COMPARISON OF PROTON MIGRATION ENERGIES OF THE PEROVSKITES BaTiO₃, BaZrO₃, AND BaCeO₃ BY QUANTUM MOLECULAR DYNAMICS

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ABSTRACT

In SOFCs, the most common separator materials are oxide ion conductors, in particular YSZ, requiring operation temperatures of more than 800°C. However, several oxides are known to incorporate significant amounts of water at low temperatures and high water partial pressures. Thus protonic defects are generated and proton conductivity exceeding that of oxygen ions can be achieved in this temperature range. In this contribution, we discuss some of the material constraints for the application of perovskite-type proton conductors as separator material in SOFC fuel cells. At this stage thermodynamic stability data may be obtained from experiments only while both experiments and quantum molecular dynamics simulations provide mobility parameters. The calculated results for the model systems ABO₃ (A=Sr, Ba; B = Zr, Ce) are in reasonable agreement with experimental single crystal data. This provides some confidence into the predictive power of the simulation technique. The calculations may also be used as a tool to support the development of new proton conducting oxides in particular with respect to applications as separator material in SOFC fuel cells.
INTRODUCTION

Oxide ion conductors such as YSZ are the most common separator materials for SOFC applications. Owing to large activation enthalpies of their conductivities and electrode polarization effects high operation temperatures are required. Perovskite-type oxides which frequently show good oxide ion conductivity at high temperatures often exhibit significant protonic conductivity exceeding that of oxide ions at low temperatures and large water partial pressures (1-3). In view of the relevance of these materials for fuel cells different groups are intensively investigating their transport properties, e.g. (3-8,11).

Due to the fairly large number of possible compounds with perovskite structures it is worthwhile to identify decisive chemical parameters controlling proton content and migration at given thermodynamic conditions. It is shown in the following section how both thermodynamical data and numerical results of quantum molecular dynamics simulations can be combined to identify possible compounds which have a large protonic charge carrier concentration and also high protonic mobility. Here quantum chemical simulations are used to assess proton mobilities (9,10). It is envisaged, however, that the determination of other relevant material properties such as hydration energies or disorder energies may also be evaluated by numerical simulations and work in this direction is currently underway. Special consideration is devoted to BaTiO₃, BaZrO₃, and BaCeO₃.

FORMATION OF PROTONIC DEFECTS IN PEROVSKITES

Protonic defects in perovskites are found as hydroxide ions on oxide ion sites, i.e. OH⁻. Protonic defects are generated in the presence of water according to

\[ H_2O + V_0^+ \leftrightarrow 2OH^- \]  \hspace{1cm} (1)

with K being the equilibrium constant for this reaction. The other defect reactions of importance are the oxygen incorporation reaction and the band band equilibrium. All other reaction equilibria are either unimportant in this context, e.g., Schottky reaction, or linear combinations of these. Together with the electroneutrality condition

\[ [OH^-] + [h^+] + 2[V_0^-] - [R'_B] = 0 \]  \hspace{1cm} (2)

with \([R'_B]\) being the acceptor dopant concentration, this set of equations determines the equilibrium defect concentrations \([OH^-], [V_0^-], [h^+],\) and \([e']\) as functions of the temperature \(T\), \(H_2O\)- and \(O_2\)- partial pressures for given acceptor dopant concentrations \([R'_B]\).
Unfortunately, numerical values of the equilibrium constants are not very well known experimentally except for SrCeO$_3$ (12), BaCeO$_3$ (3,11), BaZrO$_3$ (13), and Ba$_2$CaNb$_2$O$_9$ (14). Since the formation of protonic defects on oxygen ion vacancies by dissociative water absorption is a pure acid/base reaction not involving electronic defects, the standard hydration enthalpies are found to decrease with increasing basicity of the corresponding oxides for Sr \rightarrow Ba on the A- position and for Nb \rightarrow Zr \rightarrow Ce on the B- position. The standard hydration entropy approximately scales with the hydration enthalpy until it eventually coincides with the standard entropy of water incorporation for oxides with the lowest hydration enthalpies.

Another important parameter determining the protonic defect concentration is the apparent limiting protonic defect concentration [OH$^-$]$^*$ which is in general lower than the effective acceptor dopant concentration, e.g. (3). The cause of this phenomenon is not quite clear; however, it has been suggested that it might be due to lattice relaxation effects around defects (3) or even the result of a contamination of the samples with other species, e.g. F$^-$ (15). The limiting protonic defect concentration varies significantly for different oxides, e.g., ranging from about 1% of the effective acceptor dopant concentration in a 3% Y-doped SrZrO$_3$ (16) to about 80% in a 13% Y-doped BaCeO$_3$ (3). The experimental data seems to indicate that the limiting protonic defect concentration is lower for rather densely packed perovskites such as KTaO$_3$, CaZrO$_3$, or SrZrO$_3$ in comparison to rather loosely packed systems such as BaCeO$_3$ or Ba$_2$CaNb$_2$O$_9$ (2). Also the covalency of the chemical bonds involved may be important (2).

For fuel cell applications significant contributions of electronic charge carriers to the total conductivity ought to be avoided. The numerical value of the band band equilibrium constant, i.e., the thermal band gap, is also important for the regimes where the electronic conductivity can be neglected. In general the thermal band gap is lower than the optical one (17) with the electrons generally being associated with a M$^{4+}$ (M$^{4+}$ + e$^-$ \rightleftharpoons M$^{3+}$) and holes with oxide ions and O$^{2-}$ (O$^{2-}$ + h$^+$ \rightleftharpoons O$^-$) (2, 18). For BaCeO$_3$ the ionic conductivity domain extends over more than 20 orders of magnitude of oxygen partial pressure for temperatures lower than 800°C (11).

**MOBILITY OF PROTONIC DEFECTS IN PEROVSKITES**

In the temperature range in which the protons are the predominant ionically conducting species, see e.g. (1), the proton diffusion coefficient is found to be significantly larger than that of the oxygen ions. This suggests that the proton rather diffuses via transfer between neighbouring oxygen ions than via hydroxide ion diffusion. The diffusion mechanism is therefore assumed to be of Grotthuss-type, i.e., it involves both a proton transfer step between neighbouring oxygen ions, and, subsequently, a reorientation step of the proton and its ionic environment. For Grotthuss-type proton
conduction the dynamics of the oxygen atoms in the intimate neighbourhood of the hydroxide ion has an immediate impact on both the proton transfer- and the reorientation step. The dynamics of the oxygen atoms and, in particular, those modes which have an effect on the oxygen/oxygen separation enhance proton transfer rates by lowering the energetic barrier for proton transfer when oxygen/oxygen separations are shortened. The OH$^-$-reorientation rate is also affected by the dynamics of the oxygen atoms since reorientation is facilitated by increasing the oxygen/oxygen separations, thus lowering the hydrogen bond interaction between nearest neighbour oxygens. Both QNS (19) and quantum molecular dynamics simulations (9,10) suggest that the latter is a fast process and not rate-limiting. If we regard the proton transfer step to be rate-limiting it is rather surprising, however, that the highest proton diffusivities are observed for perovskites with large lattice constants, i.e., large structural oxygen/oxygen separations and, subsequently small hydrogen bond interaction. For BaCeO$_3$ with a mean oxygen/oxygen separation $Q_0$ of 312 pm a proton transfer barrier of 1.9 eV is estimated by quantum chemical calculations (10). The impact of the ionic dynamics on the proton migration has therefore been studied by a quantum molecular dynamics technique for the three model perovskite systems BaTiO$_3$ ($a$=399 pm), BaZrO$_3$ ($a$=419 pm), and BaCO$_3$ ($a$=440 pm). Technical details of the simulations and the simulation procedure are described in (9,10,20).

The numerical simulations for the three model materials demonstrate that the protons rotationally diffuse around an oxygen ion in the plane perpendicular to the B-O-B axis at 1200 K, see figure 1. The rotational diffusion of the proton results in rotational motion around the oxygen ion on a timescale of $10^{-12}$ s for a complete turn. The diffusion process is activated with an activation energy of the order of 0.02 - 0.03 eV. The timescale of the rotational diffusion process may be considered as the relevant timescale for the reorientation process which is found to be very similar for the three materials.

Since the simulation procedure is numerically rather complex, simulation times longer than a few $10^{-11}$ s and/or large simulation cells are currently not tractable. Experimentally, the proton transfer step is found to occur on a timescale of $10^{-9}$ s at 1200 K (3). Therefore it was not possible to observe the proton transfer step directly in the simulations. However the energetics of the proton transfer step is still accessible by numerical simulations. While the oxygen/oxygen separation coordinate $Q$ fluctuates by thermal excitations, the activation energy for proton transfer is lowered for $Q < Q_0$ and increased for $Q > Q_0$. The statistics of the thermal fluctuations of $Q$ can be detected in the pair correlation function $g_{00}(Q)$, and, by assuming Boltzmann-statistics, the fluctuations can be related to a change of the Helmholtz energy of the system by

$$\Delta A(Q) = -kT \log \left( \frac{g_{00}(Q)}{g_{00}(Q_0)} \right)$$

(3)
where \( k \) is Boltzmann's constant and \( T \) the temperature of the system. The numerical results of \( \Delta A(Q) \) for \( Q \leq Q_0 \) are shown in figure 2 for \( \text{BaTiO}_3, \text{BaZrO}_3, \) and \( \text{BaCeO}_3 \). By comparison of the three Helmholtz energy surfaces the Ce-O bond allows for the largest fluctuations of \( Q \), e.g., for a rather short oxygen-oxygen separation \( Q \) of 250 pm the numerical results yield \( \Delta A \) values of 0.46 eV for \( \text{BaTiO}_3 \), 0.82 eV for \( \text{BaZrO}_3 \), and 0.65 eV for \( \text{BaCeO}_3 \). The stiffness of the Zr-O- and Ti-O bond may be partly compensated by the shorter structural mean oxygen/oxygen separation \( Q_0 \) in comparison to that of \( \text{BaCeO}_3 \). A lower numerical value of \( \Delta A \) is found for \( \text{BaTiO}_3 \). Calculating (by a static simulation) the energy barrier \( E_b(Q) \) for proton transfer within a hydrogen bond as a function of \( Q \) using the same numerical model both the activation energy \( E_a \) for (adiabatic) proton transfer and the transition state oxygen/oxygen separation \( Q_T \) can be estimated by evaluating the minimum of \( \Delta A(Q) + E_b(Q) \), see figure 3. A significantly lower activation energy is found for \( \text{BaTiO}_3 \) (\( E_a = 0.45 \) eV) than for both \( \text{BaZrO}_3 \) (\( E_a = 0.69 \)) and \( \text{BaCeO}_3 \) (\( E_a = 0.65 \) eV). The experimental value of \( E_a \) for proton transfer is found to be 0.53 eV for both \( \text{BaCeO}_3 \) (3) and \( \text{BaZrO}_3 \) single crystals (13). The slightly shorter \( Q_T \) for \( \text{BaCeO}_3 \) in comparison to the \( Q_T \)'s of \( \text{BaTiO}_3 \) and \( \text{BaZrO}_3 \) may indicate that the rather low value of \( E_a \) is indeed due to the softness of Ce-O bond, see figure 2. Considering that the quantum mechanical nature of the proton has been ignored along with other simplifications of the numerical model the agreement of the numerical simulations and the experimental data for the activation energy is quite reasonable. However, further calculations are needed to determine the activation enthalpy at higher accuracy.

For the three model compounds \( \text{BaTiO}_3, \text{BaZrO}_3, \) and \( \text{BaCeO}_3 \) at \( T=1200 \) K, the reorientation step of proton migration is found to be fast \( (10^{-12}s) \) in comparison to the transfer step \( (10^{-9} s) \). For \( \text{ABO}_3 \) cubic perovskite structures the stiffness of the B-O bond and the mean oxygen/oxygen separation have been shown to be of significant importance for the proton diffusion process. Both a rather "soft" B-O bond and a short mean oxygen/oxygen separation decrease the activation energy for proton transfer. Despite a large mean oxygen/oxygen separation of 312 pm in \( \text{BaCeO}_3 \) the softness of the Ce-O bond allows for a rather low activation energy \( (0.53 \) eV (exp.)). A similar numerical value is found by \( \text{BaZrO}_3 \) with an increased stiffness of the Zr-O bond but shortened mean oxygen/oxygen separation \( (297 \) pm). A significantly lower activation energy has been computed for \( \text{BaTiO}_3 \) which may be attributed to a mean oxygen/oxygen separation of 285 pm with a rather similar stiffness of the Ti-O bond in comparison to the Zr-O bond. If it were possible to realize an even much shorter mean oxygen/oxygen separation, this may not increase the mobility of protonic defects since eventually hydrogen bond interaction may slow down the reorientational diffusion of the proton by increasing the activation energy for this process.
OUTLOOK

If significant amounts of protonic defects can be incorporated into BaTiO$_3$, the numerical simulations suggest that due to a high proton mobility this compound may also be a interesting proton conductor. However, it is an open question whether high protonic solubility can be achieved for this compound (21,22). The estimated activation energy for proton transfer in BaTiO$_3$ which is assumed to be rather similar to SrTiO$_3$ is in agreement with very recent experimental data by Sata et al. (23) for SrTiO$_3$ which suggests an activation energy for protons to be 0.35 eV and 0.41 eV for deuterium. Further calculations and experiments are underway to verify the simulation results and to collect more data.

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Figure 1: The traces of the oxygen atoms of two octahedra and that of a proton sampled for 10 ps are shown. The rotational diffusion of the proton generates the ring-like object around an oxygen atom in the centre ($T = 1200$ K).
Figure 2: The change of the Helmholtz energy $\Delta A$ of the oxygen lattice is shown as a function of the oxygen-oxygen separation $Q$. The mean oxygen/oxygen separation $Q_0$ is also indicated for BaTiO$_3$, BaZrO$_3$, and BaCeO$_3$. The Helmholtz energy is calculated from the O-O pair correlation data assuming Boltzmann statistics.
Figure 3a-c: $\Delta A$, $E_b$, and $E_b + \Delta A$ are plotted as a function of $Q$ for BaTiO$_3$ (a), BaZrO$_3$ (b), and BaCeO$_3$ (c). By combining $\Delta A(Q)$ and the energy barrier for proton transfer in a hydrogen bond $E_b(Q)$ the transition state energy can be estimated.