

# CO<sub>2</sub> electroreduction on copper catalysts investigated by *in situ* X-ray spectroscopy

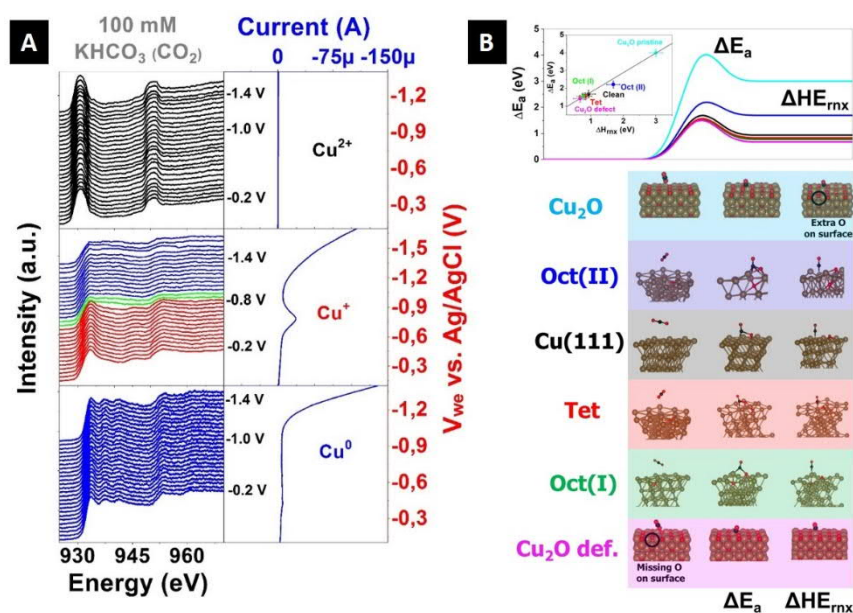
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The electrocatalytic route of energy conversion becomes a key issue because the electricity produced by renewable sources of energy, like solar and wind, can be used to convert CO<sub>2</sub> into valuable chemical feedstocks. Over the last decades several materials able to reduce electrochemically CO<sub>2</sub> in aqueous solution to produce hydrocarbons have been identified not efficient and stable for practical use. In this direction, copper is unique due to its ability to electro-reduce CO<sub>2</sub> to hydrocarbons and alcohols in aqueous electrolytes, as was probed by Hori et al.<sup>1</sup>

Nevertheless, the selective electroreduction of CO<sub>2</sub> into fuels is challenging due to the multiple complex proton-coupled electron transfer steps that must occur<sup>2</sup>. This complex network makes the cathodic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) behave with relative low current density and high overpotential as well as electrode deactivation over time. By tracking the electronic structure of the Cu catalysts, using *in situ* X-ray spectroscopies, we were able to tune and precisely set the initial Cu redox state, such as Cu<sup>0</sup>, Cu<sup>+</sup> and Cu<sup>2+</sup>, by controlled applied potential protocols<sup>3</sup>. Figure 1A shows the variation in the electronic structure that the different catalysts undergo depending on the applied potential revealing the formation of reduced copper during the reactions as well as the formation of a passivation copper carbonate layer onto cupric oxides. The magnitude of this dissociation barrier depends on the degree of surface oxidation and nature of surface defects. Therefore, we calculated the barrier associated with dissociative CO<sub>2</sub> adsorption (CO<sub>2,ads</sub> → CO<sub>ads</sub> + O<sub>ads</sub>) on several copper catalysts, as shown in Figure 1B, indicating that the dissociation barrier is lowered in the presence of missing oxygen on the surface and enhanced in presence of extra oxygen on the surface.

## References

1. Y. Hori et al. Chem. Lett. **15**(6), 897-898 (1986)
2. R. Kas et al. Chem. Phys. **16**(24), 12194-12201 (2014)
3. J.J. Velasco-Velez et al., ACS Sus. Chem. & Eng. 7(1), 1485-1492, (2018)



**Figure 1:** A Cu L<sub>2,3</sub>-edges spectra depending on the cathodic polarization in a 100 mM KHCO<sub>3</sub> solution saturated with CO<sub>2</sub>(gas) and different initial oxidation state: Cu<sup>0</sup>, Cu<sup>+</sup> and Cu<sup>2+</sup> catalysts. **B** Calculation of the adsorption barrier and heat of reaction of different copper structures. The inset shows the E<sub>a</sub> versus H<sub>rxn</sub>.