

Mechanistic Insights about Electrochemical Proton-Coupled Electron Transfer Derived from a Vibrational Probe

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Proton-coupled electron transfer (PCET) is a fundamental step in a wide range of electrochemical processes, including those of interest in energy conversion and storage. Despite its importance, several mechanistic details of such reactions remain unclear. Here, we have combined a proton donor (tertiary ammonium) with a vibrational Stark-shift probe (benzonitrile), to track the process from the entry of the reactants into the electric double layer (EDL), to the PCET reaction associated with proton donation to the electrode, and the formation of products. We have used *operando* vibrational spectroscopy and periodic density functional theory under electrochemical bias to assign the reactant and product peaks and their Stark shifts. We have identified three main stages for the progress of the PCET reaction as a function of applied potential. First, we have determined the potential necessary for desolvation of the reactants and their entry into the polarizing environment of the EDL. Second, we have observed the appearance of product peaks prior to the onset of steady state electrochemical current, indicating formation of a stationary population of products that does not turn over. Finally, more negative of the onset potential, the electrode attracts additional reactants, displacing the stationary products and enabling steady state current. This work shows that the integration of a vibrational Stark shift probe with a proton donor provides critical insight into the interplay between interfacial electrostatics and heterogeneous chemical reactions. Such insights cannot be obtained from electrochemical measurements alone.