Density-Functional Study of the $La_2Zr_2O_7$ Low-Index Faces

Yves A. Mantz[1] and Yuhua Duan[2]

[1] US Department of Energy, National Energy Technology Laboratory, Morgantown, WV 26507; [2] US Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA 15236

Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

Introduction

- Lanthanum zirconate ($La_2Zr_2O_7$, LZ) and doped forms of LZ have been shown to be effective catalysts.
  - Doped forms of LZ can catalyze reactions to make syngas (CO + H_2), used as a fuel in solid oxide fuel cells (SOFCs) or to make various chemicals:

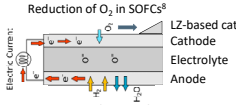
Partial oxidation of fuel into syngas[1,2]	$2C_nH_m + nO_2 \longrightarrow 2nCO + mH_2$
Dry reforming of methane[3,4]	$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$
Bi-reforming of methane[5]	$3CH_4 + CO_2 + 2H_2O \longrightarrow 4CO + 8H_2$
Oxy-reforming of methane (slow deactivation)[5]	$3CH_4 + CO_2 + O_2 \longrightarrow 4CO + 6H_2$

  - LZ and doped forms can catalyze CH_4 combustion:[6] $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
- LZ-based compounds have also been studied to catalyze other processes:

Higher alcohol synthesis by CO hydrogenation[7]

$2nH_2 + nCO \longrightarrow C_nH_{2n+1}OH + (n\text{-}1)H_2O$

Reduction of O_2 in SOFCs[8]



- To explain the effectiveness of LZ and doped form of LZ as catalysts, an understanding of LZ surfaces is needed.
- From previous experimental work, the structure of bulk LZ is pyrochlore, with four different atom types (LZ = $La_2Zr_2O_6O'$). The low-index surfaces, (001), (011), and (111), are likely to be well represented.[9-13]
- Recently, the first theoretical study of LZ surfaces was published:[14]
  - An ideal surface is defined as a surface with a surface termination or top atomic layer or layers that can be formed by cleaving the bulk crystal.
  - By computing surface free energies of different surface terminations at the level of density-functional theory (DFT), evidence is provided that the (001) surface is nonideal over a large set of temperature T and oxygen gas partial pressure p_{O_2} conditions.
- Building on ref 14, the main goal of this work is to provide evidence that all three low-index surfaces are nonideal.

Computational Approach

- Results are obtained at the level of DFT using, unless otherwise noted:
  - PW91 functional
  - Plane-wave basis set with 400 eV cutoff
  - PAW pseudopotential set
  - Monkhorst-Pack k-point meshes for bulk materials and surfaces (e.g., 4 × 4 × 4 for LZ bulk and 4 × 4 × 1 for LZ surfaces)
- Surfaces are modeled using the periodic slab technique and a slab model plus 16 Å vacuum region.
- Different types of computations are performed, such as geometry optimizations, using the VASP and PHONON software packages.

Surfaces of LZ

- All possible ideal surface terminations of the (001), (011), and (111) surfaces are examined. They are labeled (001) t1-t4, (011) t1-t4, and (111) t1-t8.

Ideal surface terminations of LZ (001), (011), and (111) surfaces, described by specifying the top atomic layer for the smallest possible surface unit cell. For surface terminations that are identical, the underlying layer is given in a footnote.

(001)		(011)		(111)			
tx	top layer	tx	top layer	tx	top layer	tx	top layer
t1	O[a]	t1	O_4[c]	t1	O[e]	t5	O_3[g]
t2	La_2Zr_2	t2	La_2Zr_2	t2	La_2Zr	t6	O_3[h]
t3	O_4O'	t3	O_4[d]	t3	O_3	t7	O_3[i]
t4	O[b]	t4	$La_2Zr_2O_4O_2'$	t4	O[f]	t8	$LaZr_3$

[a] O_4O' [b] La_2Zr_2 [c] $La_2Zr_2O_4O_2'$ [d] La_2Zr_2 [e] O_3 [f] La_2Zr [g] O' [h] $LaZr_3$ [i] O_3

- In addition, selected defective surface terminations are examined, formed by adding one or two oxygen atoms or an O_2 molecule to, or by removing one or more oxygen atoms from, an ideal surface termination. They are labeled (001) d1-d10, (011) d1-d12, and (111) d1-d7.
- In total, 45 different surface terminations are examined.

Preferred (001), (011), and (111) Surface Termination versus $\Delta\mu_O$

The surface free energy Ω is the energy to form a surface from the bulk crystal taking into account environmental conditions:

$$\Omega = \frac{1}{A}(\phi_{Zr} - \Gamma_{Zr,O}\Delta\mu_O - \Gamma_{Zr,La}\Delta\mu_{La})$$

$$\Delta\mu_O = \mu_O - \frac{1}{2}E^{gas}_{O_2}, \quad \Delta\mu_{La} = \mu_{La} - E^{bulk}_{La},$$

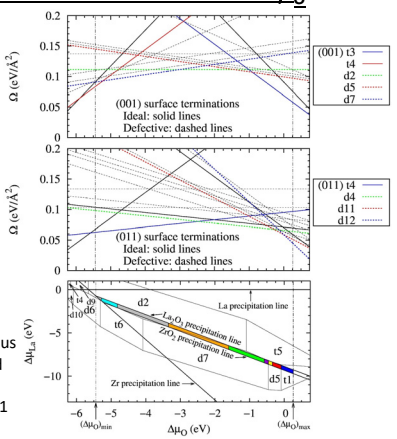
$$\phi_{Zr} = \frac{1}{2}(E_{slab} - \frac{N_{Zr}}{N^{bulk}_{LZ}}E^{bulk}_{LZ}) - \frac{1}{2}\Gamma_{Zr,O}E^{gas}_{O_2} - \Gamma_{Zr,La}E^{bulk}_{La}, \ \Gamma_{Zr,a} = \frac{1}{2}(N_a - N_{Zr}\frac{N^{bulk}_a}{N^{bulk}_{Zr}})$$

μ_a : chemical potential of element a = O and La

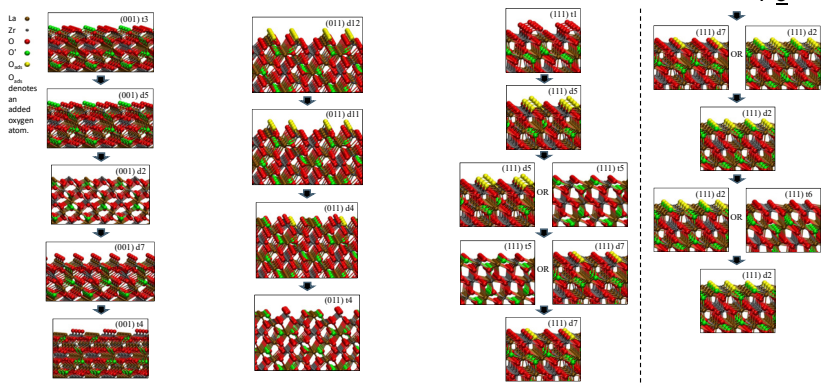
$E_{slab}, E^{bulk}_{LZ}, E^{gas}_{O_2}, E^{bulk}_{La}$: energies of the slab model, bulk LZ per formula unit (FU), O_2 molecule, and bulk La per FU, respectively (from DFT)

N_X, N^{bulk}_X, A : numbers of atoms of element X = La, Zr, and O in the slab and in bulk LZ per FU and area of one side of the slab, respectively

- For all (001) and (011) surface terminations, the Ω are linear functions of $\Delta\mu_O$ (right, top and middle plots). The preferred surface termination versus $\Delta\mu_O$ is readily identified.
- The (111) surface termination with the smallest value of Ω versus $\Delta\mu_O$ and $\Delta\mu_{La}$ is shown on the right, bottom plot. The preferred (111) surface termination versus $\Delta\mu_O$ is given by the regions in color where bulk LZ is stable. For example, in the blue region, t1 is preferred; in the orange region, d2 or d7.



Side View of the Preferred Surface Termination for Decreasing $\Delta\mu_O$



Preferred (001), (011), and (111) Surface Termination versus T and p_{O_2}

The values of $\Delta\mu_O$ for which a surface termination is preferred are converted into conditions of T and p_{O_2} using the equation below:

$$\Delta\mu_O = \frac{1}{2}[G^{gas}_{O_2}(T, p^\circ_{O_2}) - G^{gas}_{O_2}(T^\circ, p^\circ_{O_2}) + kT\ln(\frac{p_{O_2}}{p^\circ_{O_2}})] + \delta\mu^\circ_O$$

$$\delta\mu^\circ_O = \frac{1}{2}\sum_{M_xO_y}\frac{1}{y}(E^{bulk}_{M_xO_y} - xE^{bulk}_M - \Delta H^\circ_{f,M_xO_y}) - \frac{1}{2}(T^\circ S^\circ_{O_2} + E^{gas}_{O_2})$$

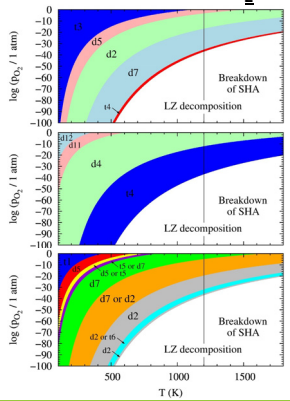
$G^{gas}_{O_2}(T, p_{O_2})$: experimental Gibbs free energy of O_2 at T and p_{O_2}, T° = 298.15 K, $p^\circ_{O_2}$ = 1 atm

$E^{bulk}_{M_xO_y}, E^{bulk}_M$: energies per FU of bulk M_xO_y = La_2O_3 and ZrO_2 and M = La and Zr, respectively (from DFT)

$\Delta H^\circ_{f,M_xO_y}$: experimental standard heat of formation of M_xO_y

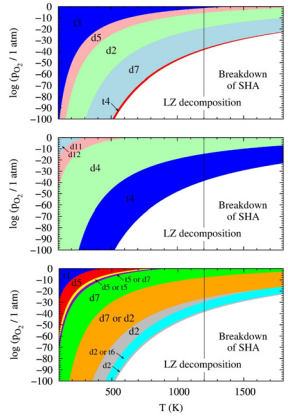
$S^\circ_{O_2}$: experimental standard entropy of O_2

The preferred (001), (011), and (111) surface termination versus T and log (p_{O_2} / 1 atm) is shown on the right (top, middle, and bottom plots, respectively). Above 1200 K, results can only be estimated due to the breakdown of the SHA or standard harmonic approximation, as discussed in the next section.



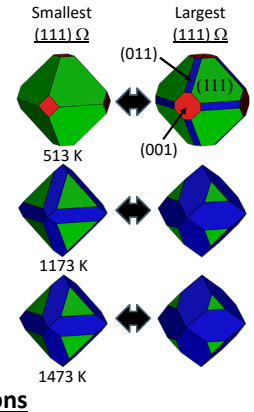
Validation and Implications of Results

- Vibrational contributions to the functions Ω and in determining precipitation lines (left, bottom plot) may be important. They are taken into account by computing phonon densities of states to make new diagrams (right), similar to the original diagrams.
- The SHA made to determine vibrational contributions is expected to breakdown above roughly half of bulk LZ's melting point. Thus, the original diagrams cannot be verified above 1200 K.
- Diagrams are also obtained within the local density approximation (not shown), similar to the original diagrams.
- Thus, for all three surfaces, conditions are identified where the preferred surface termination is nonideal.



Comparison to Experiment

- Using Ω values of preferred ideal (001), (011), and (111) surface terminations, Wulff shapes, or crystal shapes having minimal Ω, are made at LZ synthesis conditions of 0.2 atm O_2 and 513, 1173, and 1473 K (right). At every T, a set of shapes is obtained, because Ω of the preferred ideal (111) surface termination will span a range of values.
- If the experimental shape made at 0.2 atm O_2 and a T given above is different from the two shapes shown at that T or any shape in between, then one or more surfaces of the experimental shape may be nonideal.
- Before this comparison can be made, the experimental shapes need to be determined.



Conclusions

- In this work, the (001), (011), and (111) surfaces of LZ are studied theoretically, complementing a previous theoretical study.[14]
- Only certain surface terminations of a given surface are preferred.
- Evidence is provided for a nonideal (001), (011), and (111) surface under large sets of conditions of T and p_{O_2}.
- The above two conclusions are not affected by vibrational effects.
- A comparison to experiment is proposed.

Acknowledgment

SOFC Program at the National Energy Technology Laboratory

References

[1] DJ Haynes et al., *Catal. Today* **2008**, *136*, 206 [2] MW Smith et al., *Appl. Catal., A* **2015**, *502*, 96 [3] S Gaur et al., *Appl. Catal., A* **2011**, *403*, 142 [4] F Polo-Garzon et al., *J. Catal.* **2016**, *340*, 196 [5] N Kumar et al, *Appl. Petrochem. Res.* **2016**, *6*, 201 [6] J Cheng et al, *Catal. Commun.* **2009**, *10*, 1170 [7] V Abdelsayad et al, *Catal. Today* **2013**, *207*, 65 [8] S Lee et al, *J. Electrochem. Soc.* **2011**, 158, B735 [9] Y Tong et al, *J. Alloy Compd.* **2008**, *465*, 280 [10] K Koteswara Rao et al, *Mater. Lett.* **2002**, *54*, 205 [11] AK Bhattacharya et al, *J. Mater. Sci.* **1994**, *29*, 6076 [12] D Chen and R Xu, *Mater. Res. Bull.* **1998**, *33*, 409 [13] H Zhou et al, *J. Alloys Compd.* **2007**, *438*, 217 [14] YA Mantz, *J. Phys. Chem. C* **2016**, *120*, 7522

Science & Engineering To Power Our Future