MECHANISTIC INSIGHTS INTO HYDRATION OF SOLID OXIDES

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EXECUTIVE SUMMARY

Some solid oxide materials used in solid oxide fuel and electrolysis cells are known to conduct protons once the materials are hydrated. However, the mechanisms by which solid oxide materials become hydrated are not clear. By performing detailed density functional theory (DFT) calculations, we investigate hydration of two typical solid oxides with a single-crystal structure—a proton-conducting yttrium-doped strontium zirconate (SZY) and an oxide ion-conducting yttria-stabilized zirconia (YSZ). We suggest a four-step process to understand the hydration of solid oxides—water adsorption on the surface, proton migration from the surface to bulk, proton migration in the bulk, and oxide ion vacancy migration in the bulk. Our analysis provides mechanistic insights into the hydration of single-crystal SZY and nonhydration of single-crystal YSZ. Our study not only explains the hydration of materials, but also illustrates the importance of structural rearrangement when a proton is incorporated into the bulk of the solid oxide material.

RESEARCH CHALLENGE

Hydrogen production has attracted great interest as it is a clean and sustainable fuel and is a promising choice for the storage of intermittent renewable energies such as solar and wind power [1]. Water electrolysis using renewable energy is considered to be one of the cleanest methods to produce hydrogen [2], and electrolysis cells are widely used for this purpose. Compared to a commercially available polymer electrolyte membrane (PEM)-based low-temperature electrolysis cell, a solid oxide electrolysis cell (SOEC) operating at a high temperature can take advantage of thermal energy to reduce electrical energy demand. This results in a reduced cost and enhanced efficiency for hydrogen production [3]. However, the design and development of solid oxide electrolytes with sufficient stability and enhanced conductivity for SOEC are still a challenge.

Oxide ion conductors are commonly used as electrolytes in SOECs. For example, ZrO_2 doped with Y_2O_3 (YSZ) exhibits sufficient oxide ion conductivity as well as thermal and chemical stability at high temperature [2]. Comparing SOECs with oxide ion-conducting electrolytes, SOECs with proton-conducting electrolytes such as Y-doped $SrZrO_3$ (SZY) can produce pure and dry hydrogen. In order to design high-conductivity proton conductors, a fundamental understanding of what determines whether an oxide ion conductor can become a proton conductor is needed. The origin of proton conduction, which is attributed to the hydration process, is of significant importance for the development of proton conductors. The hydration reaction can be written in Kröger-Vink notation [4] as $H_2O(g)+V_O^{..}+O_O^x$ ä $2OH_O^.$, where $V_O^{..}$, O_O^x, and $OH_O^.$, denote the oxygen vacancy, lattice oxygen, and protonic defect in the hydrated structure, respectively. Significant effort has gone into correlating hydration thermodynamics (hydration enthalpy and entropy) and material properties such as the type and concentration of acceptor dopant on the B-site of perovskites [6,7], the difference in electronegativity between B- and A-site constituents in perovskites [5], and chemical expansion of perovskites [8]. However, the existing approaches have not been able to describe the detailed dynamic process of hydration. In this work, density functional theory (DFT) calculations are performed to investigate the hydration behavior of solid oxides.

METHODS & CODES

All DFT calculations are performed using the Vienna Ab initio Simulation Package (VASP) [9–11]. The Perdew–Burke–Ernzerhof [12] exchange-correlation functional is employed based on the projector augmented wave method [11]. The cutoff energy for the plane-wave basis set was 500 eV for all calculations. All the calculations are spin polarized. Bader population analysis is performed to calculate the atomic charges [13]. The migration energy barriers are calculated using the climbing image nudged elastic band method [14].

RESULTS & IMPACT

Based on DFT calculations, we investigated the hydration processes in two different solid oxides with a single-crystal structure—a proton-conducting SZY and an oxide ion-conducting YSZ.

The water adsorption calculations show that both the SrO (001) surface of SZY and (111) surface of YSZ are favorable for the dissociative adsorption of water. The structural minimization and charge analyses indicate that the water molecule is adsorbed as two hydroxide ions on the surface. The calculations for proton migration from the surface to bulk show that the energy barrier for YSZ is larger than that of SZY for both hydroxide ion migration and proton hopping. In addition, the energy barriers for proton migration in both bulk SZY and YSZ structures are relatively small and comparable. The energy barrier for the oxide ion vacancy migration in bulk SZY is slightly larger than that of bulk YSZ, but the results confirm that bulk SZY shows oxide ion conductivity. The migration of the oxide ion vacancy from the bulk to the surface of the oxide ensures that water is not only adsorbed on the surface but also hydrates the interior (in the case of SZY). Our results
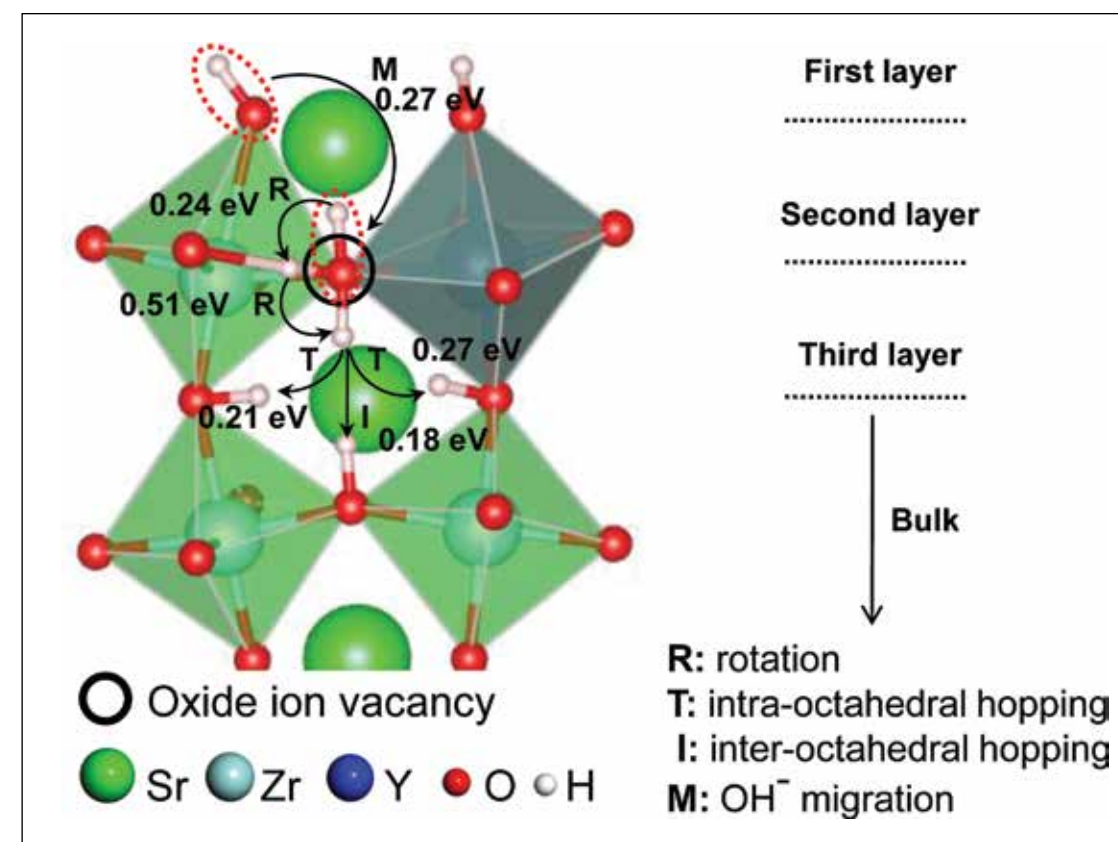

Figure 1: NEB results for proton migration from the surface to bulk of perovskite structure.

indicate that the primary difference between the hydration of SZY and YSZ comes from the energy barriers for proton migration from the surface to the bulk of the oxide material.

Our results not only provide mechanistic insights into the hydration of single-crystal SZY and nonhydration of the single-crystal YSZ, but also the importance of structural rearrangement when a proton is incorporated into the bulk of the solid oxide material.

WHY BLUE WATERS

In our work, large-scale *ab initio* simulations are needed to obtain the dynamics of hydration in solid oxides. For the proposed DFT calculations, using eight to 10 nodes (256 to 320 cores) for each job can achieve the best performance, which is attributed to the power of Blue Waters and the support of project staff. Thus, we could run *ab initio* simulations on Blue Waters easily and quickly and speed up our research greatly.

PUBLICATIONS & DATA SETS

Jing Y., H. Matsumoto, and N.R. Aluru, Mechanistic Insights into Hydration of Solid Oxides. *Chem. Mater.*, 30 (2018), pp. 138–144.