

ATOMIC LEVEL COMPUTATIONAL STUDIES OF IONIC DEFECTS AND TRANSPORT PROPERTIES OF SOLID STATE IONIC CONDUCTORS

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Solid state ionic conductors (or electrolytes) are a vital component for electrochemical devices or systems for chemical and energy transformation. The chemical composition, crystal structure, defects, morphology, and electronic structure of these materials greatly affect their electrochemical properties such as ionic and electronic conductivity.

Similar to barium zirconate (BaZrO_3), barium hafnate (BaHfO_3) is one of the most promising proton-conducting electrolytes for solid oxide fuel cells (SOFCs) because of their high proton conductivity at 400~700 °C. In this study, I have investigated dopant solubility, proton concentration, mobility, and chemical stability of A/B-site co-doped BaHfO_3 using density functional theory calculations coupled with statistical thermodynamics. Specifically, I have calculated defect formation energy in charged supercells, finite temperature vibrational energy *via* phonon calculations in the harmonic approximation, proton migration energy *via* transition state theory, and defect-defect interactions *via* cluster-expansion method. A wide range of relevant properties are predicted, including the degree of hydration governed by hydration Gibbs free energy, proton diffusion coefficient derived from proton migration barrier search, and defect-defect interactions using cluster expansion method. These properties are sensitive to the type and

amount of chemical dopants in the lattice, including Li, Na, K, Rb, and Cs on A-site and Sc, Y, La, Gd, Lu, Al, Ga, and In on B-site. The mismatch in the size of the dopant and the host ion induces local strain or elastic interactions. However, the electrostatic interactions between them are much less dependent on the ionic radius of dopant ions. Accordingly, the dependence of the dopant-proton binding energy on ionic radius of dopant has a “volcano” shape. In addition, the electronegativity of dopant ions also affect the affinity of acceptor-type dopants with donor-type protons. Hydration is promoted by both the A-site and the B-site dopants, although the effect of the latter is less pronounced. In general, a “trade-off” relation between proton concentration and mobility is observed in all cases, regardless of the ionic radius or the lattice site (A- or B-site) of the dopants.

Defects play an important role in ionic transport and in enhancing catalytic activities for chemical and energy transformation processes. Thus, it is crucial to understand how to effectively enhance ionic transport by rationally design preferred defect structures, including 0D (point defects such as vacancies), 1D (dislocation), and 2D (grain boundary) defects. For example, local ion segregation may result in a space charge region, leading to accumulation of mobile charge carriers or improved mobility near those 1D/2D defects. The effect of the space charge layer, strain near 1D/2D defects, as well as collective defect-defect interactions pose an extreme challenge for both experiments and computations. In this study, the effect of an edge dislocation in Y:BaZrO₃ on oxygen ion transport is evaluated. To probe the ion mobility, a reactive molecular dynamics simulation based on ReaxFF is utilized to simulate the super-large Y:BaZrO₃ supercell with two edge dislocations. Radial distribution functions and thermal/chemical expansion coefficients are used to benchmark the local and global structure properties, and mean-square displacements are used to calculate diffusivity and conductivity. Dislocation is found to lower the activation energy

of ionic transport, possibly because of distinct oxygen cage structures locally at the dislocation core. However, optimal Y% for oxygen ion conductivity is shifted to higher levels with increasing temperature. This could be due to the weakening of Y's electrostatic "trapping effect".

Besides materials chemistry and microstructural features, the mechanical strain is another factor affecting ionic properties. Ceria (or CeO_2) is a prototypical ionic material for catalyst and electrolyte applications. Chemo-mechanical coupling in ceria significantly affect the bulk defect properties of ceria. In this study, the effect of chemo-mechanical coupling is extended from the bulk to the (111) surface of ceria. There have been extensive theoretical and experimental research on the configurations of vacancies and polarons on the (111) surface, the dominantly exposed surface, which is crucial to surface catalytic activity. It was reported that surface oxygen vacancy on ceria's (111) surface is not necessarily the most stable vacancy; however, the sub-surface vacancy could be. Similarly, polarons are not necessarily at the 1st-nearest-neighbor (1NN) of the corresponding vacancy either; they could be at the 2nd-nearest-neighbor (2NN). All those counter-intuitive phenomena were unveiled and validated both theoretically and experimentally. Inspired by previous research, I have identified a unique way of tuning defect configurations by applying tensile and compressive epitaxial strain on (111) slab. Across the magnitude of the applied strain from -5% compression to +5% tension, stability relationships of the surface vs. the sub-surface vacancy, the 1NN vs. the 2NN polaron, and the vacancy monomer vs. the dimer are surprisingly reversed. Elastic, electrostatic and electronic excitation energies are found to be dependent on defect-configuration. This gives us a new perspective to interpret the various vacancy patterns observed on (111) surface of the prepared ceria samples.