Solid State Ionics 296 (2016) 71–77

Contents lists available at ScienceDirect

Solid State Ionics

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

# Factors controlling oxygen migration barriers in perovskites

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ARTICLE INFO

*Article history:*
Received 17 June 2016
Accepted 5 September 2016
Available online xxxx

ABSTRACT

Perovskites with fast oxygen ion conduction can enable technologies like solid oxide fuel cells. One component of fast oxygen ion conduction is low oxygen migration barrier. Here we apply ab initio methods on over 40 perovskites to produce a database of oxygen migration barriers ranging from 0.2 to 1.6 eV. Mining the database revealed that systems with low barriers also have low metal-oxygen bond strength, as measured by oxygen vacancy formation energy and oxygen p-band center energy. These correlations provide a powerful descriptor for the development of new oxygen ion conductors and may explain the poor stability of some of the best oxygen conducting perovskites under reducing conditions. Other commonly-cited measures of space, volume, or structure ideality showed only weak correlation with migration barrier. The lowest migration barriers (<0.5 eV) belong to perovskites with non-transition-metal B-site cations, and may require vacancy-creation strategies that involve no dopants or low-association dopants for optimal performance.

## 1. Introduction

Fast oxygen migration is a critical property for technologies that involve oxygen transport and exchange with the environment [1], including solid oxide fuel cells (SOFCs), gas-separation membranes, oxygen sensors, chemical looping devices, and memristors. Many of the best oxygen ion conductors are perovskites, and searching this crystal class for fast, stable, and application-compatible oxygen conductors has been an active area of research for decades [2,3].

Optimized vacancy content and low oxygen migration barrier are typically the dominant factors leading to fast vacancy-mediated oxygen transport in perovskites. This paper assumes that doping strategies can optimize vacancy content [1,4] and instead focuses solely on oxygen migration barrier. Sections 3 and 4 discuss briefly where information about vacancy concentration and dopant association effects would be valuable additional knowledge.

As an example of the scale of the effect of oxygen migration barrier on oxygen transport, for a hypothetical material at 1073 K (800 °C), a decrease of 0.4 eV in migration barrier energy corresponds to a 100 times increase in oxygen ion conductivity, potentially allowing a 100 times increase in the thickness of an SOFC electrolyte (see Supporting Information (SI), Section S2.1). Lowering the migration barrier by 0.6 eV at the same temperature could reduce the cathode area specific resistance (ASR) by 100 times (see SI, Section S2.2). These effects could enable significantly more stable, lower-temperature, cheaper SOFCs.

Descriptors for oxygen migration barrier could help identify low barrier materials prior to synthesis efforts. Previously-proposed descriptors for oxygen migration in perovskites include Kilner critical radius [5–8], Goldschmidt tolerance factor [5], volumetric factors [5], crystal structure ideality [9], oxygen vacancy formation energy [10,11], and metal-oxygen bond strength (fluorites [12]), both average [5] and related to vacancy trapping (summarized in Ref. [13]). This study focuses solely on perovskites, considers over 40 A-site and B-site combinations, uses oxygen migration barrier data from a single source and method, and evaluates dozens of descriptors at once, looking for a simple functional relationship between oxygen migration barrier and each proposed descriptor.

## 2. Methods

### 2.1. Choosing and evaluating descriptors

Because the descriptors are meant to be predictive, this study focuses on descriptors that do not require prior knowledge about the activated transition state. That is, we focus on descriptors from the bulk or initial defected state, and leave out descriptors which must be obtained from a transition-state calculation itself, such as transition state geometry [7] or actual path length.

Evaluating a descriptor consists of looking for the presence of a simple function, though not necessarily linear, between oxygen migration barrier and that descriptor. While combining descriptors might produce better correlations, evaluating descriptors individually provides a clear picture of the controlling physics without the risk of over-fitting.

Although fewer than two dozen descriptors appear in this study's main text and SI Section 3, we actually looked for correlation with

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http://dx.doi.org/10.1016/j.ssi.2016.09.007

hundreds of possible descriptors, of which only the most well-known, often-suggested, best-performing, and/or representative of key physics were included. These descriptors include those we have invented, those that have been proposed as important when comparing across crystal structures, and those that are commonly cited as being important within the perovskite crystal structure [5,9].

Most of the descriptors that were discarded were permutations of a single descriptor type, for example, the distance between a specific B-site cation and its neighboring oxygen in the positive z direction; in the negative z-direction; and so on.

### *2.2. Choosing systems*

Compounds were generated and screened in the following order:

- $La^{3+}$[3d transition metal, excluding Cu and Zn, plus Ga]$^{3+}O_3$ due to the prevalence of 3d transition metals and Ga in known and studied devices.
- [Pr, Y]$^{3+}$[3d transition metal, excluding Cu and Zn, plus Ga]$^{3+}O^3$: the chemical similarity but different radii of $Pr^{3+}$ and $Y^{3+}$ compared to each other and to $La^{3+}$ allows A-site cation size effects to become evident.
- $La^{3+}$[Al, In, Tl]$^{3+}O_3$ due to the B-site similarity with fast conductors with B-sites Sc and Ga.

Assorted other compounds were partially or fully evaluated. Some were chosen because of A-site similarity to $La^{3+}$ and guidance from observed correlations that suggested low barrier materials, e.g., $SmGaO_3$. Others were chosen for 4d or 5d transition metal B-site cations similar to those previously studied, e.g. $LaRuO_3$. Finally, a few $A^{2+}B^{4+}O_3$ systems were evaluated to check the behavior of the correlations in the $A^{2+}B^{4+}O_3$ system.

### *2.3. 2.2. Computational methods*

Vacancy-mediated oxygen diffusion in these systems was modeled by a single hop from oxygen position o29 to o30, which should be taken to be sampling possible hopping barriers that range over 0.4 eV based on calculations of all hops within three supercells (see Ref. [14] electronic supplementary information (ESI) Fig. S2.1 for atomic positions, and Ref. [14] ESI Section S8 and this work's SI Section S4 for the range of hops). The exception was the barrier for $LaRuO_3$, where we believe specific geometry in that hop forced it to exceed the range of reasonable migration barrier values for the system as a whole; therefore, the o29 to o30 migration barrier (1.847 eV) was substituted out and an in-plane migration barrier (oxygen position o31 to o30) was used instead (1.428 eV).

Climbing nudged-elastic-band calculations [15,16] were automated using the MAterials Simulation Toolkit (MAST) [17,18] and performed using the Vienna Ab-initio Simulation Package (VASP) [19] on a 2x2x2 formula unit supercell where internal relaxation allowed octahedral tilting [20,21], and with settings and approaches, including pseudopotentials picked for accuracy, as described previously [14].

GGA + U [22–25] calculations were not used in this study due to the uncertainty in selecting U values [26–28], the computational expense of performing such selection for a wide variety of cations, and convergence issues in GGA + U calculations, particularly in Co and Ni. Due to the cancellation of errors between initial and activated states in migration barrier calculations, and due to the absence of any redox occurring in our models, we expect GGA calculations to be fairly accurate for the key values in this paper. The decision to use GGA methods has also been made in other perovskite migration barrier studies [7,11].

Because mobile oxygen vacancies in a typical host perovskite will be charge-compensated [1,29,30], all migration barriers discussed in the main text use a charge-compensated oxygen vacancy, where the electrons donated by the vacancy are removed from the system either through explicit electron-removal or through explicit Strontium doping on the A-site, as described previously [14]. (See the SI for more discussion.) Table A.1 also includes non-charge-compensated data, in which the electrons donated from the vacancy are left in the system, often to reduce a nearby B-site cation.

Vacancy formation energies were calculated as in Lee et al. [31] Where the oxygen vacancy was charge-compensated by explicit electron removal, an extra term was applied to the vacancy formation energy in order to account for the removal of those electrons to the electron reservoir of the bulk, as in Section 3.1 of Lin et al. [32] The potential alignment correction in such cases used, for each species, the mean for all atoms of that species in the supercell. These vacancy formation energies are intended for use as descriptors rather than as energy values that can be compared to experiments, and they may not be accurate for the latter. In particular, no finite-size scaling correction was applied, the errors in the GGA approximations may affect the absolute value of each vacancy formation energy [31], and the given oxygen partial pressure and temperature, while possible in an SOFC, may not be appropriate for all systems. Furthermore, the values do not take into account the full defect chemistry model of the perovskites and therefore are in most cases not representative of experimental vacancy formation energies. For the purposes of this study, the important value is the relative difference in oxygen vacancy formation energy between different systems.

Radii for use in descriptors were picked from the Shannon crystal radii [11,33] based on an estimate of high-spin and low-spin state from undefected bulk magnetic moment calculations, using 6-coordination for $O^{2-}$, $B^{3+}$, and $B^{4+}$, and 12-coordination, or 9-coordination if 12-coordination was not available, for $A^{2+}$ and $A^{3+}$. For doped systems, the A-site radius was the weighted average of the radii for the A-site occupations.

## 3. Results

This section compares the calculated barriers with experiment where applicable, then plots migration barrier versus Mendeleev number to show the scale of the results, and then plots migration barrier versus the two best-performing descriptors, oxygen vacancy formation energy and oxygen p-band center energy. SI Section 3 contains the results for the other descriptors.

Each oxygen hop followed a curved migration path around a B-site cation [13,34]. Calculating all oxygen hops for three systems indicates that each hop should be considered to have been sampled from an approximately uniformly distributed range of about 0.4 eV (see Ref. [14] ESI Section S8, and SI for this paper, Fig. S4.1 and Fig. S4.2). Dopant positions may also contribute to a spread of barriers, with a spread estimated by select studies to be about 0.3 eV (see Ref. [14], ESI Section S7). Supercell size is estimated to have a non-systematic effect of approximately 0.1 eV (see Table A.1).

Fig. 1 compares our calculations to migration barriers from experimental data, whose details are given in SI Table S1.1. (For a comparison with calculated rather than experimental literature data, see SI Fig. S1.2.) For each computed value there is a comparable experimental value within the range bar of the calculation. However, the large spread in the experimental values and the uncertainty in the calculations makes any quantitative comparison very difficult. We note that many of the non-transition-metal B-site cations have predicted values lower than any of the experiments, and some of our predictions for this class of compounds (discussed in Section 4.3) also have very low values. Although these values are within the range bars of the experiments, they may also be lower because of dopant effects. Where the calculations were performed on undoped systems, with the vacancy compensated as though it had been created with dopants, which would be a requirement for these non-transition-metal B-site systems [3,4], the