The Effect of an Oxygen Vacancy on Proton Conduction Pathway in Scandium-doped $BaZrO_3$

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Acceptor-doped proton conductive barium zirconate is a promising fuel cell electrolyte candidate. Experiments and simulations suggest that an oxygen vacancy (OV) can significantly alter proton binding energies and pathways in scandium-doped barium zirconate [1, 2]. Starting from literature potential energy parameters and ab initio calculations, a few empirical potentials are tested. Each is used to find minima and transition states using the conjugate gradient optimization and the nudged elastic band method. The minima and transition states are used to create a proton conduction graph. Graph theory ideas, kinetic Monte Carlo and time-based centrality measures were used to find periodic proton conduction pathways, dynamic proton conduction pathways, and a map of highways and junctions near and far from the oxygen vacancy. We discovered that the most probable pathway far from the OV is consistently dark, which indicates high centrality, suggesting that it is a fast motion area for proton transfers. The pathway close to the OV contains both light and dark bonds, which indicates high contrast of high and low centrality, suggesting that this path has higher energy barrier. In addition, protons tend to have very limited movements in the KMC pathways, regardless of the distance from the oxygen vacancies.

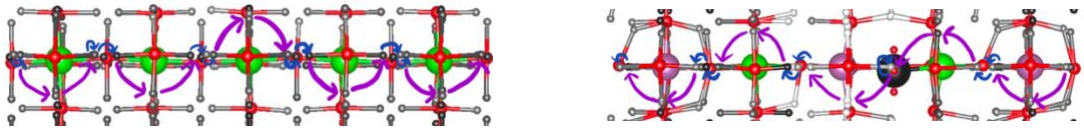

Figure 1. The left image shows the centrality of most probable long-range pathway far from the oxygen vacancy, while the right image shows the centrality of the most probable long-range pathway close to the oxygen vacancy. The black atom shown in the right image represents the oxygen vacancy. The arrows indicate the movement of proton. Purple arrows represent “rotation”, and blue arrows represent “intra-octahedral transfer”.

[1] Oikawa, I.; Takamura, H. Correlation among Oxygen Vacancies, Protonic Defects, and the Acceptor Dopant in Sc-Doped $BaZrO_3$ Studied by 45Sc Nuclear Magnetic Resonance. Chem. Mater. 2015, 27, 6660– 6667, DOI: 10.1021/acs.chemmater.5b02441

[2] Lin, Z., Lin, S., Tian, Y., Van Bokkelen, A., Valerio, M., Gomez, M.A., 2020. Oxygen Vacancies Altering the Trapping in the Proton Conduction Landscape of Doped Barium Zirconate. The Journal of Physical Chemistry C 124, 27954–27964. DOI:10.1021/acs.jpcc.0c09461