Multi-step Kinetic Monte Carlo Simulations and Topological Analysis to Determine Proton Conduction Pathways and Binding Site Relationships in Perovskite Systems

Rachel A. Krueger, Maria A. Gomez
Department of Chemistry, Mount Holyoke College, South Hadley, MA

Fuel cells featuring solid oxide electrolytes (SOFCs) have attracted increasing interest as efficient alternatives to hydrocarbon-combustion based means of energy production. Perovskites doped with lower-valance cations have displayed mechanical stability and high proton conductivity in the key 500-700 ℃ temperature range, making investigation of the proton conduction mechanism and probable conduction pathways in such materials an important step in the fuel cell development process[1,2]. Our inquiry has focused on three perovskite systems: Y-doped $BaZrO_3$, Y-doped $SrZrO_3$, and Al-doped $SrZrO_3$

Because proton conduction in perovskite systems involves a series of relatively rare proton rotation and transfer steps, it can be modeled with kinetic Monte Carlo (KMC) simulations over longer periods of time than would be practical for molecular dynamics (MD) simulations. The standard KMC algorithm involves moving the system from one energy well to another—moving the proton from one binding site to another—using a random number and rate constants for each possible escape path to ensure that moves are picked in proportion with their probability. The simulation's clock is advanced after each move by a random time picked from an exponential distribution[3,4]. Our group has modified the standard KMC algorithm to generate n-step pathways from each site using graph theory and dynamic programming. At each iteration of the algorithm, an n-step pathway rather than a single move is selected. Times selected and pathways generated for each system from this multistep KMC algorithm have been in good agreement with standard KMC results, and for long KMC runs (10,000,000 iterations), two to four-step escape paths display optimal runtimes.

Topological methods have been employed to provide additional insight into the relationships between binding sites. When the binding sites in a perovskite system are represented as vertices in a graph, information about the connections between sites and the probability of proton transition from one site to another can be given in the form of several matrices. Diagonalization of one of these matrices, the Laplacian matrix, has been used to rank vertices' contributions to the graph in graphs representing proteins, successfully identifying residues important for folding[5]. Diagonalization of Laplacian matrices representing the perovskite system has been used to rank sites according to the same criteria. The contrasting rankings for Al-doped and Y-doped $SrZrO_3$ have been generally consistent with contrasting trends in conduction pathways for the two systems[5], suggesting that such ranking may prove a quick, useful tool for predicting general conduction pathway trends for perovskite systems. A second method of system representation and site ranking involving an asymmetric Laplacian matrix, which has been recommended for wireless network problems[7], has also been considered.

[1]B.C.H. Steele and A. Heinzel. Nature, **414**, 6861 (2001).
[2]L. Malavasi, C. A. J. Fisher, and M. S. Islam, Chemical Society Reviews. **39**, 4370 (2010).
[3]Voter, A. F. *Radiation Effects in Solids;* Springer: Netherlands, 2007.
[4]Chatterjee, A. and D. G. Vlachos, J. Computer-Aided Mater Des. **14**, 253 (2007).
[5]S. Vishveshwara, K. V. Brinda, and N. Kannan, Journal of Theoretical and Computational Chemistry, **1**, 1 (2002).
[6]M. A. Gomez, M. Chunduru, L. Chigweshe, L. Foster, S. J. Fensin, K. M. Fletcher, and L. E. Fernandez, J. Chem. Phys. **132,** 214709 (2010).
[7]D. Boley, G. Ranjan, and Z. Zhang, Linear Algebra Appl. **435**, 224 (2011).