Proton relays in molecular electrocatalysis: how do they allow for reversible behavior?

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Hydrogen is now confirmed as a key component of a CO_2-neutral economy, we need to transition towards. The production of large quantities of hydrogen now requires breakthroughs in finding new catalysts that are *efficient, stable and cheap,* i.e. based on *abundant* elements. Indeed fuel formation involves multi-electron multi-proton reactions that are inherently kinetically sluggish. Efficient catalysts can be found in living micro-organisms producing or metabolizing hydrogen thanks to hydrogenases. Catalysis in these enzymes only requires Earth-abundant metal centers, the reactivity of which is enhanced thanks to the presence of basic sites acting as proton relays [1] at their vicinity. Such active sites have been used as an inspiration to design new synthetic catalysts for H_2 evolution [2-4] and oxidation [5-6]. Specification, catalytic platforms with installed proton relays display bidirectional [7] and, in rare cases, reversible catalysis [5]. In this presentation we will show how a detailed molecular electrochemistry study can help understanding and quantifying the role of the protons relays related to these remarkable behaviors.

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