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ABSTRACT:

Topochemical Hydrogenation Transition in (Ba, Sr)(M, In)$O_{3-\delta}$ Perovskites

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This study investigates the topochemical transformation of $BaM_{1-x}In_xO_{3-0.5x}$ (M = Zr, Ce, Ti) from a proton-conducting oxide phase (BMI) to a hydride-ionic oxyhydride (H-BSI) under ambient hydrogen pressure. The transformation is driven by the reduction of B-site In(III) cations and the incorporation of hydride (H^-) ions, with notable variations depending on the M cations. In BSI with x = 0.7, both Sn and In are reduced, leading to the formation of oxygen vacancies at Sn-O-In bridge sites, which enables efficient H^- ion conduction via a three-dimensional vacancy network. This structure supports H^- ion hopping through a nearest-neighbor (1NN) path, with an activation energy of 56 kJ mol^{-1}, consistent with theoretical predictions. In contrast, the BSI with x = 0.5 predominantly exhibits Sn reduction, with oxygen vacancies restricted to Sn-O-Sn bridges, resulting in a one-dimensional vacancy arrangement. This configuration increases the activation energy (~320 kJ mol^{-1}) for ion hopping along the second nearest neighbor (2NN) path, leading to poor H^- ion conductivity. Density functional theory (DFT) calculations reveal that the covalent bond between H^- ions and Sn^{2+}/In^{+} stabilizes the hydride-ionic phase. Additionally, DFT indicates that H^- ion hopping occurs in a mechanism similar to Grotthuss, in which H^- ion breaks the covalent bond with the originally coordinated Sn1(II) cation and forms a new bond with nearby In(I) or Sn(II) cations as it moves to the adjacent anion vacancy site. These findings demonstrate the potential of highly oxygen-deficient perovskites with lone-pair B-site cations as thermodynamically stable, fast H^- ion conductors, with significant implications for energy-related applications.

[1] H. Toriumi et al, Chem. Mater. 34, 7389–7401 (2022).
[2] T. Takahashi et al, Chem. Mater. doi/10.1021/acs.chemmater.4c02903.