

Density Functional Theory Modeling on: 1. The Effect of H₂O in Hydrogen Oxidation Reaction on the Perovskite Surfaces 2. Hydrogen and Cation Diffusion in Bulk Tetragonal Zirconia for Solid-Oxide Fuel Cells

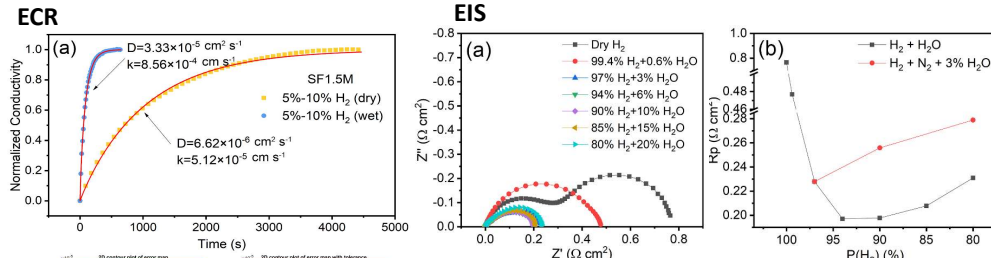
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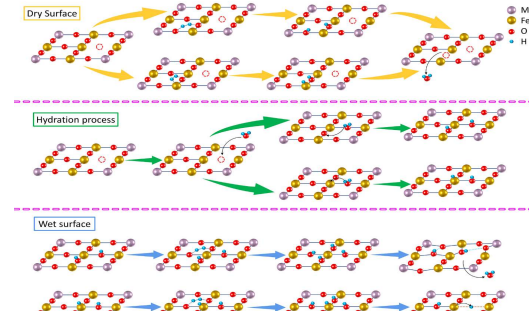
Yueh-Lin Lee^{a,b}, Qi He^c, Tao Yang^{a,b}, Wenyuan Li^c, Wei Li^c, Liang Ma^c, Shanshan Hu^c, Yuhua Duan^a, Dan Sorescu^a, Dane Morgan^d, Harry Abernathy^{a,b}, Thomas Kalapos^{a,b}, Xingbo Liu^c, Gregory A. Hackett^a
^aNational Energy Technology Laboratory, U.S. Department of Energy; ^bLeidos Research Support Team; ^cWest Virginia University, Morgantown, WV; ^dUniversity of Wisconsin-Madison, Madison, WI

1. Effects of H₂O in Hydrogen Oxidation Reaction on the Perovskite Surfaces

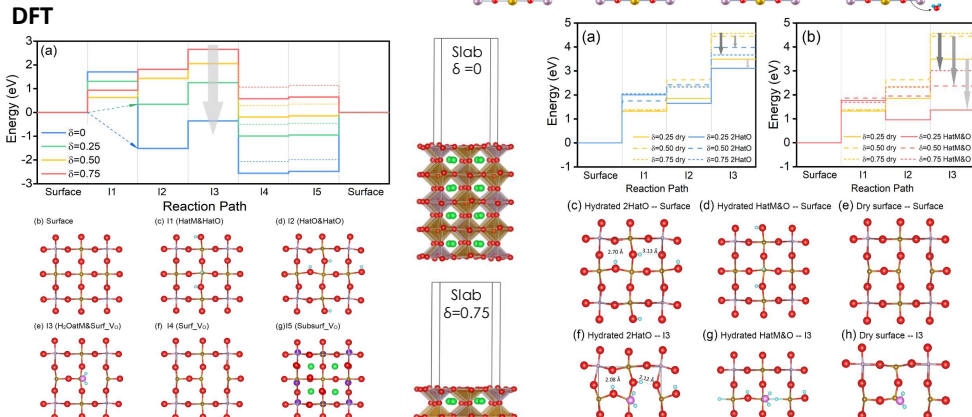
The electrochemical performances of perovskite materials Sr₇Fe_{1.5}Mo_{0.5}O_{6.5} (SF1.5M) and the Pr- and La-substituted series for the hydrogen oxidation reaction (HOR; H₂(g) + O₂^{δ-} = H₂O(g) + V_O^{••} + 2e⁻) in dry and humidified H₂ are investigated by Density Functional Theory (DFT) based thermodynamic modeling, electrical conductivity relaxation (ECR), and electrochemical impedance spectroscopy (EIS) techniques [1]



Surface Models Used to Describe the HOR Reaction Steps



Both ECR and EIS measurement results indicated a promoted electrochemical performance on tested SF1.5M material in humidified H₂

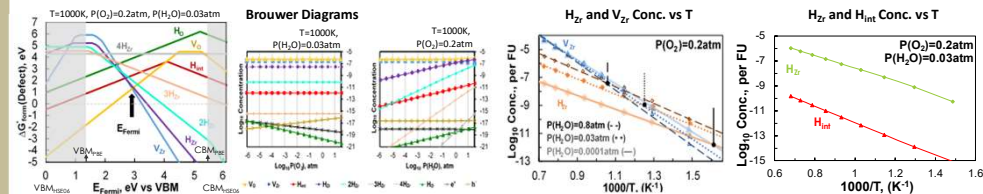


DFT-based thermodynamic modeling revealed nonstoichiometry of SF1.5 (001) slab models significantly alters the HOR energy landscape

DFT energy analysis showed enhanced interaction of surface H species with the hydrated SF1.5M surface

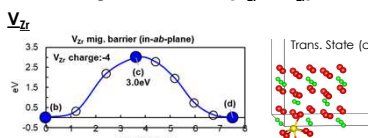
2. Hydrogen and Cation Diffusion in Bulk Tetragonal Zirconia

Density functional theory based thermokinetic modeling was performed to determine the effect of H₂O and O₂ gas pressure on the defect chemistry, hydrogen solubility and diffusivity, and on cation transport in tetragonal ZrO₂ [2]

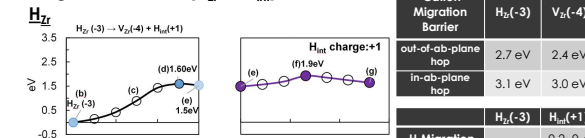


The DFT based defect thermodynamic modeling results provide information related to the stable defect complexes and hydrogen-related defect species relevant to bulk cation transport kinetics at different gas pressure and T conditions

Cation migration barriers (V_{Zr} vs H_{Zr})

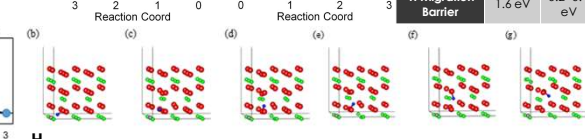
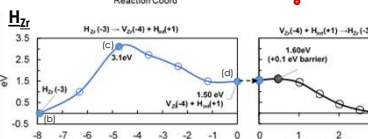


H migration barriers (H_{Zr} vs H_{int})



Cation Migration Barrier	H _{Zr} (-3)	V _{Zr} (-4)
out-of-ab-plane hop	2.7 eV	2.4 eV
in-ab-plane hop	3.1 eV	3.0 eV

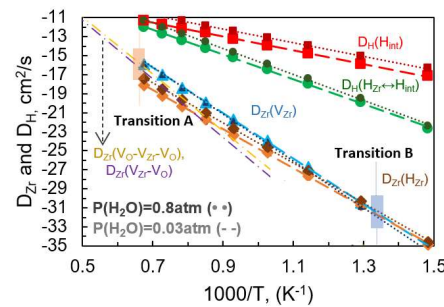
H Migration Barrier	H _{Zr} (-3)	H _{int} (+1)
	1.6 eV	0.2~0.4 eV



Summary

- Most of the stable hydrogen defect species in tetragonal bulk ZrO₂ is H_{Zr}(-3), and its concentration is 4~6 orders magnitude higher than that of H interstitial (H_{int}). Nonetheless, the most active hydrogen transport occurs via H_{int}(+1) with migration barriers 0.2~0.4 eV than through the stable H_{Zr}(-3) defect which has a larger migration barrier of 1.6 eV
- The calculated diffusion coefficients reveal that cation diffusion in tetragonal bulk ZrO₂ will transit from the V_{Zr}(-4) mechanism at high temperatures to the H_{Zr}(-3) mechanism upon lowering the operating temperature and/or increasing the humidity content
- The model further predicts another transition in the bulk cation transport mechanisms, V_{Zr} → fully- or partially-bound Schottky defects above T=1573 K (attributed to enhanced gas entropic stabilization) [2,3]:
 - Formation of V_{Zr}(-4), Zr₂O₃ + O₂ → V_{Zr}(-4) + ZrO₂ - (-4) · h⁺, involves the O₂ gas phase (or H₂O - H₂) on the reactant side, which destabilizes the reaction with increasing temperature; this gas effect was further balanced in the Schottky defect formation.

Dependence of Modeled D_{Zr} and D_H on 1/T



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