**CO₂ Electro-reduction on three dimensional Cu skeleton catalysts**

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The electrochemical reduction of CO₂ into products of higher value (in the following referred to as CO₂RR) offers the unique chance to make a significant contribution to the closing of the anthropogenic CO₂ cycle and is therefore currently in the focus of research activities worldwide. Energy needed for such electro-conversion processes might originate from excesses of renewables like hydro, wind and solar energy (power to value concept). Among the vast number of materials screened so far, it is Cu which deserves particular attention since it is the only catalyst which is capable to convert CO₂ into hydrocarbons and alcohols in considerable amounts. The activity and product selectivity of 3D Cu skeleton type of catalysts were studied with regard to CO₂RR applications thereby focusing on C₂ hydrocarbon formation. The 3D skeleton (sponge) itself reveals only a poor catalytic activity towards CO₂RR which can mainly be assigned to contaminations/residuals from the production process which can hardly be removed even by electropolishing. It will be demonstrated that an activation of the largely inactive Cu skeleton can be achieved either by (i) thermal annealing or (ii) by Cu form electrodeposition. The concept of HER (hydrogen evolution reaction) assisted Cu foam electrodeposition was successfully transferred from planar supports to 3D skeletal supports. Both treatments lead to active Cu catalysts which favor the C₂ pathway (C₂H₄ and C₂H₆) whereas the C1 pathway (CH₄) towards hydrocarbons remains fully suppressed. Both modified catalysts can be considered as oxide-derived and both show a preferential (100) texturing in their XRD analysis thus favoring the C₂ pathway. Differences in their C₂ reaction pathway concern the particular ratio of C₂H₄/C₂H₆ product formation which is higher in case of the electrodeposited Cu foam. This observation could be rationalized by the presence of µm-sized pores within the Cu foam thus leading to a more efficient trapping of reaction intermediates (e.g. C₂H₄) as compared to the annealed skeleton sample and by this to a longer mean residence time of the intermediates inside the catalyst modified by the foam electrodeposition. This effect clearly favors the fully reduced C₂ product.

![Image of Cu skeleton catalysts](image)

**Fig.1** Optical images of the Cu skeleton type of catalysts used in this study: (i) electropolished Cu skeleton; (ii) annealed Cu skeleton (at 300°C for 12h); (iii) functional Cu foam electrodeposited on the Cu skeleton.