

## Electrocatalytic generation of metal hydrides promoted by concerted proton electron transfer mediators for the transformation of small molecules

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Transition metal hydrides (M-H) have been identified as key intermediates in a variety of catalytic transformations ranging from the conversion of energy in biological system to industrial processes. As such, M-H are involved in the electrochemical or thermochemical reduction of CO<sub>2</sub> to formic acid<sup>[1]</sup>, the reversible interconversion of H<sup>+</sup>/H<sub>2</sub><sup>[2]</sup> and in a wide number of hydrogenation reactions<sup>[3]</sup>. In this context, the facile electrocatalytic generation of M-H species presents one of the main limitations for the catalytic transformation of small molecules by utilizing renewable energy sources. Particularly, in the reduction of CO<sub>2</sub> to formic acid one of the main activation pathways involves the insertion of CO<sub>2</sub> into M-H bonds.<sup>[1]</sup> Current classical strategies for electrochemical M-H formation necessitate the initial reduction of a metal center followed by the sequential transfer of a proton and an electron in either a proton transfer-electron transfer (PT-ET) or a ET-PT mechanism. This stepwise process often requires considerably high cathodic potentials to promote the reaction and the use of a strong acid as proton source. Alternatively, generation of M-H species may occur in a single kinetic step, based on the homolytic coupling of a singly reduced metal center with a hydrogen atom (concomitant proton and electron transfer) in a so called concerted proton-electron transfer (CPET) mechanism.

We have recently identified a novel strategy for the electrocatalytic generation of M-H species via a proton coupled electron transfer mechanism utilizing bioinspired CPET mediators to promote the formation of a manganese hydride species.<sup>[4]</sup> Utilizing this approach, we are exploring the extension of this concept to a variety of transition metal based catalysts to acquire a fundamental understanding of the thermodynamic boundary conditions and the kinetic limitations which govern electrocatalytic M-H generation. The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) was investigated to understand the product selectivity and a variety of spectroscopic techniques were employed to develop a mechanistic understanding of the reaction.

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