# Steering the structure and selectivity of electrocatalysts by potential pulses

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Electrochemical energy conversion driven by renewable energy is a cost-effective, environmentally friendly route to convert undesired substances (such as CO2) into valuable chemicals and fuels, but a suitable catalyst is needed. Here, Cu-based catalysts are particularly attractive due to their unique ability to convert CO2 into more complex hydrocarbons [1]. A challenge for the practical application of complex electrochemical processes as the CO2 electrocatalytic reduction reaction (CO2RR) is however the selectivity control. Convoluted selectivity trends and a missing link between reaction product distribution and the catalyst properties hinder practical applications of the CO2RR for multi-carbon product generation [2,3].

One of the critical parameters affecting the catalyst’s properties and function - its oxidation state - can be conveniently manipulated *in situ* by choosing appropriate applied potentials [4]. In particular, under pulsed reaction conditions, where pulses of a working (cathodic) potential are intermitted with short pulses of anodic potential, the desired structural motifs and preferred oxidation state can be (re-)generated [5,6]. Here, we steer the CO2RR selectivity of a Cu2O nanocube-derived catalyst by varying the type and amount of copper oxide formed during the restoring pulses. In particular, ethanol formation is doubled, as compared to stationary conditions, within a narrow range of pulse durations, where a balance between metallic Cu and distorted copper oxide species is achieved on the catalyst surface. The latter was revealed by time-resolved operando X-ray absorption spectroscopy (XAS), high energy X-ray diffraction (XRD), and quasi-*in situ* X-ray photoelectron spectroscopy (XPS). Our study demonstrates the great prospect of pulsed electrolysis for tailoring the catalyst performance, and highlights the role of operando investigations for the mechanistic understanding of a new generation of catalysts operating under dynamically changing reaction conditions [7].

References

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