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Predicting oxygen vacancy non-stoichiometric concentration in perovskites from first principles

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ABSTRACT

Formation of oxygen vacancies by introducing various mixed-valent cation dopants is a common practice to improve the cathode performance in solid oxide fuel cells. A computational procedure is developed in this work to predict the equilibrium oxygen vacancy non-stoichiometric concentrations at experimentally relevant temperatures and oxygen partial pressures for both bulk and surface oxide phases. The calculations are based on the first-principles density functional theory and a constrained free-energy functional. Quantitative agreements are found by direct comparisons to the thermogravimetry and solid electrolyte coulometry measurements for the strontium-doped lanthanum cobalt iron oxides at different compositions. Our results indicate that the oxygen vacancies are energetically stabilized at surfaces for all temperatures and all oxygen partial pressures, while such surface stabilization effects become stronger at higher temperatures and lower oxygen partial pressures.

1. Introduction

Because of the unique combination of mixed ionic and electronic conductances (MIEC) [1–4], perovskite oxides have been widely used as the cathode materials for solid oxide fuel cells (SOFC) [5]. Typical A-site cations in these perovskite cathode materials contain rare and alkaline earth elements such as La, Sr, Ca, and Ba, and typical B-site cations consist of reducible transition metal elements such as Mn, Fe, Co, and Ni [6]. Over the past two decades, extensive scientific research efforts have been focused on optimizing the materials compositions in lanthanum strontium transition metal oxides such as $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ (LSCF) to improve the catalytic performance in oxygen reduction reactions, chemical and mechanical stabilities at high temperatures, and thermal expansion properties, as well as to lower the materials and processing costs [7,8].

It has been well recognized that the MIEC of these perovskite cathode materials may be modified through controlling the oxygen non-stoichiometry $O_{3-\delta}$ concentration δ [9], which in turn is a complicated function of the materials compositions, temperature T, and oxygen partial pressure P_{O_2}. These non-stoichiometric anion vacancy defects were often introduced into perovskites in the growth, annealing, and redox reaction processes. However, if the resulting dopant and defect concentrations were not thermodynamically favorable, metastable microstructures could undergo degradations [10] and consequentially affect the overall device performance.

Experimentally, oxygen vacancy non-stoichiometric concentrations in LSCF were measured through oxygen mass changes using the thermo-gravimetry (TG) [9] and solid electrolyte coulometry (SEC) [11] techniques. Various empirical defect models [9,12,13] were introduced to explain these measurements, but all shared the following common problems. Firstly, all the cation and anion defects were treated as classical particles existing only in their pre-assigned integer valence states and only on the lattice sites such that the quantum nature of electrons and holes was completely ignored. Secondly, these defect models typically required three or four empirical fitting parameters in the forms of enthalpy, entropy, or equilibrium constants. But these fitted thermodynamical functions did not have any explicit temperature and pressure dependences. Thirdly, although the importance of surface defects were often acknowledged in the perovskite oxide literatures [9,13], these existing empirical defect models [9,12,13] did not consider

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any surface effects. In this work, we present a first-principles density functional theory (DFT) based free-energy approach to predict the oxygen vacancy non-stoichiometric concentrations $O_{3-\delta}$ for the well documented LSCF system. In this new approach, the cation and anion defects are allowed to displace away from well-defined lattice sites, and their valence states are the natural consequence of continuous wave function and charge distributions. With only one single excess Gibbs free-energy parameter describing the non-ideal solution effects which can be estimated from existing experimental measurements, we expect that the same numerical procedures described in this work for LSCF can also be applicable to other perovskite oxide materials. To the best of our knowledge, our present approach is the only model that explicitly incorporate the essential surface effects on the oxygen vacancy non-stoichiometric concentrations.

2. Computational details

Electronic-structure calculations based on the first-principles DFT provides a generic and powerful tool for predicting many important thermodynamic and kinetic properties of complex oxides [14–17]. The ground state energy calculations are performed using the standard Quantum Espresso software package [18], which gives all the equilibrium crystal structures, atomic geometries, vibrational entropies under the harmonic oscillator approximation, and electronic wave function and density distributions.

We used plane waves as the basis set with an energy cutoff of 450 eV, ultrasoft pseudopotentials, and generalized gradient approximation (GGA) for the exchange-correlation functional with the on-site Hubbard repulsion U (GGA + U) [19] corrections. Standard Coulomb repulsion parameter U = 5 eV and exchange parameter J = 1 eV are applied to the 3d orbitals of the B-site transition metals including Fe and Co [14]. The spin polarization effects are fully treated in all the calculations. A representative supercell with the periodic boundary conditions applied along all the three x, y, and z directions is given in Fig. 1(b) for $La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_3$ which contain a total of 40 atoms. A corresponding $2\times2\times2$ Monkhorst–Pack k-point mesh in the first Brillouin zone was used for the total energy calculations [20]. The equilibrium lattice constant of such a cubic perovskite oxide is 3.91 Å computed by DFT, consistent with the experimental value of 3.925 Å for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ [21]. To mimic the surface phase, a large vacuum of 10 Å is used and the atoms on the bottom layer are fixed at their bulk geometry.

Going beyond the total energy calculations directly from DFT, we need to construct a free-energy functional to obtain the oxygen vacancy non-stoichiometry concentration as a function of T and P_{O_2}. As shown in Fig. 1(a), a macroscopic sample LSCF perovskite oxide may be represented as an ensemble of N cubic perovskite unit cells. In each unit cell, there are one A atomic site, one B atomic site, and three oxygen atomic sites. For a LSCF sample with a Sr molar dopant fraction of x, there are xN Sr-containing perovskite unit cells and $(1-x)N$ La-containing perovskite unit cells, corresponding to the dark blue and light blue unit cells shown in Fig. 1(a), respectively.

Because it is highly energetically unfavorable to create oxygen vacancies in the La-containing cells as compared to the Sr-containing cells and it is both energetically and entropically unfavorable to create two oxygen vacancies in one single Sr-containing cell, we can further divide the LSCF supercell ensemble of Fig. 1(a) into three different categories, $(1-x)N$ $LaBO_3$ as the Solvent, $(x-2\delta)N$ $SrBO_3$ as the Solute 1, and $2\delta N$ $SrBO_2$ as the Solute 2. Therefore, the oxygen vacancy formation can only occur between the Solute 1 and Solute 2, as shown in Fig. 1(c). Here the charge neutrality condition is enforced between the Sr dopants and O vacancies as

$$[Sr'_{La}] = 2[V_O^{\bullet\bullet}]. \quad (1)$$

Following such an LSCF defect ensemble representation as shown in Fig. 1, we can express the overall reaction Gibbs free-energy

$$\Delta G = \Delta H - T\Delta S, \quad (2)$$

as the sum of the reaction enthalpy

$$\Delta H = H_{Solute1} - H_{Solute2} - \frac{1}{2}H_{O_2}, \quad (3)$$

directly from DFT and the reaction entropy

$$\Delta S = \Delta S_{solid} - \frac{1}{2}\Delta S_{gas} = (\Delta S_{config} + \Delta S_{vib}) - \frac{1}{2}\Delta S_{O_2}. \quad (4)$$

As shown in Eq. (4), the latter consists of the configurational entropy and vibrational entropy contributions of the solids, as well as the

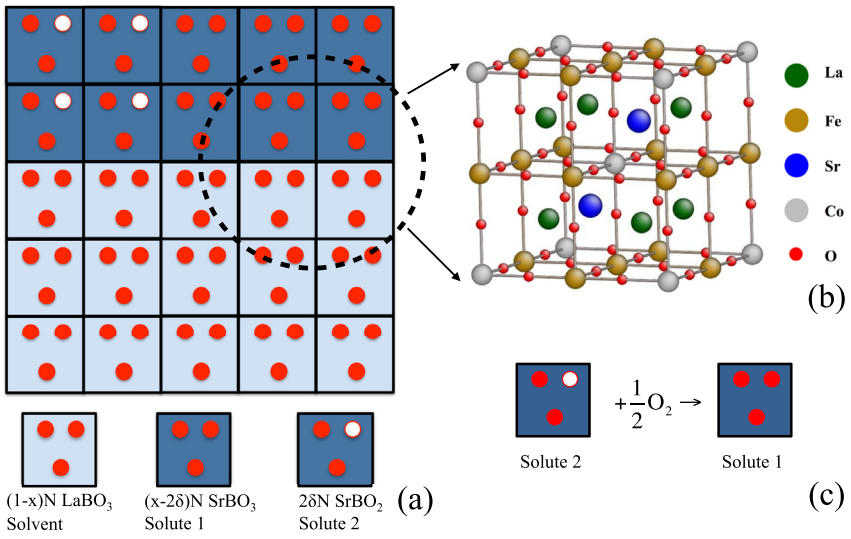

Fig. 1. (a) Schematic supercell ensemble, where the dark and light blue cells represent the Sr and La unit cells, respectively. A red filled circle indicates that the corresponding oxygen site is filled with an oxygen atom, and an empty red circle represents an oxygen vacancy site. The chance of forming two oxygen vacancies in one single unit cell is ignored. (b) Representative $2\times2\times2$ supercell of $La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_3$ used in our DFT calculations. (c) Because the oxygen vacancy formation energy in a La unit cell is much greater (> 1.2 eV) than that in a Sr unit cell, the $LaBO_3$, $SrBO_3$, and $SrBO_2$ cells are treated in our free-energy model as the Solvent, Solute 1, and Solute 2, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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