Structural and electronic parameters governing proton migration barriers in $BaFeO_{3-\delta}$: a computational study

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Ceramic materials capable of conducting protons exhibit superior ionic conductivity compared to oxide ion conductors, particularly within the intermediate temperature range of 300-600°C. Optimized cathode materials for protonic ceramic fuel cells (PCFCs) with mixed protonic and electronic conductivity (e.g. $(La,Ba,Sr)(Co,Fe,Zn,Y)O_{3-\delta}$)[1] are crucial for its performance. In our investigation, we utilized DFT calculations to analyze $(La,Sr)FeO_{3-\delta}$[2] and $(Ba,Sr)FeO_{3-\delta}$[3], elucidating the influence of La/Sr or Ba/Sr content and the formal oxidation state of Fe on hydration energies. Our findings align well with experimental observations[1].

Here[4], we employ PBE+U and HSE06 density functionals to analyse the migration trajectories and barriers in $BaFeO_{3-\delta}$. The analysis of structural changes and chemical bonding in individual proton trajectories indicates that the proton transfer occurs as a two step-process: an early stage where donor and acceptor oxygens approach, i.e. the O...H hydrogen bond is strengthened, and a second stage when the covalent O-H bond is broken. We find that the initial O...O and O-H distances exhibit the strongest correlation with the calculated migration barriers, suggesting their significance as key structural parameters. Other properties used in our analysis include the atomic charges and magnetic moments, Fe oxidation state, the electronic density of states and associated oxygen p-band centres, and crystal orbital hamiltonian population (COHP).

Notably, we observe[4] a decrease in proton migration barriers from 0.17-0.28 eV for $BaFeO_3$ to values ranging from 0.10 to 0.26 eV for $BaFeO_{2.75}$ with oxygen deficiency and correspondingly decreased formal Fe oxidation state. This correlation between proton barriers and electronic structure represents a distinctive characteristic of redox-active materials. The fact that the proton migration barriers in $BaFeO_{3-\delta}$ are comparable to or even slightly lower than in $BaZr_{1-x}Y_xO_{3-x/2}$ electrolyte materials indicates that $BaFeO_{3-\delta}$ cathodes may achieve the protonic conductivity required for good PCFC performance.

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