Scientific report for proposal CH-6570 – Author: Floriane Rollier

11.05.2023 to 16.05.2023 at ID31, ESRF synchrotron facility, Grenoble, France

The experiments carried out at ID 31 had the goal of characterizing the phase transformation occurring in Cu-Ag bimetallic catalysts during CO electroreduction (CORR). Several compositions were tested: Cu, $Cu_{0.95}Ag_{0.05}$, $Cu_{0.9}Ag_{0.1}$, and $Cu_{0.5}Ag_{0.5}$. From ex-situ WAXS, it was found that the Ag and Cu phases in Ag containing samples are partially interacting, likely being the reason for enhanced CORR selectivity on these samples. Upon reduction, the material transforms significantly and other phases might be formed.

First, three cyclic-voltammetry cycles (CV) were recorded in N_2-purged electrolyte (3M KOH) to mimic the pre-reduction step carried out before CORR in our catalytic testing. Fig. 1. shows the results of the first CV of $Cu_{0.9}Ag_{0.1}$, being the sample demonstrating the highest selectivity to C_{2+} products. We observed that once potentials more negative than +0.16V vs RHE were reached, the initial CuO phase reduced to a typical polycrystalline Cu. For all the samples and here $Cu_{0.9}Ag_{0.1}$, we observed roughly 100% reduction after the first CV cycle. The initial Cu (002) reflection measured 24 nm and the resulting Cu (111) and Cu (200) measured, 17 and 11 nm, respectively. These values were similar for all the samples. Moreover, the crystallite size of Ag upon reduction decreased slightly (from 28 nm to 23 nm), likely due to the loss of initially mixed phase with CuO. We observed that the change in crystallite size was more pronounced for low Ag content sample (5 and 10 %mol). Additionally, the as-prepared Cu-Ag catalysts displayed Ag peak shifts towards lower angles, indicating lattice expansion. We observed that upon reduction of the CuO phase, the Ag peaks shifted towards higher angle due to the loss of interactions with CuO. The shift difference was larger for low Ag content (5 and 10 %mol) than for 50%mol Ag. However, the final position was located still at lower angles compare to pure Ag, demonstrating the presence of Cu and Ag interactions after reduction. We speculate the formation of alloy in this case. This demonstrated that most of the Ag in fresh samples having less than 10%mol Ag was interacting, conversely to high Ag content. These interactions are modified upon reduction but the resulting material has likely alloyed Cu and Ag. Chronoamperometries were recorded for all the samples in CO-purged 3M KOH at -0.4V vs RHE. We observed that the phases formed during the CV in N_2 were stable in CO and/or prolonged exposure to negative bias. The crystallite sizes are stable over time and no sintering occurred.

This data brought crucial insights for the research questions we had before the beam trip and will be part of a publication, together with other in situ characterization confirming the findings of these experiments. Moreover, thanks to the experiments carried out at ID 31, we were able to understand which phases were formed during reduction and confirm the presence of interactions between the two metals.

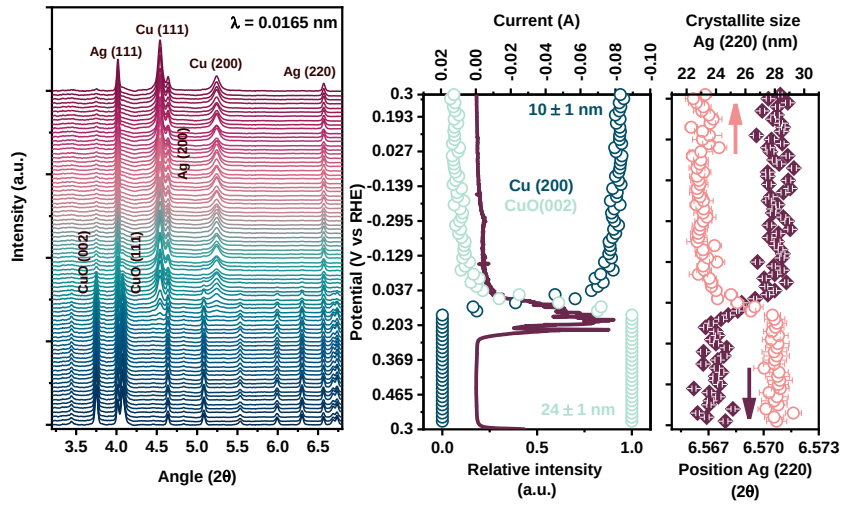

Figure 1 - In situ WAXS measurement of the first CV of $Cu_{0.9}Ag_{0.1}$