Cation Diffusion in Bulk Tetragonal ZrO_2 for Solid Oxide Fuel Cells: Effects of Defect Clusters and Hydrogen on Cation Transport

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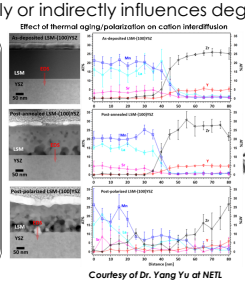
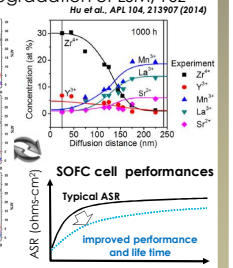
Motivation

Cation diffusion directly or indirectly influences degradation of LSM/YSZ

- **Defects:** [Vö], [V_A'''], [V_B''], [V_{Zr}''''], [V_Y'], etc.
- **Transport:** D_{ij}^*(LSM), D_{ij}^*(YSZ), ΔE_{mig}
- **Composition:** C_{ij}(interface)
- **Microstructures, TPB Density, etc** vs. **T, P(O_2)**, and **time**
- **Effect of H_2O, CO_2 and other impurities (Cr, Si, etc.).**





Develop quantitative models to assess defect chemistry and cation diffusivities in bulk YSZ and LSM vs T and P(O_2) based on *ab initio* energetics and exp.

- **Cation diffusion in bulk YSZ and LSM**
- **Property assessment of diffuse interfaces**

Defect Interactions in t-ZrO_2

V_{Zr}-V_O Interactions (dry conditions)

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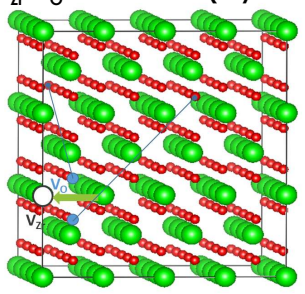
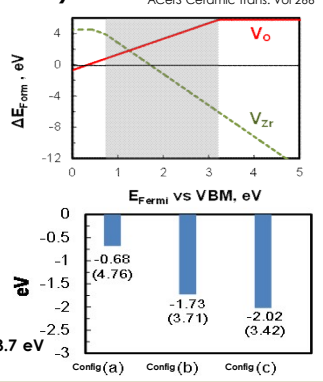
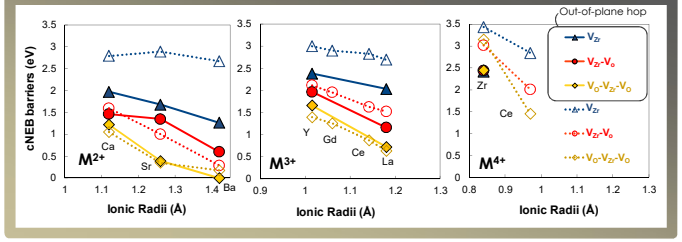


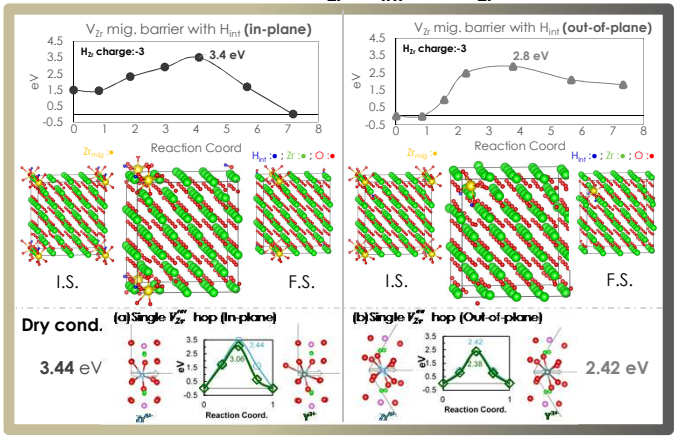


ΔE_{Form} of non-interacting Schottky : **5.4 eV**
(a) Separate Schottky (V_{Zr}+2V_O far):**4.8 eV**
(b) Partially bond Schottky (V_{Zr}-V_O+V_O far):**3.7 eV**
(c) Fully bond Schottky (V_O-V_{Zr}-V_O): **3.4 eV**

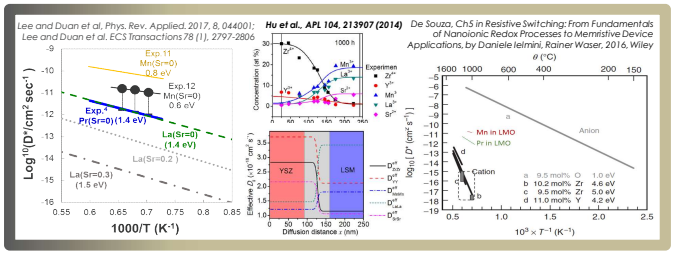
Trends in the cation migration barriers



Zr Migration Barriers (V_{Zr}+H_{int} vs. V_{Zr})



Cation Diffusivities in Bulk LSM and YSZ



Cation Diffusion Pathways in t-ZrO_2 (Dry Cond.)

Migration barriers of various pathways

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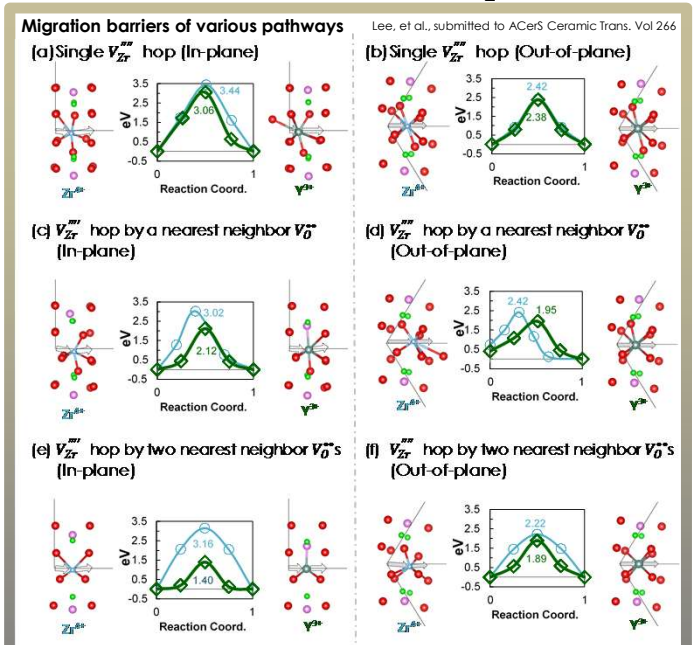
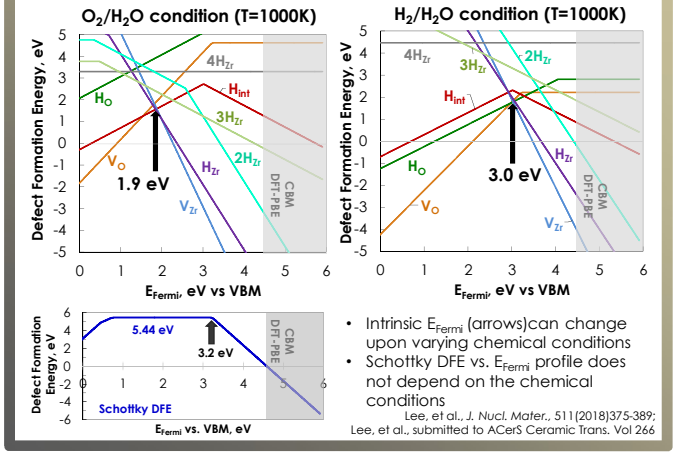


		$V_O^{\bullet\bullet}$- V_{Zr}''''-$V_O^{\bullet\bullet}$		V_{Zr}''''-$V_O^{\bullet\bullet}$		V_{Zr}''''	
		ΔE_{form}(eV)	ΔE_{mig}(eV)	ΔE_{form}(eV)	ΔE_{mig}(eV)	ΔE_{form}(eV)	ΔE_{mig}(eV)
Zr^{4+}	In-ab-plane	3.42	3.16	3.71	3.02	5.44	3.44
	Out-of-ab-plane		2.22		2.42		2.42
Y^{3+}	In-ab-plane	3.42	1.89	3.71	2.12	5.44	3.06
	Out-of-ab-plane		1.40		1.95		2.38

Ab Initio Charged Defect Analysis for t-ZrO_2

$$\Delta E_{form}(X^q) = E^T_{defect}(X^q) - E^T_{perf}[bulk] + \Sigma n_i\mu_i + q\mu_e + E_{corr}$$



- Intrinsic E_{Fermi} (arrows)can change upon varying chemical conditions
- Schottky DFE vs. E_{Fermi} profile does not depend on the chemical conditions

Lee, et al., *J. Nucl. Mater.*, 511(2018)375-389; Lee, et al., submitted to ACerS Ceramic Trans. Vol 266

Summary

1. Ab initio charged defect analysis was performed for the defect energetics of t-ZrO_2 under the SOFC operating conditions:
   - Intrinsic E_{fermi} depend on chemical conditions
   - Including H defects shifts intrinsic E_{fermi}; H_{Zr} can also be cation transport carriers.
2. Strong attractive interactions (1~2 eV) found for V_{Zr} and V_O (also V_{Zr} and H_{int})
3. Partial and full bound Schottky defect clusters significantly alter cation migration barriers
   - **1~2 eV difference in barriers** among the **V_{Zr}, V_{Zr}-V_O, and V_O-V_{Zr}-V_O** pathways
4. Both thermodynamic stability of transport defect complexes and the corresponding barriers for cation migration are needed from atomistic modeling for resolving cationic diffusivities
5. Modeled activation energies of D(Zr) in t-ZrO_2 and in YSZ are in the range of 6~8 eV (Exp. 6.3-6.5 eV; Kilo, Defect. Diffus. Forum, 194-199 1039-44 (2001); Chokshi, Scripta Mater., 48[6] 791-96 (2003))
6. At presence of H defects
   - Symmetry of migration energy landscape was broken due to interaction of H_{int} and V_{Zr}
   - Comparable migration barriers for the H trapping states (H_{Zr}) vs. the dry condition (however, attractive interaction between V_{Zr} and H_{int} may stabilize H_{Zr} vs. V_{Zr}+H_{int})
   - Lower cation migration barriers when involving the H_{int} untrapped states

Acknowledgements

This research was supported in part by an appointment to the National Energy Technology Laboratory Research Participation Program, sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education. Y.-L Lee and Y. Duan would like to thank Dr. Kirk Gerdes for his helpful comments to this work