

Atomic structure and energetics of oxygen vacancy in CeO₂ grain boundaries

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Cerium oxide (CeO₂) is one of the most promising candidates for electrolyte materials in solid oxide fuel cells due to its high oxygen ion conductivities at relatively low temperature¹. It is believed that the grain boundaries (GBs) play an important role on the transport properties, which governs the macroscopic properties of those CeO₂-based materials in practical use. Although some approximated models explain a part of reasons for the decrease of ionic conductivities in GBs², the governing mechanisms and underlying physics are still unclear in atomic scale at the present stage, due to the limited information of local atomic GB structure.

In this study, we systematically investigated 5 different model GBs of $\Sigma 5$ (ref.3), $\Sigma 3$ (ref.4), $\Sigma 9$, $\Sigma 11$ and $\Sigma 13$ GBs by scanning transmission electron microscope (STEM) and theoretical calculations. STEM images confirm that neither amorphous nor secondary phase precipitates are present at the GBs. Electron energy loss spectroscopy (EELS) result and theoretical calculations reveal that for the $\Sigma 5$, $\Sigma 11$ and $\Sigma 13$, nonstoichiometric GB core structure with oxygen vacancies is found to be the most plausible. On the other hand, the $\Sigma 3$ and the $\Sigma 9$ GB have the stoichiometric GB core structures. (Details will be shown in the presentation) These results suggest the oxygen nonstoichiometry in CeO₂ GBs are largely dependent on the GB characters, and therefore different GBs may have different degree of effects to the oxygen transportation properties. Thus, we further investigated the energetics of oxygen vacancy in the $\Sigma 3$ and $\Sigma 5$ GBs, as two examples, to understand the relationship between GB structure and V_O formation.

The formation energies of V_O at the GBs were studied by the lattice-statics method by the GULP program⁵ with the two-body Buckingham-type interatomic potentials reported by Minervini⁶. Mott-Littleton method was used here⁷: the supercell containing model GB is divided into region 1, 2a and 2b. After a defect center is defined, region 1 is assumed to be strongly affected by the defect around the defect center; the region 2 is assumed to be less perturbed compared with region 1. In region 2a, forces of short-range interatomic potentials, Coulomb term are explicitly calculated and the displacement is considered, with some approximation, while only the polarization of sublattice from a defect charge is considered in region 2b. The size of region 1 and region 2a were set to 12 Å and 24 Å respectively. The charge of V_O is assumed to be +2. The $\Sigma 3$ and $\Sigma 5$ stoichiometric GB models reported before were used in this study^{3,4}.

Oxygen vacancy formation energies of at $\Sigma 3$ and $\Sigma 5$ GBs were calculated at different atomic sites in Figure 1. In order to get rid of the influence of chemical potentials, the calculated vacancy formation energies were obtained as the difference from that in perfect crystal, which is defined as ΔE . Then formation energy of V_O at the site n is defined as

$$\Delta E'(n) = \Delta E(n) - \Delta E(1),$$

Where n represents the atomic site shown in Figure 1, and the site 1 is taken in the bulklike regions in the supercells.

Formation energies of V_O is largely affected by the Ce-O distance (coordination number) and O-O, due to the attracting force between Ce-O and the repulsion force between O-O. This can be found from the Tables 1 and 2, which list the $\Delta E'(n)$, coordination number, and distance change (only the coordination bonds are considered) between Ce-O (Δ_{Ce-O}) and O-O (Δ_{O-O}) in the GBs.

Almost all of the atomic sites at the GBs have negative value, indicating that formation of V_O is preferred at the GBs. $\Delta E'(n)$ are dependent on the atomic sites at both the $\Sigma 3$ and $\Sigma 5$ GBs. The lowest $\Delta E'(n)$ at the $\Sigma 5$ GB (site 6) is lower than that of $\Sigma 3$ GB (site 5), suggesting that oxygen vacancy forms easier at $\Sigma 5$ GB as compared with $\Sigma 3$ GB. As a consequence, the oxygen nonstoichiometric GB core is stable for the $\Sigma 5$ GB while the $\Sigma 3$ GB maintains oxygen stoichiometric core structure. Our results suggest that different atomistic environment due to different GB characters cause different V_O energetics, which leads to different oxygen nonstoichiometric behavior.

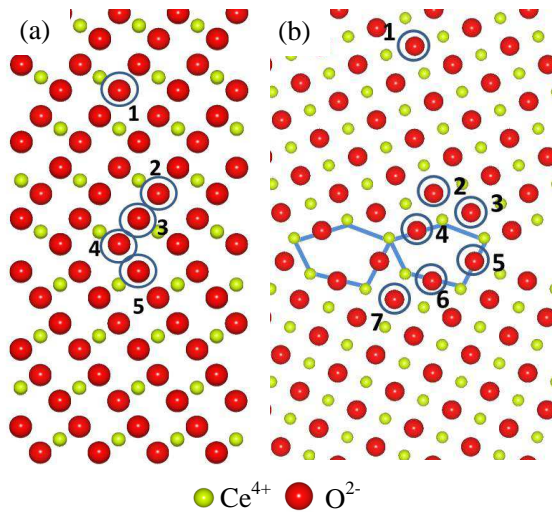


Figure 1. Supercells used in the present study. (a) $\Sigma 3$ GB viewed with [110] projection and (b) $\Sigma 5$ GB viewed with [100] projection

Table 1. $\Delta E'$, coordination number, and distance change (only the coordination bonds are considered) between Ce-O (Δ_{Ce-O}) and O-O (Δ_{O-O}) at the $\Sigma 3$ GB

Atomic site	$\Delta E'$ (eV)	CN	Δ_{Ce-O} (%)	Δ_{O-O} (%)
5	-1.92	3	-1.9	+3.9
4	-1.90	4	+4.3	+1.6
3	-0.17	4	-3.1	+0.3
1	0	4	Bulk-like	Bulk-like
2	0.26	4	-2.7	-3.1

Table 2. $\Delta E'$, coordination number, and distance change (only the coordination bonds are considered) between Ce-O (Δ_{Ce-O}) and O-O (Δ_{O-O}) at the $\Sigma 5$ GB

Atomic site	$\Delta E'$ (eV)	CN	Δ_{Ce-O} (%)	Δ_{O-O} (%)
6	-2.47	3	-6.5	+39.6
5	-0.63	3	-4.9	+45.7
7	-0.62	4	+3.7	+3.4
4	-0.53	3	-5.0	+51.4
3	-0.53	4	+6.2	+17.6
2	-0.46	4	+2.9	+4.2
1	0	4	Bulk like	Bulk like

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