

## CER over Cu - formate production and clathrate hydrate effects

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Even though CO<sub>2</sub> electroreduction (CER) over copper catalysts has attracted considerable attention over the last decade, several aspects remain poorly understood, pertaining to e.g. formate production and the effects of CO<sub>2</sub> clathrate hydrate formation.

The precise formation mechanism of formate on extended electrodes has not yet been thoroughly investigated and compared to the well studied CO and CH<sub>4</sub> formation pathways. In particular, knowledge of the reaction and activation energies is needed to understand why, on regular polycrystalline Cu electrodes, CO and formate production take off at a similar overpotential [1], even though the two pathways do not necessarily proceed via a common intermediate.

The selectivity towards formates furthermore generally increases when rougher copper substrates are employed, in particular in the case of Cu nanofoams [2,3]. As the distribution of low-index planes in these materials is not so different from smooth Cu electrodes [3], it is expected that the relevant active sites are rather to be found on surface defects such as step edges.

When CO<sub>2</sub> clathrate formation is induced by adding tetrahydrofuran and lowering the temperature to 2 °C, a high CO Faradaic efficiency of 70% has been observed at a low overpotential (-0.44 V vs RHE) [2], instead of the usual predominance of hydrogen evolution under these conditions. Possible explanations include the relative increase of the CER rate as a consequence of the increased CO<sub>2</sub> concentration inside the clathrates, and different solvation properties of the metal-clathrate interface.

To address these questions, we carry out periodic DFT calculations using the VASPsol code, where the electrolyte is described as an implicit solvent containing a counterion charge distribution screening the electrode charge. The computational work is supplemented by additional experimental measurements of the Faradaic efficiencies as a function of electrode material (Cu and Pt) and its roughness, in both the absence and presence of CO<sub>2</sub> clathrates.

[1] Y. Hori et al., J. Chem. Soc., Faraday Trans. 8 (1989), 2309-2326.

[2] D. DeCiccio et al., Electrochem. Comm. 52 (2015), 13-16.

[3] S. Sen et al., ACS Catal. 4 (2014), 3091-3095.