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

A. L. Walker[1], M. Inoue[1], V. Mougel[1]*

[1]ETH 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 CO_2 formic acid[1], the reversible interconversion of H^+/H_2[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 CO_2 to formic acid one of the main activation pathways involves the insertion of CO_2 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 CO_2 reduction reaction (CO_2RR) was investigated to understand the product selectivity and a variety of spectroscopic techniques were employed to develop a mechanistic understanding of the reaction.

[1] Robert Francke, Benjamin Schille, Michael Roemelt, *Chemical Reviews,* **2018**, 118, 4631-4701.
[2] Morris R. Bullock, Monte L. Helm, *Accounts of Chemical Research,* **2015**, 48, 2017-2026.
[3] Jingyun Ye, Ryan C. Cammarota, Jing Xie, Matthew V. Vollmer, Donald G. Truhlar, Christopher J. Cramer, Connie C. Lu, Laura Gagliardi, *ACS Catalysis*, **2018**, 8, 4955-4968.
[4] Subal Dey, Fabio Masero, Enzo Brack Marc Fontecave, Victor Mougel, *Nature*, **2022**, 607, 499-506.