

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

A. L. Walker¹, M. Inoue¹, V. Mougel^{1*}

¹ETH Zürich, Departement of Chemistry and Applied Bioscience, Laboratory of Inorganic Chemistry

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 CO₂ to formic acid^[1], the reversible interconversion of H⁺/H₂^[2] and in a wide number of hydrogenation reactions^[3]. 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 CO₂ to formic acid one of the main activation pathways involves the insertion of CO₂ into M-H bonds.^[1] 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.^[4] 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 CO₂ reduction reaction (CO₂RR) 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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