O}C_{H_2O}) \tag{10}$$

where $\mu_{H_2O}^o$ is the standard state chemical potential of H_2O at the temperature, and C_{H_2O} and γ_{H_2O} are the concentration and the activity coefficient of H_2O, respectively. The incorporation of the thermodynamic relation into equation (9) becomes

$$j_{H_2O} = -\frac{C_{H^+}D_{H^+}C_{O^{2-}}D_{O^{2-}}}{C_{H_2O}(C_{H^+}D_{H^+} + 4C_{O^{2-}}D_{O^{2-}})}\left(1 + \frac{\partial\ln\gamma_{H_2O}}{\partial\ln C_{H_2O}}\right)\nabla C_{H_2O} \tag{11}$$

where the term $\left(1 + \frac{\partial\ln\gamma_{H_2O}}{\partial\ln C_{H_2O}}\right)$ corresponds to the thermodynamic factor of water, w_{H_2O}. Thus, the chemical diffusion coefficient of H_2O is given by

$$\tilde{D}_{H_2O} = \frac{C_{H^+}D_{H^+}C_{O^{2-}}D_{O^{2-}}}{C_{H_2O}(C_{H^+}D_{H^+} + 4C_{O^{2-}}D_{O^{2-}})}w_{H_2O} \tag{12}$$

The initial concentration of oxygen vacancies, $X_{V_O^{\cdot\cdot}}^0$, is equal to $x/2$ when the stoichiometric formula of the perovskite is given by $AB_{(1-\chi)}BO_{(3-\chi/2)}$. If the amount of water added per formula unit is $y/2$ the stoichiometric formula of the partially hydrated perovskite is given by $AB_{(1-\chi)}B'_\chi O_{(3-\chi/2+y/2)}H_y$. There are N formula units per unit volume. Thus, the initial oxygen vacancy concentration is $C_{V_O^{\cdot\cdot}}^0 = \frac{Nx}{2} = NX_{V_O^{\cdot\cdot}}^0$. The proton concentration is given by $C_{H^+} = Ny$, and the oxygen vacancy concentration is given by $C_{V_O^{\cdot\cdot}} = \frac{N(x-y)}{2} = NX_{V_O^{\cdot\cdot}}$.

The diffusion of oxygen is assumed to occur exclusively via the vacancy mechanism. This implies $C_{O^{2-}}D_{O^{2-}} = C_{V_O^{\cdot\cdot}}D_{V_O^{\cdot\cdot}}$ $= \frac{N(x-y)}{2}D_{V_O^{\cdot\cdot}}$. Recalling that the degree of hydration, X, is given by $X = \frac{y/2}{x/2} = \frac{y}{x}$, and substituting in the equation for the chemical diffusion coefficient of water, we find that

$$\tilde{D}_{H_2O} = \frac{(1-X)D_{H_i^{\cdot}}D_{V_O^{\cdot\cdot}}}{XD_{H_i^{\cdot}} + 2(1-X)D_{V_O^{\cdot\cdot}}}w_{H_2O} \tag{13}$$

where the protonic defect H^+ was substituted by $H_i^{\cdot}$. This equation shows that the chemical diffusion coefficient of water, $\tilde{D}_{H_2O}$, is, not surprisingly, dependent upon the degree of hydration X.

If the thermodynamic behavior of dissolved water, w_{H_2O}, is not available in a direct experimental method, we can consider an alternative approach. The chemical diffusion coefficient of water may be given using the thermodynamic factors for the building units H^+ and O^{2-}. The chemical potential gradient of the dissolved water is given by

$$\nabla\mu_{H_2O} = \frac{d\mu_{H_2O}}{dC_{H_2O}}\nabla C_{H_2O} \tag{14}$$

For a diffusing defect i, thermodynamic factor $w_i = \frac{d\ln a_i}{d\ln C_i}$ and thus,

$$\frac{d\mu_i}{dC_{H_2O}} = RT\, w_i\frac{1}{C_i}\frac{dC_i}{dC_{H_2O}} \tag{15}$$

The equilibrium $H_2O = 2H^+ + O^{2-}$ and Eq. (15) for oxygen ions and protons allow one to obtain

$$\nabla\mu_{H_2O} = RT\left(\frac{4w_{H^+}}{C_{H^+}} + \frac{w_{O^{2-}}}{C_{O^{2-}}}\right)\nabla C_{H_2O} \tag{16}$$

Thus the incorporation of Eq. (16) into Eq. (9) yields

$$\tilde{D}_{H_2O} = \frac{C_{H^+}D_{H^+}C_{O^{2-}}D_{O^{2-}}}{C_{H^+}D_{H^+} + 4C_{O^{2-}}D_{O^{2-}}}\left(\frac{4w_{H^+}}{C_{H^+}} + \frac{w_{O^{2-}}}{C_{O^{2-}}}\right) \tag{17}$$

Now let us consider the equilibrium of reaction (3) and choose the structure elements, $H_i^\cdot$ and $V_O^{\cdot\cdot}$ as a diffusing couple.[13,14] Using these structure elements, a similar expression to Eq. (16) can be obtained for $\nabla\mu_{H_2O}$, and Eq. (9) gives

$$\tilde{D}_{H_2O} = \frac{C_{H^+}D_{H^+}C_{O^{2-}}D_{O^{2-}}}{C_{H^+}D_{H^+}+4C_{O^{2-}}D_{O^{2-}}}\left(\frac{4w_{H^+}}{C_{H^+}}+\frac{w_{O_O^x}}{C_{O_O^x}}+\frac{w_{V_O^{\cdot\cdot}}}{C_{V_O^{\cdot\cdot}}}\right) \quad (18)$$

where $C_{O_O^x}\gg C_{V_O^{\cdot\cdot}}$, and therefore $\frac{w_{O_O^x}}{C_{O_O^x}}\ll\frac{w_{V_O^{\cdot\cdot}}}{C_{V_O^{\cdot\cdot}}}$, unless $w_{O_O^x}$ has much larger value than $w_{V_O^{\cdot\cdot}}$. This means the chemical potential of the regular structure lattice element O_O^x could be neglected.[15] Noting the relation $C_{V_O^{\cdot\cdot}}D_{V_O^{\cdot\cdot}}=C_{O^{2-}}D_{O^{2-}}$, $\tilde{D}_{H_2O}$ can be given as

$$\tilde{D}_{H_2O} = \frac{C_{H_i^\cdot}D_{H_i^\cdot}C_{V_O^{\cdot\cdot}}D_{V_O^{\cdot\cdot}}}{C_{H_i^\cdot}D_{H_i^\cdot}+4C_{V_O^{\cdot\cdot}}D_{V_O^{\cdot\cdot}}}\left(\frac{4w_{H_i^\cdot}}{C_{H_i^\cdot}}+\frac{w_{V_O^{\cdot\cdot}}}{C_{V_O^{\cdot\cdot}}}\right) \quad (19)$$

Obviously Eqs. (17) and (19) must be equal. As a result,

$$\frac{w_{O^{2-}}}{C_{O^{2-}}}=\frac{w_{V_O^{\cdot\cdot}}}{C_{V_O^{\cdot\cdot}}} \quad (20)$$

Eq. (20) is also given in [16]. Using the degree of hydration X, Eq. (17) or (19) can be rewritten as

$$\tilde{D}_{H_2O} = \frac{D_{H_i^\cdot}D_{V_O^{\cdot\cdot}}\{Xw_{V_O^{\cdot\cdot}}+2w_{H_i^\cdot}(1-X)\}}{XD_{H_i^\cdot}+2(1-X)D_{V_O^{\cdot\cdot}}} \quad (21)$$

Eqs. (13) and (21) provide the relation between the thermodynamic factors of water and the defects:

$$w_{H_2O}=\frac{X}{1-X}w_{V_O^{\cdot\cdot}}+2w_{H_i^\cdot} \quad (22)$$

Eq. (22) shows that as the degree of hydration increases the effect of the thermodynamic factor of oxygen vacancies becomes more significant. In what follows the chemical diffusion coefficient of H_2O is determined at the two extreme cases $X\to0$ and $X\to1$.

2.1. $\tilde{D}_{H_2O}$ when $X\to0$

The solubility of water is related with the water vapor pressure in the surrounding gas atmosphere. Let us assume that the relation can be given in the following expression.

$$C_{H_2O}=kp_{H_2O}^{1/n} \quad (23)$$

where k is a proportionality constant and n is an integer (not necessarily). In equilibrium, the chemical potentials of H_2O must be same in the perovskite and in the gas phase. Thus

$$\mu_{H_2O}^{perovskite}=\mu_{H_2O}^{gas} \quad (24)$$

The chemical potential of H_2O, μ_{H_2O}, in the gas is given by

$$\mu_{H_2O}^{gas}=\mu_{H_2O}^o+RT\ln p_{H_2O} \quad (25)$$

The chemical potential in the perovskite of H_2O, $\mu_{H_2O}^{perovskite}$

from Eq. (10), is rewritten as

$$\mu_{H_2O}^{perovskite}=\mu_{H_2O}^o+RT\ln(\gamma_{H_2O}C_{H_2O}) \quad (26)$$

Eqs. (23) through (26) yields

$$\gamma_{H_2O}=(1/k)^nC_{H_2O}^{n-1} \quad (27)$$

When $n=1$, $\gamma_{H_2O}=$ constant and dissolved water is expected to exhibit Henrian behavior, i.e., $w_{H_2O}=1$. Deuterium dissolution in the perovskites was found to be such a case : Baikov[17] reported a linear dependence of the deuterium pressure on the D content in $SrTiO_3$. However, in case of water dissolution in proton-conducting perovskites, Sieverts law-type behavior has been observed at high temperatures,[6-11] which corresponds to $n=2$ from Eq. (22). Accordingly, Eq. (27) gives

$$\frac{\partial\ln\gamma_{H_2O}}{\partial\ln C_{H_2O}}=1 \text{ and } w_{H_2O}=2 \quad (28)$$

And thus

$$\tilde{D}_{H_2O}=\frac{2(1-X)D_{H_i^\cdot}D_{V_O^{\cdot\cdot}}}{XD_{H_i^\cdot}+2(1-X)D_{V_O^{\cdot\cdot}}} \quad (29)$$

Eq. (29) can be derived from an alternative approach : In case of the doped oxygen-ion-conducting oxides, the chemical potential of oxygen ions is generally accepted to be constant,[18-22] i.e., $w_{O^{2-}}=0$. The perovskites are expected to be such a case so that $w_{O^{2-}}\to0$ with a varying p_{H_2O} when $X\to0$. Then from Eq. (19), clearly $w_{V_O^{\cdot\cdot}}\to0$, and thus Eq. (21) reduces to Eq. (29). So far as $w_{V_O^{\cdot\cdot}}$ exhibits a value close to zero, Eq. (29) will be effective even at an increased degree of hydration. And even if $w_{V_O^{\cdot\cdot}}$ is of a substantial magnitude, $X\to0$ will also result in Eq. (29).

2.2. $\tilde{D}_{H_2O}$ when $X\to1$

When the perovskite becomes nearly saturated with water, the activity of oxygen vacancies is expected to fall. Then most of the oxygen vacancies are filled up, and they are expected to follow Henrian ideal behavior, or $w_{V_O^{\cdot\cdot}}=1$. If $w_{H_i^\cdot}=1$ sustains to be valid, Eq. (21) is simplified to Eq. (1). Eq. (22) shows that as $X\to1$, $w_{H_2O}\to\infty$, and thus $\gamma_{H_2O}\to\infty$ or $\mu_{H_2O}\to\infty$. From Eq. (4) it is clear that as the activity of oxygen vacancies $a_{V_O^{\cdot\cdot}}$ approaches 0 (as $X\to1$), obviously must be $p_{H_2O}\to\infty$ with a given finite value of the equilibrium constant K. Eqs. (24) through (26) yield

$$\ln p_{H_2O}=const.+\ln(\gamma_{H_2O}C_{H_2O}) \quad (30)$$

Then $\gamma_{H_2O}\to\infty$ is not unreasonable when $p_{H_2O}\to\infty$.

In Fig. 1, a schematic variation of $\tilde{D}_{H_2O}$ against the degree of hydration X is given. As $X\to1$, $\tilde{D}_{H_2O}=D_{V_O^{\cdot\cdot}}$, and $X\to0$, $\tilde{D}_{H_2O}=D_{H_i^\cdot}$. And in an intermediate range of X, $\tilde{D}_{H_2O}$ is expected to change from the value of Eq. (29) to that given by Eq. (1) as shown in the figure. However, as shown in Eq. (21) or (22), the term $Xw_{V_O^{\cdot\cdot}}$ becomes more significant with an increasing the degree of the hydration. Thus more quantitative knowledge on the thermodynamic
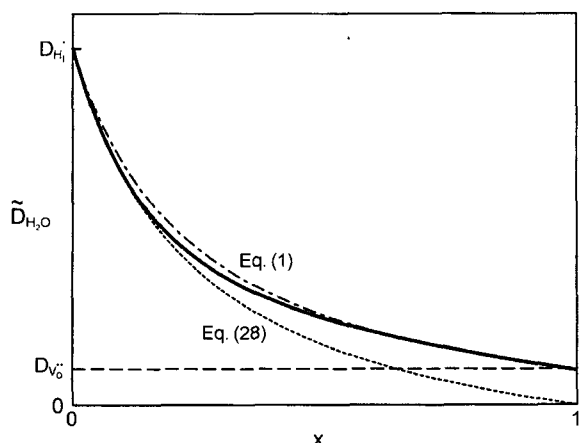
Fig. 1. A schematic plot for $\tilde{D}_{H_2O}$ vs. X. The scale is based on $D_{H_i^\cdot} \approx 10 D_{V_O^{\cdot\cdot}}$.[23]

behavior of oxygen vacancies may be needed for further analysis. Kreuer et al.[24,25] claims the behavior of oxygen vacancies corresponding to $w_{V_O^{\cdot\cdot}} > 1$, due to the lattice relaxation effect around oxygen vacancies in proton-conducting perovskites. Anyway, it is noted from Fig. 1 that Eq. (1), based on the ideal behavior of the protons and oxygen vacancies, gives a good approximation of $\tilde{D}_{H_2O}$ value in the entire range of the hydration.

A chemical diffusion coefficient is frequently expressed by a function of conductivities contributed by the diffusing species. Eq. (18) can be written, using $\sigma_i = \dfrac{C_i D_i}{RT} z_i^2 F^2$ for a species i, where z_i is the valence of i, as

$$\tilde{D}_{H_2O} = \frac{\sigma_{V_O^{\cdot\cdot}}}{\sigma} w_{H_i^\cdot} D_{H_i^\cdot} + \frac{\sigma_{H_i^\cdot}}{\sigma} w_{V_O^{\cdot\cdot}} D_{V_O^{\cdot\cdot}} \qquad (31)$$

In a mixed-conducting oxides, protons can be substituted by electronic defects (denoted by n) in Eq. (31). Assuming $w_{V_O^{\cdot\cdot}} = 1$ and $w_n = 1$, one obtains the well-known expression[16] for the chemical diffusion coefficient as follows.

$$\tilde{D} = t_{V_O^{\cdot\cdot}} D_n + t_n D_{V_O^{\cdot\cdot}} \qquad (32)$$

where t denotes transference number for the subscripted species. Eq. (32) corresponds to Eq. (1) in the case of water dissolution in perovskites. As discussed previously, in an oxide with a high concentration of oxygen vacancies, $w_{V_O^{\cdot\cdot}} \to 0$ and thus the second term of the right hand side of Eq. (32) vanishes. Thus we conclude that the term containing $D_{V_O^{\cdot\cdot}}$ in Eq. (31) or (32) can be reasonably neglected in doped oxide with a high concentration of oxygen vacancies, even though the magnitude of protonic (or electronic) contribution to the total conductivity is substantial.

Ideal behavior was assumed for the protons in our analysis. The interactions of protons, between themselves, or with dopants which may lead to the trapping of protons, affect their thermodynamic behavior. Conflicting results have been reported as to the significance of such interactions in the literature,[26] and if it is true, the chemical diffu-

sion coefficient of water may be lower than those expected by the equations given in this work.

3. Conclusions

The analysis presented here obtained two different expressions, Eqs. (29) and (1), for the chemical diffusion coefficient of water in the proton-conducting perovskites, depending on the thermodynamic behavior of oxygen vacancies : $\tilde{D}_{H_2O} = \dfrac{2(1-X)D_{H_i^\cdot} D_{V_O^{\cdot\cdot}}}{XD_{H_i^\cdot} + 2(1-X)D_{V_O^{\cdot\cdot}}}$ as the degree of hydration $X \to 0$, and $\tilde{D}_{H_2O} = \dfrac{(2-X)D_{H_i^\cdot} D_{V_O^{\cdot\cdot}}}{XD_{H_i^\cdot} + 2(1-X)D_{V_O^{\cdot\cdot}}}$ as $X \to 1$. Eq. (29) is based on the constant activity of oxygen vacancies when the water solubility is low. Eq. (1) was derived assuming Henrian ideal behavior of oxygen vacancies as the perovskite approaches full saturation. The constant activity of oxygen vacancies in the former, generally accepted for doped oxygen-ion conductors, is deduced from the experimentally reported square root dependency of water solubility on p_{H_2O}, which allows one to obtain $w_{H_2O} = 2$.

Acknowledgments

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