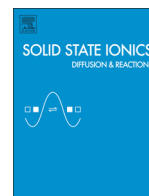




Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Two-fold stoichiometry relaxation – Simulated relaxation kinetics of ionic and electronic defect concentrations

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ARTICLE INFO

Article history:

Received 6 August 2015

Received in revised form 27 November 2015

Accepted 6 December 2015

Available online xxx

Keywords:

Proton conductor

Stoichiometry relaxation

Ambipolar diffusion

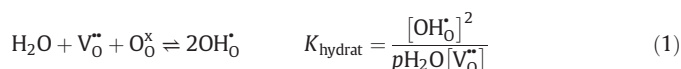
ABSTRACT

The relaxation kinetics of defect concentrations in an oxide containing protons, oxygen vacancies, and holes after an increase of water partial pressure are simulated using materials parameters representative for perovskite proton conductors. Different regimes are identified (e.g. single-fold chemical diffusion of water at low pO_2 , two-fold relaxation at high pO_2). It is shown that the analysis of ionic defect concentrations (which could be measured e.g. by thermogravimetry) and electronic defect concentrations (detectable by conductivity relaxation) yields different effective diffusion coefficients. Owing to the transition between different defect chemical and diffusion regimes, extracted effective activation energies are related to the fundamental transport parameters in a complex way.

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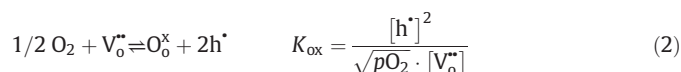
1. Introduction

Proton conducting electrolytes such as acceptor-doped $BaZrO_3$ and $BaCeO_3$ perovskites form protonic defects by the hydration reaction [1–4]



(Kröger–Vink nomenclature; square brackets denoting concentrations, expressed in molar fraction; partial pressures appearing in mass action constants are divided by $p^0 = 1$ bar). An increase in water partial pressure p_{H_2O} leads to a further proton incorporation. Under conditions where the hole concentration is sufficiently low (low temperature and/or high p_{H_2O} and low pO_2) and the surface exchange rate sufficiently high, this stoichiometry relaxation kinetics can be described by a single chemical diffusion coefficient of water $D_{H_2O}^{\delta}$, which takes values between the proton diffusivity $D_{OH_O^{\bullet}}$ and the oxygen vacancy diffusivity $D_{V_O^{\bullet\bullet}}$ depending on the degree of hydration [5].

However, when a perceptible concentration of highly mobile electron holes h^{\bullet} is available from the oxygen exchange reaction



these perovskites exhibit much more complex relaxation phenomena such as a non-monotonic change of the conductivity with two

characteristic time constants (“two-fold relaxation”). This was first observed for slightly Fe-doped $SrTiO_3$ single crystals at high T and pO_2 by space-resolved optical spectroscopy [6,7], and then also found for acceptor-doped $(Ba,Sr)(Zr,Ce)O_3$ at high T and high pO_2 . [8–12] Given a sufficient hole concentration, the holes are able to “decouple” the proton and oxygen vacancy fluxes. As first approximation, this can qualitatively be assigned to a fast hydrogen uptake (ambipolar diffusion of protons OH_O^{\bullet} compensated by holes) followed by a slower oxygen uptake (ambipolar diffusion of oxygen vacancies $V_O^{\bullet\bullet}$ and holes h^{\bullet}) so that the overall reaction still is mainly water incorporation.

Exact analytical relations to describe the diffusion and stoichiometry relaxation in such systems with three mobile carriers (e.g. OH_O^{\bullet} , $V_O^{\bullet\bullet}$ and h^{\bullet}) were derived in [13], and complemented by numerical simulations for different defect chemical regimes at constant temperature. The complex relaxation behavior can be traced back to the fact that only all three carriers together have to fulfill the electroneutrality condition. The flux of one defect depends on the concentration gradients of two defects which are not necessarily linked by simple prefactors. Consequently, in such a situation four diffusion coefficients are required to fully describe the system.

In the present article, we choose the mass action constants for the hydration reaction and the oxygenation reaction as well as the defect diffusivities $D_{V_O^{\bullet\bullet}}$, $D_{OH_O^{\bullet}}$, $D_{h^{\bullet}}$ in a range typical for proton conducting acceptor-doped $BaZrO_3$ and $BaCeO_3$ perovskites. From the simulated normalized integral defect concentrations, two pairs of phenomenological diffusivities are extracted. $D_{h^{\bullet}}^{\text{eff}}$ and $D_{V_O^{\bullet\bullet}}^{\text{eff}}$ describe the changes of OH_O^{\bullet} and $V_O^{\bullet\bullet}$ concentrations, which could be measured e.g. by thermogravimetry. In addition, also the transient behavior of the conductivity (typically predominant p-type electronic under the conditions leading to two-fold relaxation, reflecting the changes in hole concentration) is fitted by

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D_{fast} and D_{slow} which, as shown below, in general differ from D_H^{eff} , D_O^{eff} [14]. The simulations are performed for different temperatures in order to compare with experimentally determined activation energies (cf. [15] and references therein).

2. Computational details

The computational details of the one-dimensional finite difference simulations for a finite sample with a thickness of 0.001 cm with diffusion occurring from both surfaces are given in ref. [13]. The key points of the model are (i) assumption that all surface exchange reactions are infinitely fast, (ii) ideally dilute behavior of the point defects, (iii) local electroneutrality (i.e. the stoichiometry relaxation is purely determined by bulk transport, no interfacial space charge effects), and (iv) application of small p_{H_2O} changes. The simulation input parameters are the defect diffusivities and the defect concentrations as well as their change for a 10% increase of p_{H_2O} at given p_{O_2} and T [16]. These concentrations are calculated from the mass action constants $K_{hydrat} = K_{hydrat}^0 e^{-\Delta H_{hydrat}/RT}$, $K_{ox} = K_{ox}^0 e^{-\Delta H_{ox}^0/RT}$ and an acceptor concentration of 10% assuming ideally dilute behavior (absence of defect interactions, which also implies that the defect diffusivities depend only on T).

The parameters for proton diffusivity D_{OH_0} and K_{hydrat} were chosen close to the values given for $BaZr_{0.9}Y_{0.1}O_{2.95}$ in [4] with a proton migration enthalpy of 0.4 eV and $\Delta H_{hydrat}^0 = -0.8$ eV. The vacancy diffusivity D_{V_0} is taken a bit lower than the values derived in [17] for $BaZr_{0.9}Y_{0.1}O_{2.95}$ to obtain better agreement with $D_{H_2O}^{\delta}$ from [10], and a V_0 migration energy of 0.8 eV typical for many perovskites is used. The hole diffusivity is assumed T -independent (cf. the even slight decrease of hole mobility with increasing T for $SrTiO_3$, $BaTiO_3$), with a value $D_{h^{\cdot}} = 8.6 \cdot 10^{-3}$ cm²/s in the typical range for $SrTiO_3$ or $BaTiO_3$ [18–20]. At all T considered, $D_{V_0} < D_{OH_0} < D_{h^{\cdot}}$. For K_{ox} , ab initio calculations [21] for $BaZrO_3$ yielded values of ΔH_{ox}^0 in the range of +0.88 to +1.53 eV strongly depending on the chosen exchange-correlation functional (for the PBE functional which is known to strongly underestimate the band gap, even $\Delta H_{ox}^0 = -1.31$ eV is obtained). Taking a value of $\Delta H_{ox}^0 = 0.9$ eV proved suitable to reproduce the experimentally observed change from protonic to hole electronic conductivity at high T and p_{O_2} and the T -dependence of the conductivity in the hole-dominated regime. [22,23] However, the values of ΔH_{ox}^0 and the temperature dependence of $D_{h^{\cdot}}$ are strongly correlated (a nonnegligible hole migration barrier will directly lead to less positive ΔH_{ox}^0). While we choose the parameters in a range typical for acceptor-doped $Ba(Zr,Ce)O_{3-x}$ perovskite proton conductors, we do not attempt to achieve the best possible fit for an individual member of this materials family.

The effective diffusivities D_H^{eff} and D_O^{eff} were calculated from the linear initial regions of the normalized integral defect concentration versus \sqrt{t} according to $D = (\text{slope})^2 \pi^2 / 16$ [24]. The transient behavior of the total conductivity for conditions of non-monotonic relaxation was fitted by a sum of two individual diffusion-limited relaxation curves as suggested in [8], yielding D_{fast} and D_{slow} . For each of the two curves, the standard solution of one-dimensional diffusion into a finite plate was used [25], where taking five terms of the sums proved sufficient. For small p_{H_2O} changes (here: by 10%), identical conductivity relaxation curves are obtained for measurements parallel or perpendicular to the direction of diffusion (cf. appendix in [26]); for large changes the conductivity should be extracted in the same geometric configuration as applied in the experiment.

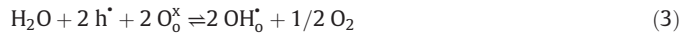
The chemical diffusion coefficients D_H^{δ} , D_O^{δ} and $D_{H_2O}^{\delta}$ (strictly valid only in situations without perceptible contribution from a third carrier) shown for comparison in Figs. 3 and 4 are calculated from $D_H^{\delta} = \frac{t_{h^{\cdot}}}{t_{h^{\cdot}} + t_{OH_0}} D_{OH_0} + \frac{t_{OH_0}^{\delta}}{t_{h^{\cdot}} + t_{OH_0}^{\delta}} D_{h^{\cdot}}$, $D_O^{\delta} = \frac{t_{V_0}}{t_{h^{\cdot}} + t_{V_0}} D_{V_0} + \frac{t_{h^{\cdot}}^{\delta}}{t_{h^{\cdot}} + t_{V_0}^{\delta}} D_{h^{\cdot}}$ and $D_{H_2O}^{\delta} = \frac{t_{V_0}^{\delta}}{t_{V_0}^{\delta} + t_{OH_0}} D_{OH_0} + \frac{t_{OH_0}^{\delta}}{t_{V_0}^{\delta} + t_{OH_0}^{\delta}} D_{V_0}$ using the transference numbers of the full three carrier defect model. These expressions deviate from the respective two carrier equations (e.g. $D_H^{\delta} = t_{h^{\cdot}} D_{OH_0} + t_{OH_0} D_{h^{\cdot}}$) by

the fact that the t_i are divided by $(t_i + t_j)$. This corresponds to hypothetically setting the mobility of the respective third carrier to zero.

3. Results and discussion

Fig. 1 summarizes the mass action constants, defect diffusivities, defect concentrations and the respective partial conductivities calculated from the chosen defect chemical parameters. Despite the elevated temperature the proton concentration is still perceptible (in agreement with experimental observations for acceptor-doped $BaZrO_3$ and $BaCeO_3$ [4]). The conductivity changes between predominant ionic at low p_{O_2} (protonic, changing to V_0^{δ} conductivity at highest T) and predominant electronic (by holes) at high p_{O_2} .

As demonstrated before, [10,13] the increase of the concentration of highly mobile holes leads to the transition between single-fold water chemical diffusion for low $[h^{\cdot}]$ to complex two-fold relaxation at high $[h^{\cdot}]$. For the present simulations, this is apparent in Fig. 2 where p_{O_2} (and thus $K_{ox} \sqrt{p_{O_2}}$ and $[h^{\cdot}]$) is varied while T and K_{hydrat} p_{H_2O} are kept constant. For the lowest p_{O_2} used, the relaxation of the ionic defect concentrations is determined by $D_{H_2O}^{\delta}$ (single-fold relaxation), as is the relaxation of the conductivity which is predominantly protonic for this case [27]. The splitting of the OH_0^{δ} and V_0^{δ} concentration curves becomes visible for $K_{ox} \sqrt{p_{O_2}} = 3 \cdot 10^{-5}$ and more pronounced for $K_{ox} \sqrt{p_{O_2}} = 3 \cdot 10^{-4}$. The overall reaction is still mainly H_2O incorporation which only marginally affects $[h^{\cdot}]$. Only at even higher $[h^{\cdot}]$ (high $K_{ox} \sqrt{p_{O_2}} = 3 \cdot 10^{-3}$, i.e. extremely high p_{O_2} in the case of electrolyte materials, or redox-active cathode materials exhibiting larger K_{ox}), the proton uptake at expense of holes (“hydrogenation”) according to the combination of reactions (1) and (2)



constitutes a perceptible share of the overall proton uptake, with corresponding changes between initial and final hole conductivity. For these conditions, one can recognize in the proton concentration curves an initial regime of faster H uptake (hydrogenation, change of $[OH_0^{\delta}]$ and $[h^{\cdot}]$), followed by a slower hydration process (change of $[OH_0^{\delta}]$ and $[V_0^{\delta}]$ while $[h^{\cdot}]$ perceives only smaller modification). For such conditions, the V_0^{δ} concentration curve is close to the D_{V_0} curve for short times (i.e. changing slower than according to $D_{H_2O}^{\delta}$, because the “drag” of the protons – those being compensated by h^{\cdot} – is missing), while it approaches the $D_{H_2O}^{\delta}$ curve for long times. Here the simulations show that the qualitative picture of sequential H and O diffusion is insufficient for a full description of the system, and that more than two diffusion coefficients are required. The total conductivity, predominantly electronic or containing at least a significant contribution from holes, exhibits the two-fold non-monotonic relaxation already for the lowest p_{O_2} in Fig. 2, with a minimum followed by an increase to a final value only slightly below the initial value. This characteristic overshooting behavior is found for all conditions investigated here, and in good agreement with measurements on acceptor-doped $(Ba,Sr)(Zr,Ce)O_3$ [8–12]. In hypothetical cases with a very large fraction of protons incorporated by the redox reaction (3), $\sigma_{h^{\cdot}}$ rather exhibits a step-like shape with only little overshooting. This will be discussed in a subsequent publication.

The extracted effective diffusion coefficients at 1000 K are displayed in Fig. 3 as function of p_{O_2} for intermediate and low degree of hydration, and in Fig. 4 in an Arrhenius plot. Although D_H^{eff} , D_O^{eff} as well as D_{fast} , D_{slow} both show the characteristic features of two-fold relaxation, these two sets of effective diffusion coefficients are not identical. The values of D_H^{eff} , D_O^{eff} calculated from the ionic defect concentration changes equal the value of $D_{H_2O}^{\delta}$ at low $[h^{\cdot}]$ (low $K_{ox} \sqrt{p_{O_2}}$, electrolytic regime) and then gradually approach the values of D_{OH_0} and D_{V_0} for increased $[h^{\cdot}]$ (increased decoupling). For high $[h^{\cdot}]$, an increased p_{H_2O} leads to predominant proton uptake by reaction (3). Correspondingly, the relaxation

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