ATOMISTIC MODELING OF DEFECT INDUCED DILATIONS IN LANTHANUM CHROMITE

R. E. Williford and T. R. Armstrong
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352

ABSTRACT

Acceptor doping combined with reducing atmospheres causes defect induced lattice dilation in lanthanum chromite SOFC interconnect materials. Energy minimization techniques were used to simulate this dilation on the atomistic scale. To test the extrapolation capabilities of the technique, interatomic potentials were derived using minimal data bases. Lattice expansions were well predicted for 16 mol% Sr doping, but underpredicted by 33% at 30 mol% Sr. Approaches to improve the extrapolative prediction capabilities of the model are described.

INTRODUCTION

The interconnect in a solid oxide fuel cell (SOFC) plays a unique role separating the air and fuel while maintaining (a) high electronic conductivity, (b) a thermal expansion coefficient matched to the other stack components, and (c) mechanical integrity. The chemical potential gradient arising from partial pressure differences between the air and fuel place severe constraints on the choice of material for the interconnect. Only acceptor substituted lanthanum chromite can adequately maintain the required material properties at high-temperature in this environment. However, of these materials, only Sr-substituted lanthanum chromite has adequate mechanical strength in reducing environments (1) to be used as a high-temperature interconnect.

In acceptor substituted lanthanum chromite, charge compensation is electronic under oxidizing conditions through the formation of Cr^{4+} (2). Under sufficiently reducing conditions, oxygen vacancies form (resulting in ionic compensation) and Cr^{4+} reduces to Cr^{3+} in order to maintain electrical neutrality. The net result is a decrease in the electronic conductivity by decreasing the number of charge carriers available to participate in small polaron hopping (3), a lattice expansion due to the change in ionic radii of Cr (4, 5), and the development of an ionic conductivity due to oxygen vacancy formation (6, 7).

The effect of reducing environments on lattice expansion has been well documented in acceptor substituted lanthanum and yttrium chromites (4, 5, 8-13). The published literature indicates that the onset of expansion is between 10^{10} and 10^{12} atm for highly...
doped samples (>15 mole% acceptor), and that nearly complete reduction of the tetravalent Cr occurs at $10^{-18}$ atm. The amount of expansion varies depending on which acceptor dopant is used and whether it occupies the A-site or the B-site in the ABO$_3$ perovskite lattice. For A-site substitution, lower expansions have been observed by doping with Sr rather than Ca. The degree of expansion is approximately 0.15% per 10 mole % of dopant for Sr substituted lanthanum chromite (4). For B-site substitution, Mg has primarily been used as a dopant. Mg additions typically result in lower expansions than Sr or Ca. However, this is not a fair comparison since additions to the B-site of both acceptors and donors have been shown to reduce the lattice expansion (4, 5, 8). It has been successfully demonstrated that the amount of lattice expansion is proportional to the initial Cr$^{4+}$ concentration in the sample, implying that the expansion is solely due to the increase in ionic radius associated with the reduction of Cr$^{4+}$ to Cr$^{3+}$ and not due to interatomic repulsive forces arising from vacancy formation (4, 8).

The use of ceramic interconnects has been limited at high-temperature due to defect induced dilation and consequent failure of the interconnect. To date, the approach to developing new rare earth chromite compositions with minimal expansion has been purely Edisonian in nature. Over the past decade hundreds of compositions have been synthesized and tested at research institutions across the globe in order to find a suitable interconnect material. Composition development and testing still continues and it is not certain whether a rare earth chromite will be developed that meets all of the SOFC requirements.

The purpose of this study is to develop a model that could eventually be used as a design tool to predict the lattice expansion of rare earth chromites without the need for synthesizing and testing hundreds of compositions. In this paper a model was developed for the lattice expansions in $(\text{La}_{1-x}\text{Sr}_x)\text{CrO}_3$ and the results were compared to experimental data collected for samples with Sr concentrations ranging from $x = 0.16$ to 0.30.

**EXPERIMENTAL PROCEDURE**

All powders for this study were prepared by the glycine-nitrate process. The powder produced by the combustion event was passed through a 100 mesh screen to break up large agglomerates, and then calcined at 1000°C for 1 hour in air. The calcined powders was uniaxially pressed (55MPa) into bars, and then isostatically pressed at 138 MPa. The pressed compacts were sintered for 2 hours in air at 1400 to 1600°C. Dilatometric measurements were used to determine the stability of synthesized chromites in highly reducing environments. The dilatometric experiments were carried out using sintered bars (=30 mm x 3 mm x 3 mm) as a function of the ambient oxygen partial pressure ($P(\text{O}_2)$) using a buffered CO$_2$/Ar/H$_2$ gas system. The buffered gas system allowed measurements to be made over a $P(\text{O}_2)$ range from $10^{-5}$ to $10^{-18}$ atmospheres at 1000°C.
The significant ionic character of the bonding in lanthanum chromites (La$_{1-x}$Sr$_x$CrO$_3$) justifies the use of static lattice energy minimization techniques in this investigation. This technique has been successfully employed for the study of defect energetics in other perovskites (14-16). The General Utility Lattice Program (GULP) (17, 18) was used in this investigation to simulate the energetics and structures of La$_{1-x}$Sr$_x$CrO$_3$ on an atomistic scale. GULP’s energy minimization facility is based on the Born model, where energy is partitioned into long-ranged Coulombic interactions computed via the Ewald summation technique, and short-ranged atomic pairwise or three-body interactions. The code is unique in that it optimizes the use of crystal symmetry to make structure generation easier and to speed up calculations through the symmetrization of the energy components and its derivatives to second order.

GULP is also a popular tool for computing the energetics of isolated defects in extended solids (e.g., 19-21) using the Mott-Littleton approximation (22). Ionic polarization is treated using the well-known Dick-Overhauser shell model (23) and includes the important coupling between short range repulsion and ion polarization, which prevents excessive polarization from occurring (i.e., the ‘polarization catastrophe’). A simple harmonic spring model is used to represent the separation of the valence electron cloud from the ionic core (nucleus plus core electrons). Within an ion, the shell charge and spring constant combine to determine the overall electronic polarizability. The net ionic (core plus shell) charge may depart from formal charges in order to approximate the effects of partial covalency.

In the present paper, the lattice dilations observed when La$_{1-x}$Sr$_x$CrO$_3$ is subjected to a reducing environment were atomistically simulated using a mean field approximation. This means that the total interatomic potential at a particular site was the sum of potentials for all species (e.g., vacancies and/or substitutions) at that site, each weighted by their partial occupancies. The potential cutoff radii were 10 Å for cation-oxygen interactions and 12 Å for oxygen-oxygen interactions. The energy minimization technique is sensitive to the details of the interatomic potentials, which will be discussed next.

**INTERATOMIC POTENTIALS**

Although interatomic potentials have been developed for defect studies in cubic perovskites (14-16), these were found to be insufficient for the orthorhombic (x=0) and rhombohedral (x>0.1) structures of La$_{1-x}$Sr$_x$CrO$_3$. It was thus necessary to derive new potentials for the present work. In this initial investigation, an objective was to test the ability of the energy minimization technique to predict defect induced dilations of the structures in an extrapolative manner. For this purpose, the following restrictions were imposed for the derivation of cation-oxygen potentials.

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1. Although the charge partition between an ion core and shell was allowed to vary, the total charge was maintained at the value of the formal charge for each species. This restriction permits a straightforward classical interpretation of oxidation states.

2. The potentials were derived by fitting to only the structural data (lattice constants and atom positions) typically obtainable from standard x-ray diffraction (XRD) data bases. The only exception was the Sr-O potential, which also used the static dielectric constant (24) because its simple Fm3m space group provided only one observable to fit two parameters (A and p in Equation 1).

3. Each potential was fit to the most fundamental (simplest) oxide for which the above data was available (La2O3, SrO, Cr2O3, CrO2). This is a traditional means to allow 'transferability' of the potentials to other materials.

4. Adjustments of the potential parameters were allowed (within the limits of a good fit) only on the basis that an ion with a larger radius should have a higher potential. Ionic radii were obtained from Shannon (25, 26) for the proper coordination numbers: Cr3+ (VI) = 0.62 Å, Cr4+ (VI) = 0.55 Å, La3+ (XII) = 1.32 Å, Sr2+ (XII) = 1.44 Å.

5. Catlow’s well-known O-O potential (27) was used because of its demonstrated success for many oxides. The dispersion term (C in Equation 1) for cubic perovskites (14-16) was used for O-O in this work. All cation-O dispersion terms were taken as zero, thus ignoring any partial covalency or multibody effects.

6. Cation-O potentials were all fit to the Buckingham form, where r is the interatomic separation:

\[ E \ (\text{eV}) = A \ e^{-r/\alpha} - C/r^6 \]  

The new potential parameters were derived using the fitting capabilities of GULP, and are shown in Table I (Y is the shell charge and Ks is the core-shell spring constant).

Table I. Interatomic potentials.

| Ion Pair | A, eV  | r, Å     | C, eV Å⁶ | Y, | Ks, eV Å² |
|----------|--------|----------|----------|----|-----------|
| La³⁺ - O | 2983.988 | 0.3236 | 0.00 | -0.250 | 145.00 |
| Sr²⁺ - O | 687.189  | 0.3945 | 0.00 | 1.530  | 11.41 |
| Cr³⁺ - O | 522.725  | 0.3876 | 0.00 | 2.995  | 67.01 |
| Cr⁴⁺ - O | 3448.231 | 0.2800 | 0.00 | 3.970  | 67.00 |
| O - O    | 22764.300 | 0.1490 | 43.00 | -2.240 | 42.00 |

These potentials are also plotted in Figure 1 to show their relative values over the range of the cation-oxygen bond distances in La₁ₓSrₓCrO₃: (La, Sr) - O = 2.49 - 3.00 Å, Cr - O = 1.95 Å. The Cr³⁺-O potential is greater than the Cr⁴⁺-O potential for interatomic separations greater than about 1.91 Å, which is consistent with relative ionic radii for the Cr - O bond distance given above. The Sr²⁺-O potential is greater than the La³⁺-O potential for separations greater than about 2.65 Å. This is consistent for the majority of the (La, Sr) - O bond distances (six bonds at 2.74 Å and three at 3.00 Å), but is not
consistent for the three shortest bonds at 2.49 Å. The La and Sr potentials could not be further adjusted to correct this situation and still give good fits to the simple oxides La2O3 and SrO. They were therefore used as given in Table I to simulate the defect induced dilation of La1-xSrxCrO3, as described in the next section.

**SIMULATION RESULTS**

Benchmarking of the above potentials was performed by comparisons of measured (28) versus computed structures and volumes for LaCrO3 and La0.75Sr0.25CrO3. The structures, lattice constants, and atom positions for LaCrO3 (orthorhombic, Pbnm) and La1-xSrxCrO3.8 (rhombohedral R-3c for x>0.15) were obtained from Khattak and Cox (28). For La1-xSrxCrO3, the neutron powder diffraction data for x = 0.25 was assumed applicable for defining the atom positions for x = 0.16 to x = 0.30. Structural comparisons for both materials agreed within ~1%. For orthorhombic LaCrO3, the measured/predicted volumes were 58.50 / 58.20 Å³/formula unit, giving agreement within ~0.5%. For oxidized rhombohedral La0.75Sr0.25CrO3, the measured/predicted volumes were 57.93 / 58.39 Å³/formula unit, giving agreement within ~0.8%. For reduced rhombohedral La0.75Sr0.25CrO3, the measured/predicted volumes were 58.74 / 58.75 Å³/formula unit, giving excellent agreement. The measured/predicted linear expansion of the lattice (1/3 of the volume expansion for polycrystalline samples) upon reduction was thus 0.47% / 0.21%, which is reasonable agreement for this initial study considering the restrictions placed on the potential derivations.

For the data described above, lattice dilation was simulated for the reduction reaction

\[
\text{La}_{1-x} \text{Sr}_x \text{Cr}_{1-x} \text{O}_3 \rightarrow \text{La}_{1-x} \text{Sr}_x \text{Cr}_{1-x} x \text{Cr}_{x} x \text{O}_{3-x} \xch{\text{[V}_x \text{O}^\cdot \text{]\_x}} + \delta/2\text{O}_2. \tag{2}
\]

Values for the coefficient \(\delta\) as a function of the Sr fraction and the oxygen partial pressure (PO2) were obtained from Figure 6 of Yasuda and Hishinuma (29) for La1-xSrxCrO3 at 1000°C, with x = 0.1, 0.2, and 0.3. Linear interpolation was used to compute \(\delta\) at x = 0.16 and 0.24 for comparison with the experimental data described above. The results are shown in Figure 2.

The predicted and measured linear expansions for x = 0.16, 0.20, 0.24, and 0.30 are shown in Figure 3. All simulations were performed at 0°K. The agreement for 16 mol% Sr is very good. However, only about 2/3 of the measured linear expansion is predicted for 30 mol% Sr.
DISCUSSION AND CONCLUSIONS

There are several sources of uncertainty that could conceivably contribute to the underprediction observed in Figure 3, including errors associated with the determination of $\delta$ from a different set of experimental data. However, the somewhat severe restrictions placed on potential derivation (to test extrapolation capabilities) would seem more important at this stage of the investigation. Insufficiencies in the potentials were manifest in the benchmarking cases, where the volume of LaCrO$_3$ was underpredicted but the volume of oxidized La$_{0.75}$Sr$_{0.25}$CrO$_3$ was overpredicted. The latter caused underprediction of the defect induced dilation upon reduction. Since La is common to both reference cases, the implication is that either the La-O potential is too ‘soft’ or the Sr-O potential is too ‘hard’. However, raising the La-O potential or lowering the Sr-O potential would produce an effect opposite to that needed to maintain the correct relationship for the Sr/La ionic radii (see Figure 1).

It would appear that improvements are needed in the potentials. Such improvements should include simultaneous fitting to elastic and dielectric constants, since these data determine the curvatures of the potentials in Figure 1, which in turn affects the crossover points between potentials. The Cr-O potentials would also benefit from fitting to more complete data bases. Sr-O and Cr-O potentials fitted simultaneously to several materials (SrO, SrCrO, and Sr$_2$CrO$_4$) could result in substantial improvements, if sufficient data were available for these materials. Beneficial results may also be obtained by relaxing other restrictions for potential fitting, such as allowing the charges to deviate from formal values so that differences in polarizabilities and partial covalent bonding could be better represented. Finally, the role of defect clusters should also be investigated, since they can play an important role in dilation studies (30).

The general conclusion is that the static lattice energy minimization technique appears well suited to extrapolative predictions of defect induced lattice dilations in lanthanum chromite SOFC interconnects. Approximately two-thirds of the experimentally observed dilation was predicted using limited interatomic potentials developed from less than half the usual data base. The path is clear for improving the potentials and their predictive capabilities.

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Figure 1. Potentials as a function of interatomic separation.

Figure 2. Values of $\delta$ used in this study.
Figure 3. Predicted (dashed lines) and measured (solid lines) isothermal linear expansions.