Understanding of the vacancy formation, interaction, increasing its concentration and diffusion, and controlling its chemical strain will advance the design of mixed ionic and electronic conductor (MIEC) materials via element doping and strain engineering. This is especially central to improve the performance of the solid oxide fuel cell (SOFC), an energy conversion device for sustainable future.

The oxygen vacancy concentration grows exponentially with the temperature at dilute vacancy concentration but not at higher concentration, or even decreases due to oxygen vacancy interaction and vacancy ordered phase change. This limits the ionic conductivity. Using density functional theory (DFT), we provided fundamental understanding on how oxygen vacancy interaction originates in one of the typical MIEC, La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ (LSF). The vacancy interaction is determined by the interplay of the charge state of multi-valence ion (Fe), aliovalent doping (La/Sr ratio), the crystal structure, and the oxygen vacancy concentration and/or nonstoichiometry ($\delta$). It was found excess electrons left due to the formation of a neutral oxygen vacancy get distributed to Fe directly connected to the vacancy or to the second nearest neighboring Fe, based on crystal field splitting of Fe 3d orbital in different Fe-O polyhedral coordination. The progressively larger polaron size and anisotropic shape changes with increasing Sr-content resulted in increasing oxygen vacancy interactions, as indicated by an increase in the oxygen vacancy formation energy above a critical $\delta$ threshold. This was consistent with experimental results showing that Sr-rich LSF and highly oxygen deficient compositions are prone to oxygen-vacancy-ordering-induced phase transformations, while Sr-poor and oxygen-rich LSF compositions are not. Since oxygen vacancy induced phase transformations, cause a decrease in the mobile oxygen vacancy site
fraction (X), both δ and X were predicted as a function of temperature and oxygen partial pressure, for multiple LSF compositions and phases using a combined thermodynamics and DFT approach. A detailed oxygen vacancy migration barrier calculation gave the oxygen ionic diffusivity and conductivity.

Oxygen vacancy also causes chemical strain, which was treated as a scalar in the literature. However, in many materials, it should be a tensor, which is anisotropic. We illustrate this effect on CeO2, in which it explained a puzzling experiment, which shows significant amplification of measured strain on applied bias in non-stoichiometric Gd doped ceria. The presence of highly localized 4f valence orbital in Ce causes charge disproportionation on the formation of neutral oxygen vacancy, producing anisotropic chemical strain in ceria with cubic symmetry. Understanding of δ and X and anisotropic chemical strain in the lattice has led to the design of better MIEC via element doping and strain engineering of the lattice.