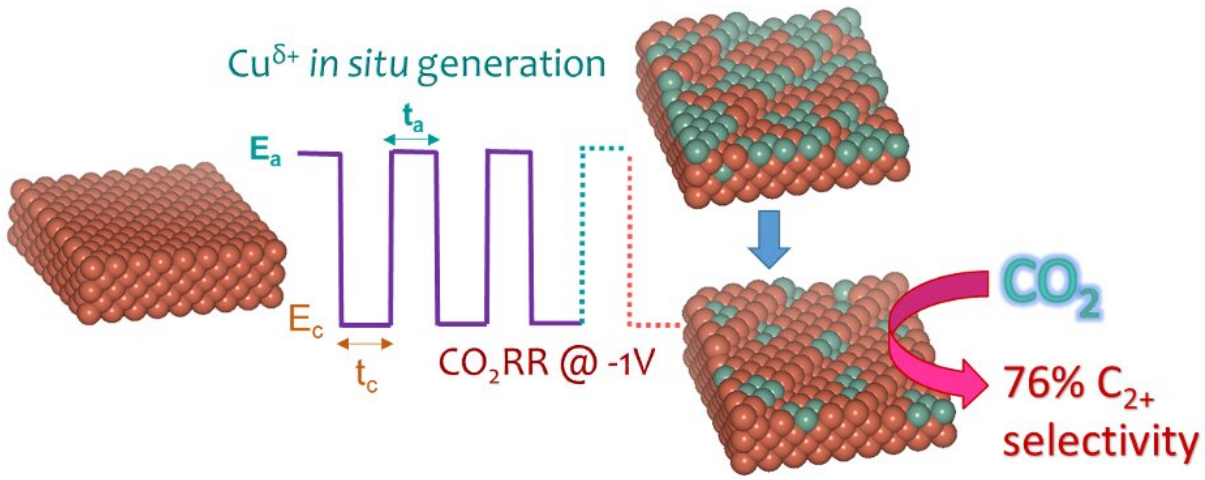
Simultaneously tuning the surface structure and oxidation state of copper catalysts

April 16 2020, by Ingrid Fadelli



Credit: Arán-Ais et al.

Electrical energy derived from renewable sources could be used to rearrange bonds in carbon dioxide (CO_2) and water molecules into complex hydrocarbons, which can then be burnt to produce new energy and CO_2, ultimately enabling a carbon cycle. Copper is a catalytic material that has been found to be promising for enabling this process and facilitating the CO_2 electroreduction reaction (CO_2RR).

Two key elements when trying to understand the parameters controlling the CO_2RR reaction are a well-defined surface structure and known

material composition. Past theoretical and experimental studies have shown that the C—C coupling pathway for generating ethylene is favored on the Cu(100) surface.

More recently, researchers noticed the key catalytic role played by $Cu^{\delta+}$ and sub-surface oxygen for the production of C2-C3 hydrocarbons and alcohol. However, stabilizing copper under the conditions necessary for the CO_2 electroreduction reaction (CO_2RR) to take place has so far proved to be very challenging.

Researchers at the Fritz-Haber Institute, part of the Max-Plank Society in Berlin, have carried out a study aimed at stabilizing Cu(I), copper in the 1+ oxidation state, in order to better understand its role in the CO_2RR reaction. In a recent paper, published in *Nature Energy*, they reported an enhanced efficiency in producing ethanol using copper, attained by tuning the structure and oxidation state of Cu (I) catalysts.

"So far, the stabilization of Cu(I) species under CO_2 reduction conditions has proved to be very difficult," Beatriz Roldan Cuenya, one of the researchers who carried out the study, told TechXplore. "The main goal of our study was to be able to generate Cu(I) species and transiently stabilize them on a well-defined surface, to then study their impact on the CO_2RR product selectivity."

In their study, Roldan Cuenya and her colleagues tuned the structure and oxidation state of copper catalysts using a technique known as pulsed electrolysis. This technique allowed them to design a pulsed potential sequence, which enabled the simultaneous tuning of both the surface structure and composition of Cu catalysts during the CO_2RR reaction.

The researchers monitored changes in the catalyst's structure as well as the chemical state of its surface. This ultimately led to interesting new findings about the mechanisms through which copper catalysts enable

the generation of hydrocarbons via the CO_2RR reaction.

"Our findings suggest that the combination of (100) domains, defect sites, and surface Cu_2O is the best configuration to enhance the CO_2RR reaction pathway leading to C_{2+} products," Roldan Cuenya explained. "In particular, an increased ethanol selectivity could be linked to the coexistence of Cu(I) and Cu^0 species, while the ethylene yield was dominated by the length of the Cu(100) terraces."

The recent study carried out by this team of researchers gathered new interesting findings that shed some light on the role of copper catalysts in facilitating the electrochemical conversion of CO_2. In the future, the technique used by Roldan Cuenya and her colleagues could be used to tune electrochemical interfaces with constrained surface structures and compositions, so that they can be used to selectively produce C_2 products.

"In our next studies, would like to explore the effect of the continuous regeneration of Cu(I) species on other surface orientations and finally apply this pulsed protocol to other nanoparticulated systems aiming more practical applications in real electrolyzers," Roldan Cuenya said.

More information: Rosa M. Arán-Ais et al. The role of in situ generated morphological motifs and Cu(i) species in C2+ product selectivity during CO2 pulsed electroreduction, *Nature Energy* (2020). DOI: 10.1038/s41560-020-0594-9

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Citation: Simultaneously tuning the surface structure and oxidation state of copper catalysts (2020, April 16) retrieved 8 May 2024 from https://techxplore.com/news/2020-04-simultaneously-tuning-surface-oxidation-state.html