In Situ and *Operando* Characterization of Electronic and Chemical States of WO_3 During Electrochemical Proton Intercalation.

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Proton intercalation in oxide materials plays a crucial role in various chemical applications, including sensors, fuel storage, battery materials, and electrochromic devices. Tungsten trioxide (WO_3) serves as a stable host for proton intercalation, forming tungsten bronzes that contribute to the hydrogen evolution reaction (HER). While numerous studies have demonstrated catalytic enhancements in WO_3 via proton-coupled electron transfer (PCET), the evolution of its electronic and chemical states during proton intercalation and HER remains poorly understood. In this work, we employ *in situ* and *operando* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to investigate the electronic and chemical transformations in WO_3 throughout the intercalation process and HER under applied reducing potentials. Our findings reveal that PCET governs the intercalation dynamics, where W is progressively reduced due to electron transfer and subsequent proton incorporation into oxygen lattice sites, forming hydroxyl species. As HER proceeds, these intercalated protons act as a reservoir, facilitating the reaction mechanism. We will present a detailed analysis of how the electronic and chemical states evolve during proton/electron intercalation and HER, offering new insights into the catalytic functionality of WO_3.

Keywords: Proton intercalation, solid-liquid interface, oxide materials, ambient pressure photoelectron spectroscopy (APXPS), materials characterization

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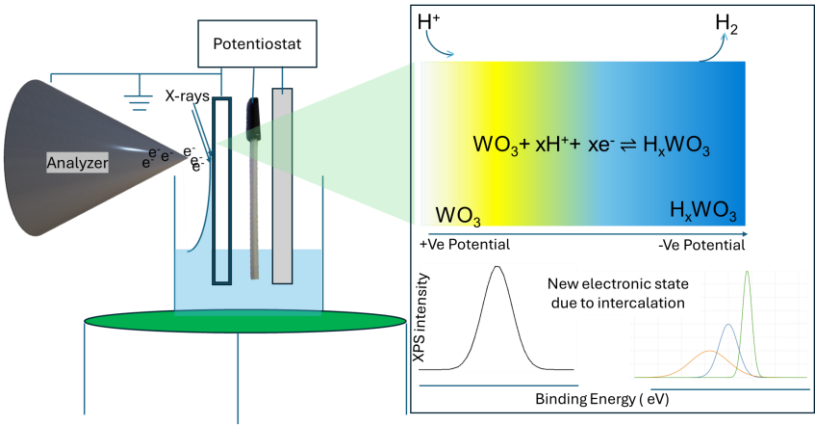

Figure: Schematic of the dip-and-pull setup for operando XPS measurements of WO_3 during proton intercalation, capturing the evolution of H_xWO_3 and associated electronic structure changes.