

	Experiment title: A new Cu-macrocyclic water oxidation catalyst: structure, anchoring, stability	Experiment number: A08-1 1078
Beamline: BM-08 LISA	Date of experiment: from: 25/01/2022 to: 31/01/2022	Date of report: 28/02/2022
Shifts: 18	Local contact(s): Michela Brunelli, Francesco D'acapito	<i>Received at ESRF:</i>
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Report:

The experiment A08-1 1078 was performed at beamline LISA BM-08 from January 25th to 31st 2022. The main goal of the experiment was to study the structure and the stability of Cu and Fe-based macrocyclic molecules used as catalysts for water splitting applications.

Two different Cu-based macrocyclic molecules were measured: $[Cu(L3)]^{2-}$ and $[Cu(L1)]^{2-}$, the structure of which is reported in Figure 1. Here, we report a preliminary qualitative analysis of the acquired spectra; a detailed analysis is in progress.

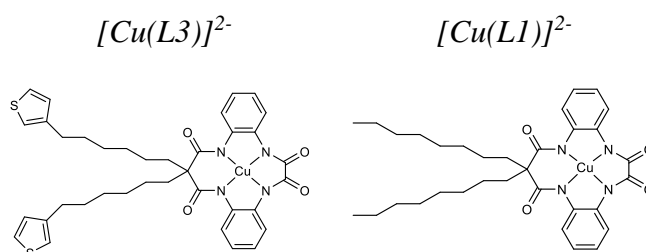


Figure 1: Structure of Cu-based macrocyclic catalysts.

We measured XANES and EXAFS spectra at Cu K-edge of samples used for different working time in an electrochemical cell and we compared them to the reference powder.

The results for $[Cu(L3)]^{2-}$ deposited on glassy carbon substrate are reported in Figure 2. Spectra of the samples are all similar to the reference powder, but with some differences, especially after 72 hours of working time.

This suggests that the Cu local structure may undergo some modifications during the electrochemical process of water oxidation.

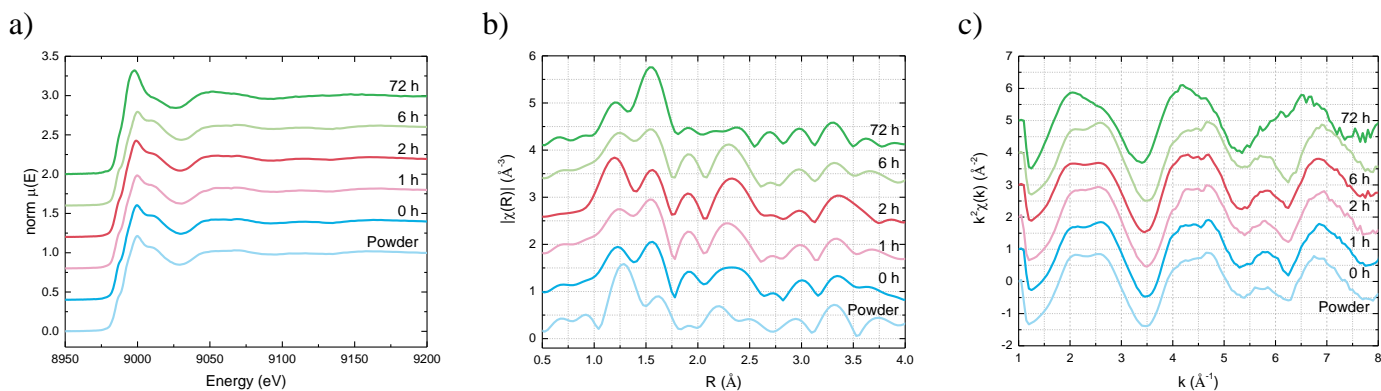


Figure 2: a) normalized Cu K-edge XANES for reference powder and for sample after different working time (reported in hours); b) experimental Fourier transforms of k^2 -weighted EXAFS and c) correspondig back Fourier transform.

For what concerns $[Cu(L1)]^{2-}$ molecules, we measured XANES and EXAFS spectra at Cu K-edge before and after a serie of cyclic voltammtries. The substrate used with these samples was FTO (Fluorine Tin Oxide) coated glass. Spectra are reported in Figure 3.

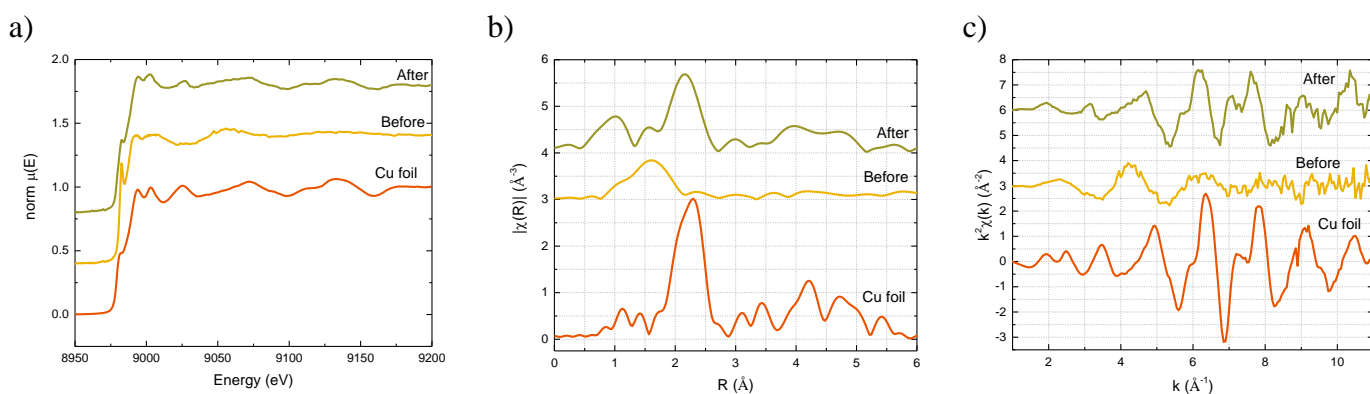


Figure 3: a) normalized Cu K-edge XANES for $[Cu(L1)]^{2-}$ sample before and after cyclic voltammetry compared with Cu foil; b) experimental Fourier transforms of k^2 -weighted EXAFS and c) correspondig back Fourier transform.

Spectra appear very different from $[Cu(L3)]^{2-}$ samples. In addition, the sample after the serie of cyclic voltammtries exhibit significant modifications.

Finally in Figure 4 a comparison between $[Cu(L3)]^{2-}$ and $[Cu(L1)]^{2-}$ in form of powder on glassy carbon substrate is reported.

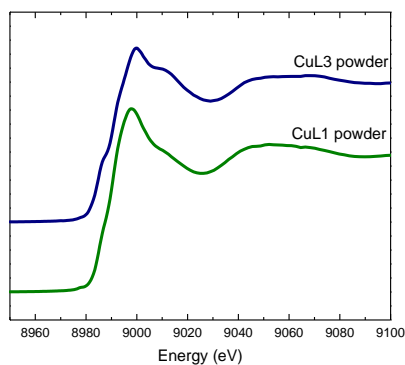


Figure 4: Comparison between XANES spectra of $[Cu(L3)]^{2-}$ and $[Cu(L1)]^{2-}$ powder on glassy carbon substrate.

It is interesting to notice that the spectral shape of these samples is different even though the expected local structure of Cu atom in the molecules is the similar.