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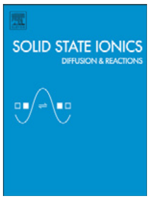

Mass relaxation vs. electrical conductivity relaxation of a proton conducting oxide upon hydration and dehydration

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ABSTRACT

Hydration or dehydration of a proton conducting oxide has been understood to be due to chemical diffusion of H_2O. Hence, mass relaxation of the oxide has often been employed to determine the chemical diffusivity and saturation solubility of H_2O. This paper shows that this approach is not correct. Applying thermogravimetric methods at 973 and 1073 K to $BaCe_{0.95}Yb_{0.05}O_{2.975}$ as model system, the mass relaxes twofold (i.e., with two different chemical diffusivities for H and O) like the electrical conductivity, but monotonically unlike the conductivity which relaxes non-monotonically. The correlation of the mass relaxation with the conductivity relaxation is established. The closed-form solution for the mass relaxation is presented in comparison with that for the conductivity relaxation and its implication is discussed in connection to water saturation.

1. Introduction

Since the discovery of proton conducting oxides in the early 80s [1], they have been a subject of active research for their scientific interest as well as for their green, electrochemical applications [2]. These proton conducting oxides are in contradistinction to other ion conducting oxides, e.g., zirconia, in that protons are not an intrinsic part of the oxide, but are only externally incorporated into the system. The thermodynamics and kinetics of hydration or dehydration have, thus, been of very fundamental interest. Through almost three decades of study, we have come to believe that these are well understood: one may prescribe the solubility limit and stability of dissolved water as a function of the thermodynamic variables of a given system, and the hydration or dehydration kinetics together with its mechanisms in a given boundary condition [3–8].

With regard to the kinetics, hydration or dehydration has long been understood to proceed via an ambipolar diffusion of protons (H^+) and oxide ions (O^{2-}) as charged components (or equivalently, interstitial protons $H_i^{\bullet}$ and oxygen vacancies $V_o^{\bullet\bullet}$ in terms of defects) or chemical diffusion of molecular H_2O [3]. If this is the case, then the mass relaxation upon hydration or dehydration should be governed by one and only chemical diffusivity of H_2O (assuming the surface reaction is fast enough), thus leading to a single-fold relaxation of the oxide mass with time [9]. One can then determine the chemical diffusivity of water from the relaxation time and the water saturation solubility from the stationary mass as time approaches infinity. This is actually what has been practiced to date to determine the chemical diffusivity and saturation solubility of water in a proton conducting oxide by thermogravimetry in particular [3,5,8,10].

Quite recently, Yoo and coworkers [11,12] have observed that upon a sudden increase of water vapor activity in the ambient with a uniformly constant oxygen activity (hydration), the electrical conductivity of proton conducting $BaCe_{0.95}Yb_{0.05}O_{2.975}$ and $SrCe_{0.95}Yb_{0.05}O_{2.975}$ first decreases fast and then increases slowly with time towards a saturation, resulting in a minimum between the two processes. Upon dehydration, the conductivity relaxes exactly in the opposite sense, resulting in a maximum. They have interpreted this non-monotonic, twofold relaxation of conductivity as being due to the fast, chemical diffusion of H (or an ambipolar diffusion of protons $H_i^{\bullet}$ and holes $h^{\bullet}$ in counter directions) followed by sluggish chemical diffusion of O (or an ambipolar diffusion of $V_o^{\bullet\bullet}$ and $h^{\bullet}$ in counter directions), and extracted these two chemical diffusivities, $\tilde{D}_{iH}$ and $\tilde{D}_{vH}$, respectively, from those twofold conductivity relaxations with a sufficient precision [11,12]. Around the same time, Yu et al. [13] also observed a similar, non-monotonic relaxation of conductivity on the system of Fe-doped $SrTiO_3$ upon hydration and verified by an optical means the two decoupled chemical diffusion processes, viz., fast H-diffusion leading to reduction of Fe_{Ti}^{x} to $Fe_{Ti}^{\prime}$ and sluggish O-diffusion leading to oxidation of $Fe_{Ti}^{\prime}$ back to Fe_{Ti}^{x}. In retrospect, such twofold relaxation of proton conducting oxides upon hydration has already been indicated in earlier experiments: for instance, Schober and Coors [14] measured the times taken for deuterium D and O^{18} to reach the lower water activity side of a $BaCe_{1-x}Y_xO_{3-x/2}$ slab under an activity gradient of D_2O and H_2O^{18}, respectively, to find that they differ by ca. two orders

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of magnitude at 700 °C. They [14] further reported that upon hydration, a specimen expands rapidly up to 85% saturation followed by slow expansion to a full saturation.

This new kinetic picture of hydration or dehydration is quite contradictory to the conventional one based on the single chemical diffusion of H_2O. If hydration or dehydration indeed proceeds by the two decoupled chemical diffusion processes, the mass relaxation thereby should also be twofold in terms of relaxation times. But, it should be monotonic unlike the conductivity relaxation, because diffusion of H and O in parallel directions always contributes in parallel to the mass change, but in anti-parallel to the total conductivity change [11,12]. As a matter of fact, the mass relaxation upon hydration or dehydration used to be employed, obviously assuming or believing the relaxation to be single-fold, to determine the chemical diffusivity of H_2O of the proton conducting oxides [3,10].

This paper aims to verify whether the mass relaxation during hydration or dehydration of a proton conducting oxide is necessarily single-fold as has been believed, or twofold monotonic in accordance with the conductivity relaxation that is twofold non-monotonic. We have, thus, measured the mass relaxation by high temperature thermogravimetry on the system of $BaCe_{0.95}Yb_{0.05}O_{2.975}$, for which the conductivity relaxation has been documented extensively [12]. We will first present the closed-form solution to the mass relaxation in analogy to the twofold non-monotonic conductivity relaxation, and analyze thereby the mass relaxations observed. By doing that we will establish the correlation between the mass and conductivity relaxation to substantiate the decoupled chemical diffusion in a water activity gradient. Finally, we will discuss the implications of the closed-form solution.

2. Closed-form solution to mass relaxation

Let us suppose that an oxide with a parallelepiped geometry, measuring $2a\times 2b\times 2c$, is subjected to an abrupt change of water vapor activity a_{H_2O}in its surrounding where the oxygen activity a_{O_2} is kept uniformly constant. Hydration or dehydration proceeds not through the ambipolar diffusion of $H_i^{\bullet}$ and $V_O^{\bullet\bullet}$ or

$$H_2O + V_O^{\bullet\bullet} = 2H_i^{\bullet} + O_O^{x}, \tag{1}$$

but through the decoupled ambipolar diffusion of $H_i^{\bullet}$ and $h^{\bullet}$ and of $V_O^{\bullet\bullet}$ and $h^{\bullet}$ or [11,12]

$$H + h^{\bullet} = H_i^{\bullet} \tag{2a}$$

$$O + V_O^{\bullet\bullet} = O_O^{x} + 2h^{\bullet}. \tag{2b}$$

The local concentrations of $H_i^{\bullet}$ and $V_O^{\bullet\bullet}$, c_i and c_v, respectively, will, thus, be determined as

$$\frac{\partial c_k}{\partial t} = \nabla\tilde{D}_{kH}\nabla c_k \ \ (k = i, v). \tag{3}$$

By assuming the chemical diffusivity of species $k(=i,v)$, $\tilde{D}_{kH}$ to be constant across an a_{H_2O} window chosen, the general solution for the spatial average concentration of species k, $\overline{c}_k$ takes the form [11,12],

$$\overline{c}_i - c_{i,0} = (c_{i,\infty} - c_{i,0})[1 - f(\tau_i)] \tag{4}$$

where $c_{k,0}$ and $c_{k,\infty}$ denote the concentration of $k(=i,v)$ at time $t=0$ (initial equilibrium) and at $t\to\infty$ (final equilibrium), respectively. The time-dependent term $f(\tau_k)$ is given as [15]

$$f(\tau_k) = \left(\sum_{\ell=1}\frac{2L^2 e^{-\beta_\ell^2\tilde{D}_{kH}t/a^2}}{\beta_\ell^2(\beta_\ell^2 + L^2 + L)}\right)\left(\sum_{m=1}\frac{2M^2 e^{-\beta_m^2\tilde{D}_{kH}t/b^2}}{\gamma_m^2(\gamma_m^2 + M^2 + M)}\right) \left(\sum_{n=1}\frac{2N^2 e^{-\beta_n^2\tilde{D}_{kH}t/c^2}}{\lambda_n^2(\lambda_n^2 + N^2 + N)}\right) \tag{5}$$

where $\tilde{k}_{kH}$ denotes the surface reaction rate constant with respect to the species $k(=i,v)$, β_ℓ, γ_m and λ_n (ℓ,m,$n=1,2,3\ldots$) are such that

$$\beta_\ell \tan\beta_\ell = L\equiv a\,\tilde{k}_{kH}/\tilde{D}_{kH}; \tag{6}$$

$$\gamma_m \tan\gamma_m = M\equiv b\,\tilde{k}_{kH}/\tilde{D}_{kH};$$

$$\lambda_n \tan\lambda_n = N\equiv c\,\tilde{k}_{kH}/\tilde{D}_{kH}.$$

If L, M, $N\gg 1$, or the overall kinetics is governed by diffusion, Eq. (5) may be reduced to

$$f(\tau_k) = \left(\frac{8}{\pi^2}\sum_{\ell=1}\frac{e^{-(2\ell+1)^2\tilde{D}_{kH}t/a^2}}{(2\ell+1)^2}\right)\left(\frac{8}{\pi^2}\sum_{m=1}\frac{e^{-(2m+1)^2\tilde{D}_{kH}t/b^2}}{(2m+1)^2}\right) \left(\frac{8}{\pi^2}\sum_{n=1}\frac{e^{-(2n+1)^2\tilde{D}_{kH}t/c^2}}{(2n+1)^2}\right). \tag{7}$$

By noting that upon hydration or dehydration, the chemical diffusion fluxes J_i and J_v are in counter directions, the overall sample mass "m" (not to be confused with the subscript "m" in Eq. (5)) may be represented as

$$(m - m_0)/V_0 = \omega_i(\overline{c}_i - c_{i,0}) - \omega_v(\overline{c}_v - c_{v,0}) \tag{8}$$

where m_0 stands for the sample mass at $t=0$, and V_0 the volume of the sample. This volume is assumed to be constant despite the possible volume change with hydration or dehydration [14]. Here, ω_k represents the mass per unit concentration of species $k(=i,v)$. If protons and oxygen vacancies themselves are solely responsible for the mass transferred, one might expect that $\omega_i=1$ g/mol and $\omega_v=16$ g/mol when c_k are given in molar concentration. Substituting Eq. (4), associated with Eq. (5) or (7), into Eq. (8), one finally obtains the closed-form solution for hydration or dehydration as

$$\Delta m = m - m_0 = (B_i + B_v) - B_i f(\tau_i) - B_v f(\tau_v) \tag{9}$$

with

$$B_i\equiv V_0\omega_i(c_{i,\infty} - c_{i,0})\,;\ B_v\equiv V_0\omega_v(c_{v,0} - c_{v,\infty}). \tag{10}$$

Here, it is noted that for hydration,

$$c_{i,\infty}\geq\overline{c}_i\geq c_{i,0}\,;\ c_{v,\infty}\leq\overline{c}_v\leq c_{v,0} \tag{11a}$$

and for dehydration,

$$c_{i,\infty}\leq\overline{c}_i\leq c_{i,0}\,;\ c_{v,\infty}\geq\overline{c}_v\geq c_{v,0}. \tag{11b}$$

Furthermore, as $f(\tau_k)\to 0$ as $t\to\infty$,

$$B_i + B_v = m_\infty - m_0. \tag{12}$$

On the other hand, the spatial mean conductivity, $\overline{\sigma}$ may be written, relative to σ_0, the conductivity at $t=0$, as

$$\overline{\sigma} - \sigma_0 = -\lambda_{pi}(\overline{c}_i - c_{i,0}) - \lambda_{pv}(\overline{c}_v - c_{v,0}) \tag{13}$$

with

$$\lambda_{pi} = e_0(u_p - u_i)\,;\ \lambda_{pv} = 2e_0(u_p - u_v) \tag{14}$$

where e_0 stands for the fundamental charge, u_k the electrochemical mobility of the carrier type k ($p=h^{\bullet}$). Again by noting Eq. (11a) and the contributions to the conductivity change by H and O being in counter directions due to Eq. (2), one may substitute Eq. (5) or (7)