A critical assessment of interatomic potentials for ceria with application to its elastic properties

Haixuan Xu (徐海譞), Rakesh K. Behera, Yanli Wang (王艳丽) [1], Fereshteh Ebrahimi, Susan B. Sinnott, Eric D. Wachsman, Simon R. Phillpot *

Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, United States

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ABSTRACT

We critically assess the materials fidelity of six interatomic potentials for ceria, based on predicted lattice constants, thermal expansion, chemical expansion, dielectric properties, oxygen migration energy and mechanical properties. While, no potential can reproduce all fundamental properties, the Gotte (2007) and Grimes potentials display the combination of highest fidelity with the widest range of applicability. The simulations show that sub-stoichiometry leads to a significant softening of the elastic constant, which is consistent with the experimental results. Similar results are observed for doped-ceria systems.

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1. Introduction

The industry standard electrolyte for solid-oxide fuel cells (SOFCs) is yttria-stabilized zirconia (YSZ) [1,2]. However, it suffers from the significant drawback that high temperature operation is required in order to produce oxygen ion mobility fast enough to support a significant current. Ceria-based materials [2–4] are being considered as a replacement for YSZ because the much higher conductivity of doped ceria compared to YSZ enables efficient operation at much lower temperatures.

A key issue for all putative electrolytes is mechanical stability. Recently some of us have characterized the elastic properties of both pure ceria and gadolinia doped ceria (GDC) [5] and found that the materials show significant elastic softening as the oxygen partial pressure decreased, i.e., as ceria becomes more sub-stoichiometric and GDC contains more oxygen vacancies. These results were interpreted using an analytic defect-equilibrium model [6].

In this paper, we address the issue of the mechanical properties of ceria and doped ceria using atomic-level simulation methods. Atomic-level simulation, molecular dynamics (MD) in particular, neatly complements the experimental and analytical approaches in that we can specify the composition of a system with atomic precision, and characterize the structure at the atomic level. The quantitative reliability of an MD simulation is determined by the materials fidelity of the interatomic potential used. There are a number of interatomic potentials for ceria in the literature. We therefore perform a survey of fundamental properties predicted using these potentials, which allows us to identify the potential(s) most suitable for the simulation of the effects of temperature and chemistry on the elastic properties. Using the most suitable potentials, our results are consistent with the experimental results in that the simulations show that sub-stoichiometry leads to a significant softening of the elastic constants. The effects of temperature and sub-stoichiometry on mechanical properties are investigated. We also find a similar degree of elastic softening in doped-ceria systems.

2. Simulation methodology

The lattice-statics and MD simulations carried out here use conventional simulation approaches. The overall ionic interactions are described as the sum of long-range and short-range contributions. The long-range interactions between different ionic species are described by a simple Coulombic interaction:

$$E_{LR}\left(r_{ij}\right) = \frac{1}{2}\sum_{i=1}^{N}\left\{\sum_{j\neq i}\frac{q_i q_j}{r_{ij}}\right\} \tag{1}$$

where N is the total number of ions in the system, q_i and q_j are the charge on ion i and j respectively, r_{ij} is the distance between ion i and j.

* Corresponding author. 162 Rhines Hall, MSE, University of Florida, Gainesville, FL –32611-6400, United States. Tel.: +1 352 846 3782; fax: +1 352 846 3355.
E-mail address: sphil@mse.ufl.edu (S.R. Phillpot).
[1] Current address: Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States.

The summations are carried out using the Ewald method. All of the potentials use the formal ionic charge for q (i.e., $q_{Ce} = +4$ and $q_O = -2$).

The most common functional form for the short-ranged interactions is given by the Buckingham form:

$$E_{Buck}\left(r_{ij}\right) = Ae^{(-r_{ij}/\rho)} - C/r_{ij}^6 \qquad (2)$$

where A, ρ and C are adjustable parameters, chosen to reproduce pertinent physical properties of the real material.

Also commonly used is the Born–Mayer–Huggins (BMH) form:

$$E_{BMH}\left(r_{ij}\right) = f_0\left(b_i + b_j\right) \exp\left\{\left(a_i + a_j - r_{ij}\right)/\left(b_i + b_j\right)\right\} - c_i c_j / r_{ij}^6. \quad (3)$$

Here a_i, b_i and c_i are the parameters for individual atom species. Although the BMH form can be simply recast into the Buckingham form, it does have the advantage that, at least in principle, parameters for individual ions can be defined, rather than for ion pairs as in the Buckingham form. For ceria-based systems, potentials using both the Buckingham and BMH forms have been developed. Since the quality of the simulations is directly determined by the quality of the potential, an evaluation of the available potentials is given in Section 3.

The calculations used in the evaluation of the potentials are carried out using GULP (General Utility Lattice Program) [7,8]. All simulations are performed on a $6 \times 6 \times 6$ supercell of cubic non-primitive fluorite unit cells, each of which contains four CeO_2 formula units, for a total of 2592 ions. Periodic boundary conditions are applied in all three spatial directions. To simulate sub-stoichiometry, Ce^{4+} ions are randomly replaced by Ce^{3+} ($q = +3$) ions. Within a single simulation the arrangement of Ce^{4+} and Ce^{3+} ions is fixed; this is a limitation of the current approach, since experimentally electron transfer allows the Ce^{3+} ions to develop an equilibrium arrangement, which may not be random. An appropriate number of oxygen ions are then removed to maintain charge neutrality. Computational annealing of the system by MD at high temperature allows the oxygen vacancies to diffuse to form a structure in which the anion and vacancy arrangements are in equilibrium with respect to the fixed cation sublattice. For sub-stoichiometric ceria and doped ceria, since the properties may depend on the arrangements of dopant cations and oxygen vacancies, several random cation structures are generated and the properties of each structure are calculated to capture the range of effects. For the $T > 0$ K calculations, the free energy is calculated using the quasi-harmonic approximation to lattice dynamics, as implemented in the GULP code.

Table 2
Parameters of Inaba [26] Born–Huggins–Mayer potential for CeO_2. No shell model is available for this potential.

		z	a (Å)	b (Å)	c (J$^{0.5}$(nm)^3 mol$^{-0.5}$)
Inaba	Ce^{4+}	2.700	1.33	0.0454	0.00
	O^{2-}	−1.350	1.847	0.166	1.294

3. Potential evaluation

There are five different parameterizations of the Buckingham potentials and one parameterization of the BMH potential available for the ceria-based systems. The parameters for the five Buckingham potentials, denoted as Grimes [9], Vyas [10], Butler [11], Gotte (2004) [12], and Gotte (2007) [30], are given in Table 1. The Grimes, Gotte (2004) and Gotte (2007) potentials have also been parameterized for Ce^{3+}, allowing the effects of off-stoichiometry to be assessed. In addition, the Grimes potential has been parameterized for a number of rare-earth ions, allowing doping effects to be determined. The parameters for Inaba's BMH potential are given in Table 2. All of the Buckingham potentials have shell-model parameters; unless otherwise indicated all of the simulation results for these systems are based on shell-model calculations. In the shell model [13], each ion is considered to be composed of a core and a shell. The total charge on each ion is the sum of the respective core and shell charges (Y_e). The core and shell of each ion interact with those of other ions via long-ranged Coulombic interactions. There is also a short-range shell–shell interaction, which takes into account the repulsion between electron clouds of the atoms. The shell model mimics the presence of the nucleus plus core electrons (core) and valence electrons (shell). For any given atom, the core and shell are coupled by a spring constant (K_1). Inaba's BMH potential is a rigid-ion potential. To evaluate the quality of each potential, the lattice constant, thermal expansion, chemical expansion, oxygen migration energy, dielectric properties and mechanical properties are determined. The detailed comparison for these properties is given in the following subsections.

3.1. Lattice constant and thermal expansion

The zero-temperature lattice constants calculated using these potentials are listed in Table 3. The values are all essentially identical and in excellent agreement with the experimental data. This is to be expected since the potentials were fitted to the lattice parameter and some other fundamental properties. However, it should be noted that the experimental data is 293 K while simulation data are for 0 K.

Table 1
Parameters of the five Buckingham potentials for CeO_2. All are formal charge models.

	Species	A (eV)	r (Å)	C (eV Å^6)	Y_e (e)	K_1 (eV Å^{-2})	Ref
Grimes	O^{2-}–O^{2-}	9547.96	0.2192	32.0	−2.04	6.3	[27]
	Ce^{4+}–O^{2-}	1809.68	0.3547	20.40	−0.20	177.84	[10]
	Ce^{3+}–O^{2-}	2010.18	0.3449	23.11			[22]
	In^{3+}–O^{2-}	1495.65	0.3327	4.33			[28]
	Y^{3+}–O^{2-}	1766.40	0.33849	19.43			[27]
	Gd^{3+}–O^{2-}	1885.75	0.3399	20.34			[22]
	La^{3+}–O^{2-}	2088.79	0.3460	23.25			[22]
Vyas	O^{2-}–O^{2-}	9547.92	0.2192	32.0	−2.04	10.3	[10]
	Ce^{4+}–O^{2-}	2531.5	0.335	20.40	−0.20	177.84	
Butler	O^{2-}–O^{2-}	22,764.3	0.149	45.83	−6.10	419.9	[11]
	Ce^{4+}–O^{2-}	1986.8	0.3511	20.40	7.7	291.8	
Gotte (2004)	O^{2-}–O^{2-}	9547.92	0.2192	32.0	60.78	−3.0	[12]
	Ce^{4+}–O^{2-}	1809.68	0.3547	24.40	166.021	7.0	
	Ce^{3+}–O^{2-}	1809.68	0.3547	24.40	166.021	7.0	
Gotte (2007)	O^{2-}–O^{2-}	9533.421	0.234	224.88	1759.8	−6.5667	[29]
	Ce^{4+}–O^{2-}	755.1311	0.429	0.0	43.451	4.6475	
	Ce^{3+}–O^{2-}	1140.193	0.386	0.0	2172.5	15.092	