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In situ observation of pH change during water splitting in neutral pH conditions: impact of natural convection driven by buoyancy effects

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Abstract:

Photoelectrochemical water splitting in near-neutral pH conditions offers a safe and sustainable way to produce solar fuels, but operation at near-neutral pH is challenging because of the added concentration overpotentials due to mass-transport limitations of protons and hydroxide ions. Understanding the extent of this limitation is essential in designing a highly efficient solar fuel conversion device. In the present study, the local pH between the anode and cathode in a water splitting cell is monitored in situ using fluorescence pH sensor foils. By this direct visualization, we confirm that supporting buffer ions effectively suppress local pH changes, and we show that electrochemical reactions induce natural electrolyte convection in a non-stirred cell. The observed electrolyte convection at low current densities (<2 mA cm^{-2}) originates from buoyancy effects due to the change in the local electrolyte density by ion depletion and accumulation. A Multiphysics simulation that includes the buoyancy effect reveals that natural convection driven by electrochemical reactions stabilizes the local pH, which is consistent with our experimental observations. In contrast, the model without the buoyancy effect predicts significant shifts of the local pH away from the pK_a of the buffer, even at low current densities. This experimentally validated model reveals that natural convection induced by electrochemical reactions significantly affects the overall mass-transport, especially in close vicinity of the electrodes, and it should, therefore, be considered in the design and evaluation of solar fuel conversion devices.

Keywords: water splitting, buoyancy effect, mass-transport, buffer ions, electrolyte convection, in situ fluorescence pH monitoring