A Platinum Emulating Solid-State Electrocatalyst for Hydrogen Evolution Reaction (HER): Unfolding the Kinetics of Proton and Electron Transfer in Sodium Tungsten Bronze Perovskite

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This work explores a viable alternative to platinum as a catalyst to perform the hydrogen evolution reaction (HER), a key step towards renewable energies. To do so, a perovskite material was developed, the sodium tungsten bronze ($Na_{0.3}WO_3$), rich in W^{V} sites. These sites give material properties like platinum — particularly its ability to adsorb hydrogen and start its reduction at the underpotential deposition of hydrogen (UPDH), a hallmark of platinum's catalytic power. To optimize the material performance, the Costentin's catalytic model was applied to obtain the kinetics of the process and mechanism details. It was tested to both strong (hydrochloric acid) and weak (acetic acid) acidic environments. Electrochemical impedance spectroscopy showed the system reached a steady state in both cases, allowing the model to apply. Interestingly, signals called inductive loops revealed that hydrogen radicals were forming through a homolytic mechanism — a pathway that favors the Tafel step, where two adsorbed hydrogen atoms combine to form H_2. In hydrochloric acid, the HER occurs in a stepwise path: an electron transfer comes followed by a proton transfer with a rate-limiting step of a reversible proton transfer and substrate reduction (PT_{Rev}-SR_{RDS}), yielding an impressive turnover frequency (TOF) of 2.0×10^5 s^{-1}. On the other hand, in acetic acid, the mechanism was different, a single step, concerted electron-proton transfer (CPET), limited by the buffer deprotonation, resulting in an unexpected lower TOF of 3.8×10^4 s^{-1}. Ultimately, $Na_{0.3}WO_3$ shows real promise as a low-cost, platinum-free HER catalyst for clean hydrogen technologies.

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References:

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