Defect Thermodynamics and Transport Properties of Perovskite and Fluorite Materials for Solid-Oxide and Proton Conducting Oxide Cells Evaluated Based on Density Functional Theory Modeling

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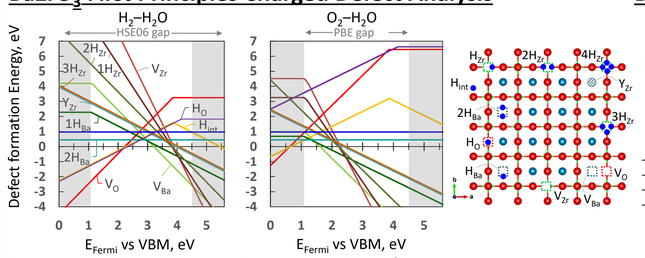
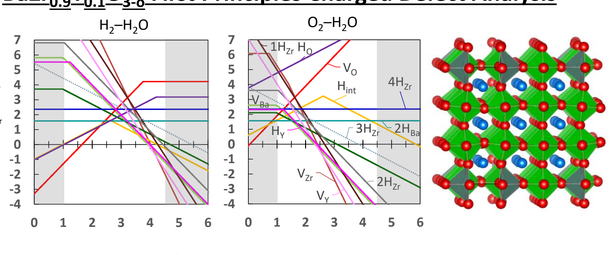
Modeling of $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) Defect & Transport Properties for Proton Conducting Electrolytes [1]

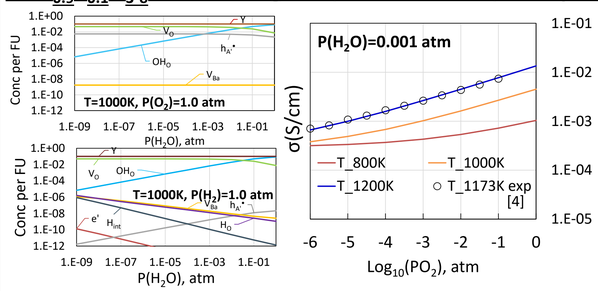
$BaZrO_3$ First Principles Charged Defect Analysis



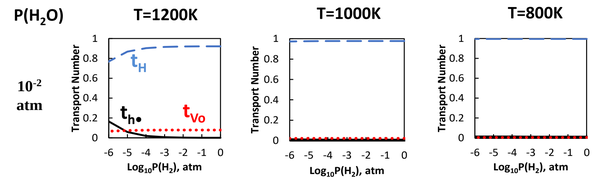
$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ First Principles Charged Defect Analysis



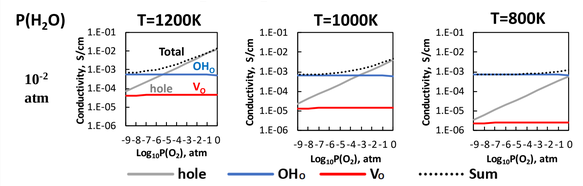
$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ Brower Diagrams, Conductivities, Transport Numbers vs. $P(O_2)/P(H_2)$ and $P(H_2O)$



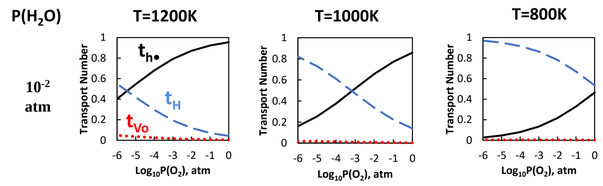
Transport Number vs. $P(H_2)$ at $P(H_2O)$= 10^{-1}, 10^{-2}, and 10^{-3} atm



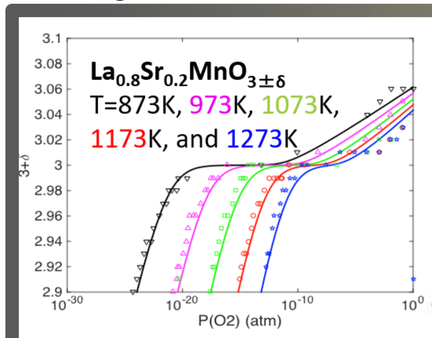
Total Conductivity vs. $P(O_2)$ at $P(H_2O)$= 10^{-1}, 10^{-2}, and 10^{-3} atm

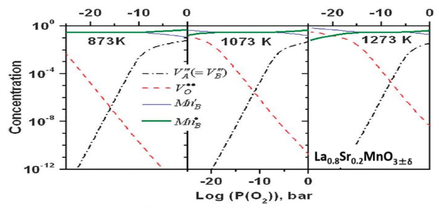


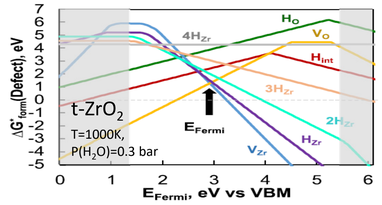
Transport Number vs. $P(O_2)$ at $P(H_2O)$= 10^{-1}, 10^{-2}, and 10^{-3} atm



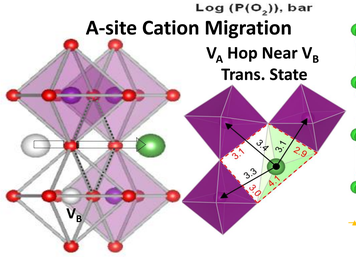
Modeling of Cation Defect and Transport Properties in Bulk LSM and YSZ [2,3]

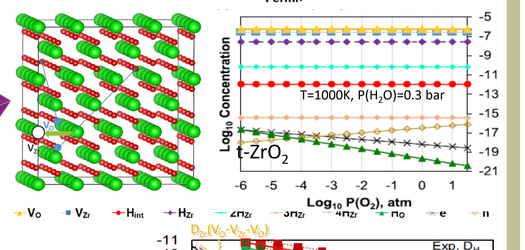




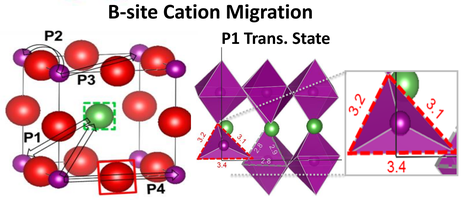


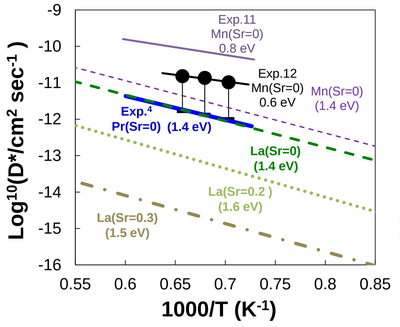
A-site Cation Migration

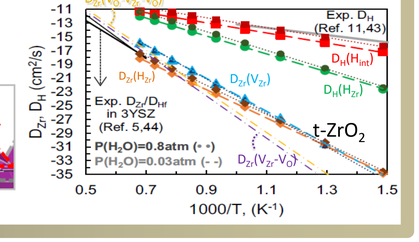




B-site Cation Migration





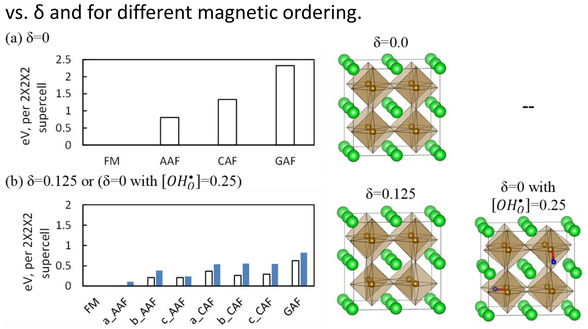


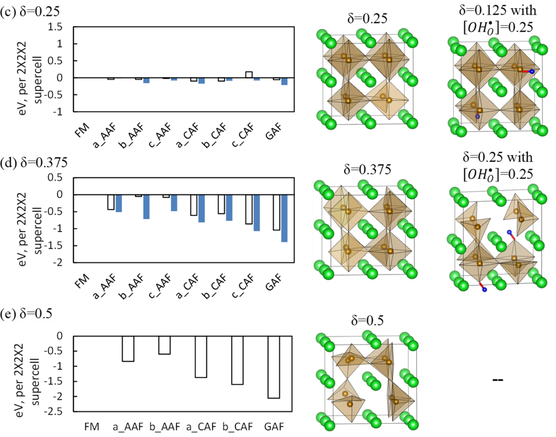
Defect Thermodynamic Modeling of $(La,Ba)Fe_{1-x}M_xO_{3-\delta}$ Triple Conducting Electrodes [4,5]

GNU-Octave scripts of the $(La,Ba)Fe_{1-x}M_xO_{3-\delta}$ defect model solver available at NETL-EDX:

https://edx.netl.doe.gov/dataset/triple_conducting_perovskite_defect_model

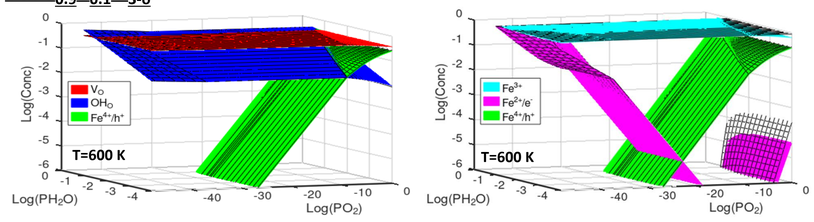
Stability of dry (white bar) and hydrated (blue bar) $BaFeO_{3-\delta}$ vs. δ and for different magnetic ordering.



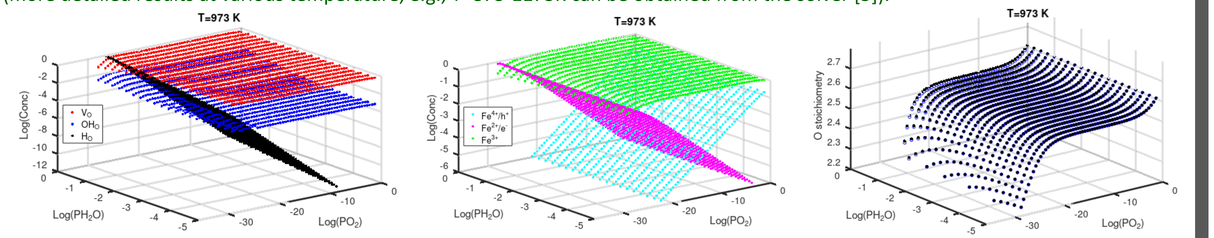


Defect reaction energies as a function of δ as obtained by DFT modeling were used to generate Brouwer diagrams of $BaFe_{0.9}Y_{0.1}O_{3-\delta}$ [4].

$BaFe_{0.9}Y_{0.1}O_{3-\delta}$



$Ba_{0.95}La_{0.05}Fe_{0.9}O_{3-\delta}$: Experimental hydration and defect formation enthalpies and entropies reported in the literature [6] were used to generate Brouwer diagrams of $Ba_{0.95}La_{0.05}Fe_{0.9}O_{3-\delta}$ [6], with addition of the modeled hydride (H_O) defect formation energies and entropies incorporated into the model to examine defect equilibria under reducing conditions at various operating temperatures (more detailed results at various temperature, e.g., T=873-1173K can be obtained from the solver [5]).



Conclusions

- Density functional theory-based defect thermodynamic modeling was performed to determine the effect of humidity and H_2/O_2 gas pressure on various defect chemistry and transport properties of perovskite and fluorite oxides for solid-oxide and proton-conducting-oxide cell applications, with inclusion of the electronic-conducting oxides (as electrodes) and insulating oxides (as electrolytes).
- A GNU Octave defect model subroutines were developed to facilitate defect modeling of electronic conducting oxides in a wide range of operating conditions guided by modeling and experiments. The model includes the hydride defect formation reaction under reducing conditions and is able to incorporate nonstoichiometry effects on the defect thermodynamic parameters.
- Automatic defect generation workflow and first principles charged defect analysis were implemented on the NETL Joule supercomputer for modeling defect equilibria and transport properties of insulating oxides as electrolytes in SOCs and proton-conducting ceramic cells.

References

1. Y.-L. Lee, et al, *Defect Thermodynamics and Transport Properties of Proton Conducting Oxide $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) Guided by Density Functional Theory Modeling*; **JOM**, (2022), 74, 4506
2. Y.-L. Lee, et al, **Phys. Rev. Applied**, 8(2017) 044001.
3. Y.-L. Lee, et al, **Physical Review Research**, (2021), 3, 013121.
4. Y.-L. Lee, et al **ECS Transactions, (2023) 111, (6) 1823-1838** for the 18th International Symposium on Solid Oxide Fuel Cells.
5. GNU-Octave scripts of (La,Ba)$Fe_{1-x}M_xO_{3-\delta}$ defect model solver are available at DOI: 10.2172/2328139
6. Zohourian et al, Adv. Funct. Mater. 2018, 28, 1801241; Bae et al, J. Electrochem. Soc. 2021, 168, 034511

Acknowledgements and Disclaimer

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