Molecular Dynamics Studies of ZrO_2 and CeO_2 Based Solid Oxide Fuel Cell (SOFC) Materials

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Abstract: Solid oxide fuel cells (SOFCs) are a class of portable primary energy devices, that stand the potential as a green and sustainable alternative to fossil fuels. However, widespread commercial adoption of these electrochemical devices demands significant advancements in their design and efficiency as well as the development of infrastructural ecosystem. The electrolyte, that is sandwiched between the electrodes, is a crucial component of an SOFC device, having a critical impact on its performance. For the efficiency, operational safety, and lifespan of SOFC devices, the electrolyte material has to meet several criteria, such as high ionic conductivity, high chemical and mechanical stability, compatibility with potential electrodes, etc. As argued in the Introduction of this thesis, zirconia (ZrO_2) and ceria (CeO_2) based ceramic solids are among the most promising choices for practical applications, though their commercial viability demands further improvements. A thorough understanding of the microscopic nature of ion transport and the factors governing it is crucial to the necessary advancement of SOFC devices.

The thesis attempts to bring out fresh insights into the microscopic mechanism of ion transport in yttria doped ceria and zirconia employing molecular dynamics (MD) simulations. The theoretical foundations and computational algorithms of MD simulations are discussed in Chapter 2 of the thesis. Chapter 3 of the thesis discusses the nature of oxide ion transport in yttria-doped ceria, in terms of the microscopic energy barriers, local environments and residence times of oxygen ions at their tetrahedral sites, and other pertinent details. Chapter 4 explores oxide ion migration in yttria- stabilized zirconia (YSZ) with a focus on the energetic aspects of different pathways linking oxygen sites as well as of the saddle points due to the specific cationic edges. The study suggests a significant degree of oxide ion correlations in YSZ matrix. In Chapter 5, the impact of cationic distribution (Zr^{4+}/Y^{3+}) on oxide ion transport in the YSZ matrix is examined. The study finds that certain cationic ordering can enhance the ionic conductivity up to four orders of magnitude relative to the randomly ordered structures. The findings of the studies are summarized in Chapter 6, along with a glimpse at possible future directions.