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In situ TEM/EELS and spatially resolved XAS/XRF analysis of CuO electrocatalyst for CO2 reduction

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Background

Electrochemical devices such as fuel cells and electrolysers enable chemical and energy transformations that are required to help achieve net-zero targets by 2050. One of the emerging technologies is electrochemical reduction of CO2 into value-added products, such as carbon monoxide, formic acid and ethylene. [1] The best performing cathode catalyst for producing ethylene and other C2+ products in a CO2 electrolyser is oxide-derived copper (OD-Cu), which is metallic coper formed in situ via reduction of a copper oxide-based electrode in the electrolyser. The activity of OD-Cu tends to be significantly higher than that of similar Cu catalysts that have been reduced ex situ prior to being incorporated into the electrolyser, which suggests that additional or superior active sites are generated during the in situ electrochemical reduction [2]. In addition, the catalyst can experience significant structural changes under CO2 electroreduction conditions [3]. Obtaining structure-performance relationships of copper requires in situ characterization, which is due to the surface oxidation and possible restructuring the metal experiences when exposed to open circuit potential and air during disassembly of the electrochemical cell. In situ characterisation imaging techniques such as XAS and XRF are therefore a crucial step to capture the active catalyst formation and the morphology dynamics under electrochemical conditions. These techniques suffer from lower spatial resolution, which limits the level of understanding of the underlaying dynamics for reactions involving gases or liquids. This motivated our investigation of the hypothesis that specific conditions of thermal reduction experiments can led to the Cu structures formed under electrochemical conditions. In this way, a higher spatially-resolved analysis could be done by extrapolation from gas-phase investigation.

Methods

In this work we present in-situ TEM gas phase thermal reduction experiments of CuO samples and correlate them with in-situ liquid phase electrochemical reduction of CuO samples carried out on the i14 nanoprobe beamline (Diamond Light Source). Synchrotron-based spectroscopy techniques, such as X-ray absorption spectroscopy (XAS) and X-ray fluorescence spectroscopy (XRF) are very powerful methods to study the chemical nature of the catalyst under relevant conditions [4]. Combining the i14 nanoprobe beamline(down to 50 nm resolution) with aberration corrected electron microscopy (Å resolution) allows to use spatially resolved XRF imaging to study morphology and dynamics in a liquid biasing environment and link it to gas-phase experiments on the nanoscale.

Results/Conclusion

We will show the benefit of combining these techniques to reveal the effect of the thermal reduction on the CuO particles (morphology / oxidation state) through a combination of in-situ STEM imaging and EELS versus the electrochemical reduction as revealed by the in-situ liquid cell i14 XRF/XANES experiment (Figure 1). We will also address the challenges with liquid biasing experiments such as beam-induced damage, especially to the ionomer that is commonly present in catalyst layers (e.g. Nafion), and challenges involved with sample preparation.

Graphic:

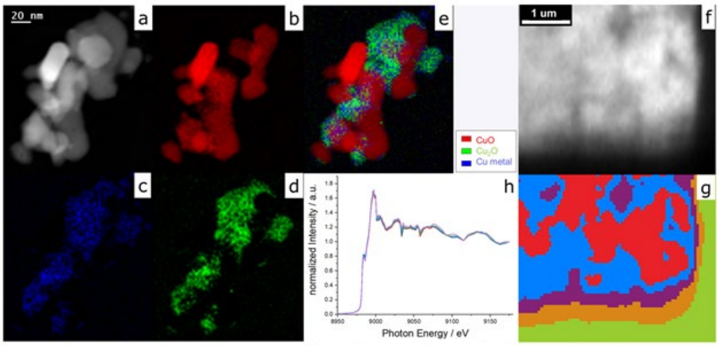

Figure 1: a) STEM HAADF image, Cu L edge EELS map of CuO b), Cu metal c), Cu_2O d) and RGB map of Cu oxidation states at 600°C e); 9.2keV XRF map f), XANES cluster map g) and extracted XANES spectra h) during liquid cell experiment

Keywords:

CO2-reduction, Cu, in-situ, TEM-synchrotron,

Reference:

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