

**Enhanced anisotropic ionic diffusion in layered electrolyte structures from density functional theory**

J. A. Hirschfeld\*

*Forschungszentrum Jülich, IAS, 52425 Jülich, Germany*

H. Lustfeld

*Forschungszentrum Jülich, PGI, 52425 Jülich, Germany*

(Received 26 March 2013; revised manuscript received 19 November 2013; published 29 January 2014)

Electrolytes with high ionic diffusivity at temperatures distinctively lower than the presently used ones are the prerequisite for the success of, e.g., solid oxide fuel cells. We have found a promising structure having an asymmetric but superior ionic mobility in the direction of the oxygen-ion current. Using a layering of zirconium and yttrium in the fluorite structure of zirconia, a high vacancy concentration and a low migration barrier in two dimensions are obtained, while the mobility in the third direction is basically sacrificed. According to our density functional theory calculations an electrolyte made of this structure could operate at a temperature reduced by  $\approx 200^\circ\text{C}$ . Thus a window to a different class of electrolytes has been flung open. In our structure the price paid is a more complicated manufacturing method.

DOI: [10.1103/PhysRevB.89.014305](https://doi.org/10.1103/PhysRevB.89.014305)

PACS number(s): 82.45.Gj, 31.15.E-, 82.20.Pm, 82.45.Xy

**I. INTRODUCTION**

Among fuel cells, the high-temperature solid oxide fuel cell (SOFC) is a very promising candidate due to its high power density and wide variety of possible fuel types. At present the main problem of the SOFC is the required high temperature. The standard electrolyte being used, yttrium-stabilized zirconia (YSZ), has insufficient ionic diffusivity below  $700^\circ\text{C}$  for SOFC application and progress was mainly achieved by fabricating extremely thin [1] electrolyte layers of  $10\ \mu\text{m}$  and less. To construct a mechanically stable and gas-tight layer of that thickness is a challenging task, however. It is obvious that decreasing the thickness of the electrolyte further will reach its limits in the not too distant future. This shows how important it is to look for alternative approaches to overcome the problem of the high operating temperatures in SOFCs.

In our approach we allow asymmetric ionic diffusivity of the electrolyte. In fact, isotropic diffusivity is not necessary since the ionic current mainly passes between the electrodes in the shortest way and only marginal currents are perpendicular to this direction. Therefore, the permission of anisotropic diffusivity *opens the possibility of enhancing, in particular, the ionic current in the main direction.*

An electrolyte material with those properties and, therefore, being appropriate for low-temperature SOFC applications is proposed here. This electrolyte is an example for a new class of anisotropic electrolyte materials with superior anisotropic diffusivity. The improvement arises from a strain effect, as in typical sandwiched structures (e.g., Refs. [2–5]), but also from two other effects, which are discussed below. *Ab initio* molecular dynamics calculations demonstrate that the activation energy of the oxygen diffusion in the proposed structure is clearly smaller than the ones in the state of the art electrolytes.

The proposed structure has alternating layers of zirconium and yttrium in the fluorite structure, exhibiting a high charge

carrier (oxygen vacancy) concentration of 12.5% and strongly reduced migration barriers in two dimensions. The low activation energy makes applications of this material in SOFCs at temperatures below  $500^\circ\text{C}$  possible. The price paid for gaining the improved performance is a complex synthesizing procedure.

**II. THE LAYERED STRUCTURE**

A systematic search for anisotropic structures having a favorable diffusivity in at least one direction seems reasonable. A layered cation structure can lead to such anisotropic behavior. Of course, layers are possible in many crystallographic directions [6]. However, criteria can be given as a guide for the search of layered structures with enhanced anisotropic diffusivity. These criteria excluding most of these structures are the following:

(1) Increase of the charge carrier concentration in the system without having to overcome very high migration barriers when passing yttrium ions. This effect requires a layering of the cations with any reasonable thickness.

(2) Obtaining oxygen lattice sites which have exactly one yttrium ion as nearest neighbor but at the same time passing only through zirconium ions in the migration pathway. This favorable arrangement requires a clear alternating layering of the cations.

(3) Increase of the lattice constant to introduce expansive strain, which decreases the migration barrier for oxygen ions. (This effect is desirable in any case.)

One interesting layered structure has been found to fulfill these criteria and have a reduced migration barrier in the direction of interest (cf. Fig. 1). In the proposed structure every second cation layer in the (111) plane is a pure yttrium layer and every other is a pure zirconium layer. The direction of oxygen-ion motion takes place in either of these two directions. The stoichiometry of this structure is  $\text{Zr}_2\text{Y}_2\text{O}_7$ , which exhibits a vacancy concentration of 12.5%. Note that in the standard YSZ material with 8 mol%  $\text{Y}_2\text{O}_3$  (8YSZ) the vacancy concentration is only 4%.

\*j.hirschfeld@fz-juelich.de

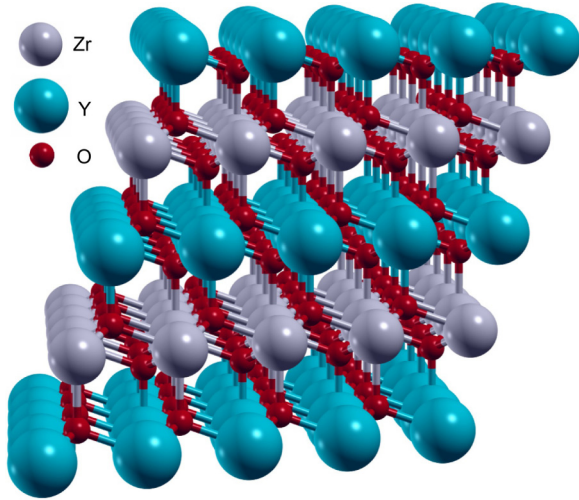


FIG. 1. (Color online) Layered structure of the  $Y_2Zr_2O_7$  compound shown in a face-centered cubic (fcc) supercell. For better visibility the oxygen vacancies are not shown [7].

The high yttrium content leads to an increased concentration of vacancies in the system. However, when oxygen passes by a yttrium ion, the migration barrier is nearly twice the one when passing only through zirconium ions [8]. This effectively limits the yttria concentration to 8 mol% in isotropic YSZ, but due to the special arrangement of the cations in this layered structure, no yttrium-induced high barriers are hindering the migration of oxygen ions between the electrodes (criterion 1). Without interactions of the vacancies, the diffusivity would increase linearly with the vacancy concentration. However, high vacancy concentrations give rise to vacancy clustering and repulsion, hindering the oxygen motion. It is shown that no stable vacancy pairs are formed in this construction, and therefore the vacancy-vacancy interaction will have a less serious impact on the oxygen motion.

Pornpasertsuk *et al.* [8] already reported a decreased migration barrier, when the initial and final lattice site of an oxygen jump have one yttrium ion as nearest neighbor (1NN) (criterion 2). The 1NN oxygen sites around yttrium ions are less favorable for vacancies, which reduces the relevant barrier in the migration pathway along the layering. Due to the high content of large yttrium ions, the lattice is expanded by 2% in comparison to 8YSZ. This is the origin of criterion 3. While this can be obtained just by increasing the yttrium content independently of the dopant distribution the conditions of criterion 1 and criterion 2 require a clear layering of the cations. Criterion 1 just requires the cations to be ordered in layers, independently of the exact stacking order. Lastly, criterion 2 can only be achieved in a structure with alternating monolayers in the (111) plane. In the fluorite structure only this configuration exhibits oxygen pathways without passing yttrium ions and with nearest neighbor yttrium ions at each oxygen lattice site.

Since the vacancies disfavor 1NN positions to yttrium ions, the lattice sites with three yttrium ions as INN ( $Zr_1|Y_3$ ) are avoided by the vacancies. This leads to a motion along zigzag paths in the zirconium layers, which is effectively limited to two dimensions. In the third geometric direction, the barriers

are very high due to the yttrium layers, making a motion into this direction basically impossible.

To represent the  $Zr_2Y_2O_7$  compound in a crystallographic cell, at least four fcc fluorite unit cells are necessary.

Our *ab initio* calculations are done in a  $4 \times 4 \times 4$  fcc supercell ( $32 Zr^{4+}$ ,  $32 Y^{3+}$ ,  $112 O^{2-}$ ,  $16 V_o^{2+}$ ).

Since the proposed structure is highly ordered, it cannot be expected to form spontaneously. Calculations concerning the stability of the cation lattice have been executed, showing that the proposed structure is similar in energy to the pyrochlore structure. Furthermore, Xiao *et al.* [9] found defect-fluorite structures being more stable than the pyrochlore structure. This shows that the proposed structure is not the ground state of the  $Zr_2Y_2O_7$  compound. However, tentative calculations indicate high migration barriers for cations in this structure ( $\approx 9$  eV without cation vacancy and  $\approx 2.5$  eV for cation-vacancy diffusion), which reflects the reported small cation diffusion at SOFC operation temperatures in YSZ [10].

It has to be considered that while for the oxygen ion movement the macroscopic scale is relevant, the diffusion of zirconium and yttrium only needs to overcome rather small distances to hinder the oxygen ion current. However, if no cation vacancy is present, no diffusion of zirconium or yttrium ions are possible due to the extremely high barrier of  $\approx 9$  eV. This means that during the fabrication process a  $\approx 20\%$  surplus of Y ions in the Zr layers is tolerable. From two-dimensional percolation theory [11] it is clear that the infinite Y cluster in a Zr layer will occur at about 50% Y in the Zr layer, but the ionic conductivity will break down earlier, since each Y ion prevents good conductivity in its neighborhood.

The case of cation vacancies is more intricate, since the migration barrier of about 2.5 eV for a jump of a cation into the vacancy is not high enough to exclude cation migration affecting oxygen diffusion. At an operation temperature of  $500^\circ C$  and with a typical vibrational coefficient of  $\nu_0 = 5$  THz for oxygen, we get the jump rate

$$\nu = \sqrt{\frac{m_o}{m_{Zr}}} \nu_0 e^{-2.5eV \cdot \beta} \approx 1 \times 10^{-4} \text{ Hz.} \quad (1)$$

The movement of zirconium or yttrium ions in their layered planes does not affect the oxygen-ion movement at all, but jumps from layered planes into neighboring layered planes can multiply the misplaced cations. Therefore, the rate of the relevant jumps is  $3 \times 10^{-5}$  Hz, meaning that after 100 days of continuous operation at  $500^\circ C$  a single vacancy may have produced about 250 relevant misplaced cations. From this we conclude that under these conditions the vacancy concentration must be less than 0.1%. Therefore, the result is that vacancies of cations have to be avoided in our structure. One possible preventive measure could be a small surplus of cations during the fabrication process.

However, this estimation shows that also for larger concentrations of cation vacancies, the layered structure is metastable to a degree, which should at least be sufficient for experimental verification of its properties. Technologically sophisticated methods like molecular beam epitaxy (MBE) [12] are available to synthesize the proposed structure layer by layer for measurements of its properties.

We want to point out that this is only one example of this type of anisotropic structure. A related example is the  $Y_2Zr_4O_{11}$  structure found by Predith *et al.* [13] having incomplete yttrium layers in the (111) plane of the fluorite structure. They found this structure to be the ground state of the  $Y_2Zr_4O_{11}$  compound being stable with respect to the monoclinic and the  $\delta$  phase. However, nothing is known about the ionic motion in this structure.

### III. VACANCY-VACANCY INTERACTIONS

The density functional theory (DFT) computations presented here are all executed in the VASP code using the projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) function. The energy cutoff was 600 eV and only the  $\gamma$  point has been used for  $k$ -point sampling. Due to the smaller electron number of  $Y^{3+}$  in comparison to  $Zr^{4+}$  the vacancies in YSZ are twice positively charged ( $V_o^{2+}$ ). For some calculations the number of vacancies was reduced and the total number of electrons in the system has been increased accordingly to obtain vacancies of the same charge state.

In a system with only two vacancies correlations between vacancies have been checked. It turned out that the vacancies repel each other in a way that [100], [110], and [111] vacancy-pairs are unstable (cf. Fig. 2). By comparing the energies of the smallest stable vacancy separation with larger separations, we observed a further decrease of energy with increasing separation, indicating repulsion of vacancies over bigger distances.

While in this system the vacancies cannot keep nearby lattice sites, such behavior is not observed in 8YSZ. In contrast, it is known that, especially at high vacancy concentrations, the

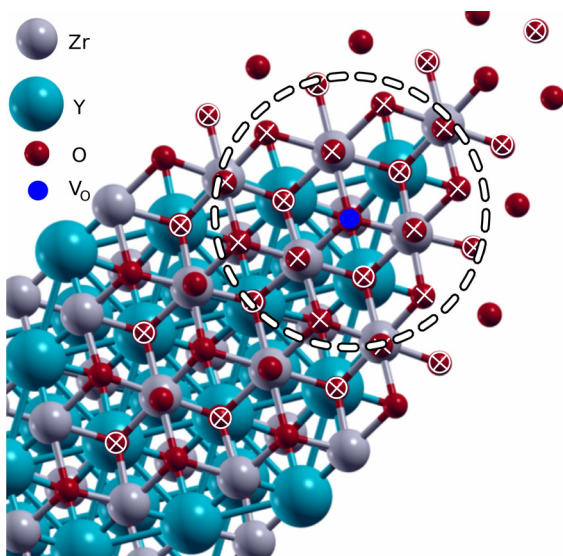


FIG. 2. (Color online) Local vacancy-vacancy correlation in one layer with two vacancies ( $V_o^{2+}$ ). When a vacancy is located at the blue (gray) spot (center of the circle), there can be no second vacancy on the surrounding oxygen sites, indicated by the circle. The simple crosses indicate unstable positions for a second vacancy due to the V-V repulsion and the circled crosses indicate  $Zr_1|Y_3$  lattice sites being generally unstable for vacancies in this system [7].

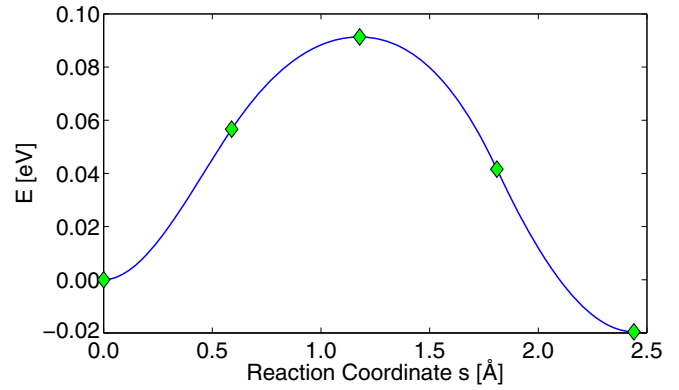


FIG. 3. (Color online) MEP of a jump in the layered structure. The ending point has the larger vacancy-vacancy distance.

vacancies will cluster and form stable pairs. In no calculation of the proposed structure has such clustering been observed.

To figure out whether the absence of vacancy clustering is a numerical artifact or in fact physical, the vacancy pairs have been calculated in pure zirconia ( $3 \times 3 \times 3$  cell with a  $3 \times 3 \times 3$   $k$ -point mesh and also with an adapted number of electrons to obtain YSZ-like  $V_o^{2+}$ ). In these simulations it turns out that the [111] pair is  $\Delta E_{[100][111]} = 0.5$  eV more stable than a [100] pair, but the [110] pair is  $\Delta E_{[110][111]} = -0.43$  eV more stable. With the ordering  $E_{[100]} > E_{[111]} > E_{[110]}$ , there is clearly a stable vacancy pairing along the [110] direction possible in pure zirconia. Although in literature typically the [111] vacancy pair is denoted as the most stable one (e.g., Ref. [14]), there are reports that in some cases the [110] pair becomes more stable. Bredow [15] assumed that this happens when the cubic phase is not fully stabilized, which is consistent with the here-investigated pure zirconia system. This shows that the formation of vacancy pairs as described in literature is reproduced in the pure zirconia system and the absence of this clustering effect is due to the specific configuration of our structure, not due to numerics.

Using again the layered  $4 \times 4 \times 4$  cell with only two vacancies, the migration barrier has been computed. In Fig. 3 the minimum energy pathway (MEP) between two stable positions is shown determined by the nudged elastic band (NEB) [16] method. Due to the second vacancy, the jump is not symmetric. Both the forward and the backward jump have a barrier of about  $\Delta E \approx 0.1$  eV. This is smaller by a factor of six than the literature values corresponding to a randomly displaced oxygen sublattice [17] of 8YSZ. However, this barrier is determined in an idealized case, in which only two vacancies are present in the system and are sufficiently far away from each other. It will become clear that in the case of small barriers it is the correlation of vacancies which mainly determines the activation energy of the diffusion process. Hence, the potential surface in the case of 16 vacancies (12.5%) in the computational cell is highly complicated and cannot fully be grasped by determining migration barriers alone, but the dynamics in the whole system needs to be accounted for.

To get an idea of how the barriers in the system with all vacancies look, the 16 vacancies have been distributed randomly throughout the two zirconium layers of the supercell. Except for choosing only  $Zr_3|Y_1$  oxygen sites, no further rules

have been applied in the distribution. After setting up the cell, the ions have been relaxed to the next local minimum. Subsequently, the MEP for the motion of one vacancy over five lattice sites has been computed. From these calculations we conclude first that vacancies can keep closer than observed in the two-vacancy case. In fact, it is possible for two vacancies to be on directly neighboring lattice sites, if further vacancies surrounding their positions prevent their departure. It has to be pointed out that this is a special case and the computations do not allow conclusions about how stable this configuration is and how likely it is for this configuration to arise in a dynamical system. Second, the observed barriers in this specific configuration vary between 0.1 and 2 eV, showing the effect of the vacancy repulsion.

Since these high barriers do not result from vacancy pair bonds but from vacancy repulsion, this means that as soon as the vacancies inducing such correlation effects move away, the barrier in this direction will drop.

From the PBE-DFT computed density of states of the layered structure including all 12.5% vacancies it can be seen that it has a wide band gap of  $E_{\text{Gap}} = 3.5$  eV, being larger than the one computed in pure zirconia ( $E_{\text{Gap}} = 3.1$  eV).

#### IV. MOLECULAR DYNAMICS

As mentioned before, the correlation effects in the layered structure due to the high number of vacancies leads to a complexity, which cannot be represented by simple interactions as, e.g., the Buckingham potential [18]. To determine the diffusion in the layered structure in spite of the complex interactions, *ab initio* molecular dynamics as implemented in VASP are employed. From the computational demand of this framework follows a rather limited size of the calculations both in spatial and temporal extent. Thus, this approach clearly has the caveat that the statistics are not as good as in classical pair-potential MD. This is especially the case at low temperatures, when the dynamics is low and the number of jumps is small.

The MD computations are executed in the  $4 \times 4 \times 4$  supercell of the layered structure including plane waves up to an energy cutoff of 300 eV by sampling the Brillouine zone using only the  $\gamma$  point. For the description of the thermodynamics, a canonical ensemble is considered, and the temperature is controlled by a Nosé thermostat. The time  $t$  dependent mean squared displacement  $\langle r^2 \rangle$  of the oxygen ions is connected to the activation energy  $E_A$  of the diffusion process by the Einstein relation

$$\langle r^2 \rangle(t) = D_0 2dt e^{-E_A/k_B T} \quad (2)$$

with the dimensionality of the diffusion process  $d$ , the temperature  $T$ , the Boltzmann constant  $k_B$ , and the diffusivity at infinite temperature  $D_0$ . The diffusion process in our structure is two dimensional, thus  $d = 2$ . Due to the periodic boundary conditions, the oxygen ions can leave the cell and enter it again on the corresponding position on the other side of the cell. This has explicitly been accounted for when computing the mean squared displacement by considering the motion of such ions as smooth trajectories out of the computational cell.

A configuration with equally distributed vacancies is used as a starting point for a series of MD runs with different temperatures to determine the diffusivity and by that the

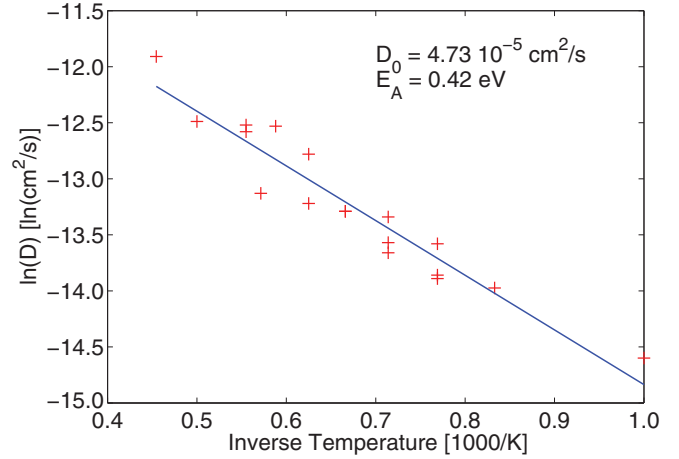


FIG. 4. (Color online) Arrhenius plot of the MD results. The crosses are the averaged diffusivities from each MD calculation and the line is the linear fit of the data points.

activation energy of the layered structure. Statistical data have been collected over up to 40 ps for each starting temperature.  $E_A$  and  $D_0$  are subsequently obtained by Eq. (2).

In Fig. 4 the MD results are shown. The effective migration barrier is  $E_A = 0.42$  eV and thus higher than the migration barrier determined with negligible vacancy interactions  $\Delta E = 0.1$  eV, but it is much lower than the high barriers of about  $\Delta E \approx 2$  eV observed in the static barrier computations with all vacancies. In fact, obtaining an activation energy of about 0.4 eV is a very good result, showing how the intelligent positioning of cations in the system leads to a reduction in activation energy. In experiments the value for 8YSZ is typically about 0.8 to 1 eV [19]. In simulations, the obtained migration barriers are usually lower than the experimental ones. Devanathan *et al.* [19] gave a summary of some numerically determined migration barriers in 8YSZ from different sources. Typical values are about 0.6 to 0.8 eV. Also in comparison to gadolinium-doped ceria (GCO), with an experimental activation energy of about 0.65 to 0.75 eV [20], and LSGM, with an experimental activation energy of about 0.7 to 1.0 eV [21], the proposed structure seems to be advantageous.

This shows that the activation energy of the oxygen diffusion in the layered structure is significantly lower than in common electrolyte materials, leading to higher performances especially at lower temperatures. Based on the activation energies in standard 8YSZ and in our layered structure, one can expect performance in the layered structure at an operating temperature of  $\approx 500$  °C to be comparable to the performance in 8YSZ at  $\approx 700$  °C.

#### V. CONCLUSIONS

Electrolytes require high ionic mobility. However, in the YSZ electrolyte, mostly used in the SOFC, the ionic mobility becomes insufficient below  $\approx 700$  °C. This serious deficiency is one of the reasons preventing a breakthrough of the SOFC as a widely used energy converter.

In the present paper we exploit the fact that the ionic mobility needs not be isotropic. Only the mobility in the direction of the oxygen-ion current is essential. Therefore, an

intelligent configuration of YSZ has been proposed, harnessing the strain-dependent barrier, the avoidance of yttrium-induced high barriers along the pathway, and the reduction of the relevant migration barrier by neighboring yttrium dopants. In this way an increased diffusivity of the compound has been achieved in two dimensions. According to our DFT computations, the activation energy of this diffusion process is only  $E_A = 0.42$  eV, resulting in superior ionic mobility and allowing a substantially lower operating temperature of  $\approx 500^\circ\text{C}$ . The mobility in the third dimension has been

sacrificed. The price to be paid for the superior mobility in the relevant directions is a nontrivial layered structure that probably needs more complicated synthesizing methods, such as molecular beam epitaxy.

#### ACKNOWLEDGMENT

The calculations have been performed on the supercomputer JUROPA at the Jülich Supercomputing Center with a grant from the FZ-Jülich.

- 
- [1] R. Hansch, M. R. R. Chowdhury, and N. H. Menzler, *Ceram. Int.* **35**, 803 (2009).
- [2] K. Suzuki, M. Kubo, Y. Oumi, R. Miura, H. Takaba, A. Fahmi, A. Chatterjee, K. Teraishi, and A. Miyamoto, *Appl. Phys. Lett.* **73**, 1502 (1998).
- [3] C. Korte, A. Peters, J. Janek, D. Hesse, and N. Zakharov, *Phys. Chem. Chem. Phys.* **10**, 4623 (2008).
- [4] N. Schichtel, C. Korte, D. Hesse, and J. Janek, *Phys. Chem. Chem. Phys.* **11**, 3043 (2009).
- [5] T. J. Pennycook, M. J. Beck, K. Varga, M. Varela, S. J. Pennycook, and S. T. Pantelides, *Phys. Rev. Lett.* **104**, 115901 (2010).
- [6] E. Lee, F. B. Prinz, and W. Cai, *Phys. Rev. B* **83**, 052301 (2011).
- [7] This picture, or part of this picture, has been done with the atomic viewer XCrysDen: A. Kokalj, *Comp. Mater. Sci.* **28**, 155 (2003). Code is available from <http://www.xcrysden.org/>
- [8] R. Pornpasertsuk, P. Ramanarayanan, C. B. Musgrave, and F. B. Prinz, *J. Appl. Phys.* **98**, 103513 (2005).
- [9] H. Y. Xiao, F. Gao, and W. J. Weber, *Phys. Rev. B* **80**, 212102 (2009).
- [10] R. Krishnamurthy, D. J. Srolovitz, K. N. Kudin, and R. Car, *J. Am. Ceram. Soc.* **88**, 2143 (2005).
- [11] D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, rev. 2nd ed. (Taylor & Francis, Basingstoke Hants, 1991).
- [12] J. N. Eckstein and I. Bozovic, *Annu. Rev. Mater. Sci.* **25**, 679 (1995).
- [13] A. Predith, G. Ceder, C. Wolverton, K. Persson, and T. Mueller, *Phys. Rev. B* **77**, 144104 (2008).
- [14] A. Bogicevic and C. Wolverton, *Phys. Rev. B* **67**, 024106 (2003).
- [15] T. Bredow, *Phys. Rev. B* **75**, 144102 (2007).
- [16] D. Sheppard, R. Terrell, and G. Henkelman, *J. Chem. Phys.* **128**, 134106 (2008).
- [17] R. Krishnamurthy, Y.-G. Yoon, D. J. Srolovitz, and R. Car, *J. Am. Ceram. Soc.* **87**, 1821 (2005).
- [18] G. V. Lewis and C. R. A. Catlow, *J. Phys. C: Solid State Phys.* **18**, 1149 (1985).
- [19] R. Devanathan, W. J. Weber, S. C. Singhal, and J. D. Gale, *Solid State Ionics* **177**, 1251 (2006).
- [20] W. Lai and S. M. Haile, *J. Am. Ceram. Soc.* **88**, 2979 (2005).
- [21] J. Wolfenstine, P. Huang, and A. Petric, in *Solid Oxide Fuel Cells VI*, edited by S. C. Singhal and M. Dokiya (Electrochemical Society, Pennington, 1999).