Enhanced electrochemical reduction of CO_2 over Cu-based catalysts modified with p-block elements

G. O. Larrazábal[1], T. Shinagawa[1], A. J. Martín[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

The coupling of electrosynthesis technologies with renewable energy sources can potentially turn CO_2 emissions into a valuable feedstock for the production of fuels and chemicals while contributing to closing the anthropogenic carbon cycle.[1,2] Copper foil electrodes prepared from the reduction of thick oxide films (OD Cu) effectively target the reduction of CO_2 to CO at moderate overpotentials.[3] However, such electrodes display modest current densities, and their preparation on bulk metallic substrates makes them unsuitable for practical applications. In this context, we have recently shown that Cu_2O nanocatalysts prepared by a simple and potentially scalable solvothermal route are more active and selective for CO evolution than OD Cu electrodes under similar conditions.[4] Additionally, the performance of these catalysts can easily be enhanced by introducing Sn and In into the Cu_2O matrix through the addition of the corresponding precursors to the synthesis medium (**Figure 1**). Based on this insight, we extend this methodology to evaluate the catalytic effect of introducing most non-hazardous p-block elements as modifiers, revealing a powerful strategy to tune the selectivity toward other eCO_2RR products while maintaining a high selectivity at reduced overpotentials.

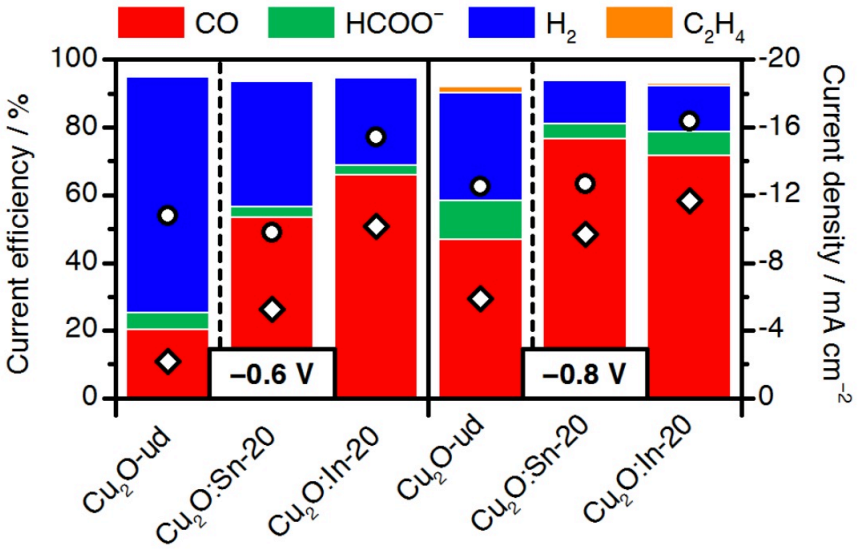

Figure 1 Current efficiency (bars), total current density (circles) and partial current density for CO (diamonds) in CO_2 electroreduction over unmodified (Cu_2O-ud) and Sn- and In-modified Cu_2O electrocatalysts prepared by a simple and potentially scalable solvothermal synthesis (potential indicated *versus* RHE in CO_2-saturated 0.1 M $KHCO_3$). The number in the codes indicates the Cu:Sn or Cu:In ratio of the catalyst.

[1] E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, J. Pérez-Ramírez, *Energy Environ. Sci.* **2013**, 6, 3112.
[2] A. J. Martín, G. O. Larrazábal, J. Pérez-Ramírez, *Green Chem.* **2015**, 17, 5114.
[3] C. W. Li, M.W. Kanan, *J. Am. Chem. Soc.* **2012**, 134, 7231.
[4] G. O. Larrazábal, A. J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez, *ChemSusChem* **2017**, 10, 1255.