

Experiment Report Form



Experiment title: In situ XAS and VtC-XES Studies of Electrocatalytic Water Oxidation Mechanisms in Dimeric Copper(pyalc) Complexes

Experiment number:
CH-6036

Beamline: ID26	Date of experiment: from: 07 July 2021 to: 12 July 2021	Date of report: 12.09.2022
Shifts: 15	Local contact(s): Sami Juhani Vasala	<i>Received at ESRF:</i>
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Report:

Background

Water electrolysis serves as one of the green approaches for the sustainable energy conversion and generation of chemical fuels.^[1] Water splitting is more complex on the oxidation side due to the thermodynamically uphill energy barrier and involvement of four electrons.^[2] Nature's water splitting machinery: the Mn₄CaO_x (OEC) has influenced the scientific community to design artificial molecular water oxidation catalysts (WOCs).^[3-4] Due to the harsh oxidative conditions molecular catalysts often transform to corresponding metal oxides during the turnover, which makes their strategic design and in-situ investigation very important. Herein we target aimed to identify the high-valent Cu-oxo species involved in the water oxidation turnover catalyzed by Cu₂(pyalc)₄ molecular WOC by application of HERFD-XANES and Valence to Core XES (VtC-XES).

In-situ HERFD-XANES & VtC-XES under electrocatalytic conditions:

The *in-situ* HERFD-XANES & VtC-XES experiments under chronoamperometric conditions were performed at the ID26 beamline. *Ex-situ* measurements were carried out on Cu reference samples pressed into pellets. For all *in-situ* measurements, a in-house built in-situ electrocatalysis flow-cell with kapton windows was used

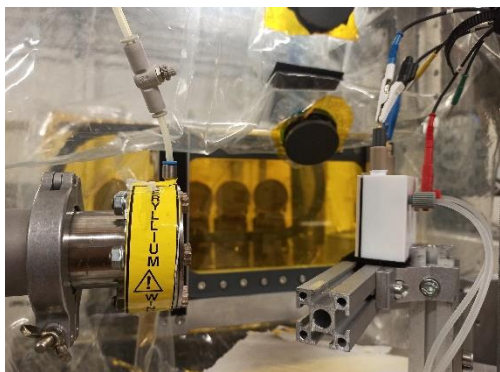


Fig.1: In-situ electrocatalytic cell in Rowland Geometry, at ID26 beamline ESRF

(**Fig.1**). In addition, an automated (programmable) peristaltic pump equipped with PTFE tubings connected to the in-situ cell was placed in vicinity of the cell, for circulation of the Cu complex solution dissolved in aqueous carbonate buffer (**Fig.1**). The applied potential was varied serially with an increment of 0.2 V vs NHE, from 1.4 – 1.75 V vs NHE. Since the experiments were conducted in solution conditions that too in dilution of 0.5 millimolar aqueous buffer, each measurement for a certain potential took 20-30 min for HERFD-XANES and around 3 hours for VtC-XES. The HERFD-XANES and VtC-XES were recorded by analyzing the Cu $K\alpha$ and Cu $K\beta$ emission lines respectively, in Rowland Geometry. Initial data treatment were performed using *PyMca* software and plotting were carried out by ESRF python library *daxs* scripts.

Results:

Analysis of the Cu references samples indicated the presence of major and minor pre-edge peaks for Cu(II) and Cu(III) valence states. In addition, the Cu(III) pre-edge is shifted by 1.79 eV to higher energies as compared with Cu(II) (**Fig.2**). In the same fashion, the Cu HERFD-XANES pre-edge intensity also increases and shifts to higher energy, from an applied potential of 1.5 V vs NHE. The pre-edge intensity increment is more profound at an applied potential of 1.65 V vs NHE (**Fig.3**) which is the long term catalytic potential where we obtain high oxygen evolution. This shows that Cu(III) species have been generated under electrocatalytic conditions at an applied potential of 1.65 V. In the VtC-XES spectrum, the $K\beta''$ satellite lines from the oxygen ligands increases in intensity as the potential is scanned above 1.5 V vs NHE and reaches a maximum in the range of 1.65-1.68 V vs NHE, indicating the increased interaction of oxygen ligands towards the Cu orbitals.

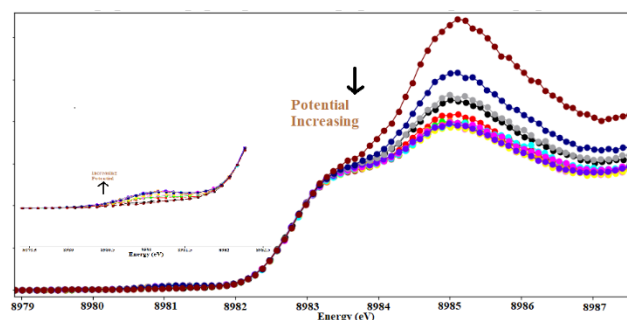


Fig.3: in-situ Cu HERFD-XANES showing pre-edge shifts and increasing intensity as potential increases

potential and not below. Additionally, a shoulder peak at 8.97 eV appears when the potential is held at 1.65 V vs NHE. (**Fig.4**)

Conclusions and Outlook:

The combined in-situ data from HERFD-XANES and VtC-XES suggest that water oxidation turnover includes a formal Cu(III) species. The pre-edge intensification and oxy ligand contribution supports the above hypothesis. Further correlations are to be drawn from DFT calculations and simulations so as to completely confirm the optimized geometry and electronic states of the active species. The experimental data clearly suggest the presence of a high valent Cu intermediate.

References:

- [1] *ACS Catal.* 2017, 7, 5, 3384–3387
- [2] *Nanoscale*, 2020,12, 4187-4218
- [3] *J. Am. Chem. Soc.* 2021, 143, 47, 19761–19768
- [4] *Sustainable Energy Fuels*, 2022,6, 1312-1318

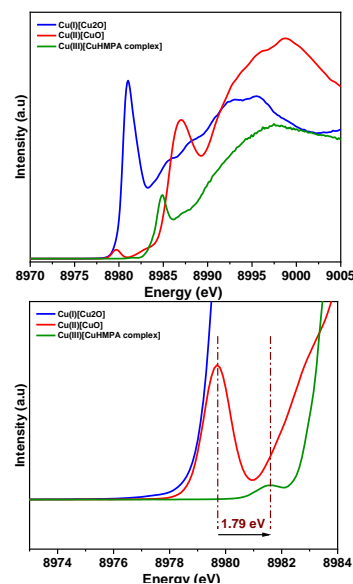


Fig.2: Cu HERFD-XANES showing pre-edge shifts

Moreover, this peak intensity lowers when the potential is lowered below 1.55 V vs NHE, notifying that the Cu-oxo/hydroxo active species are generated at the catalytic

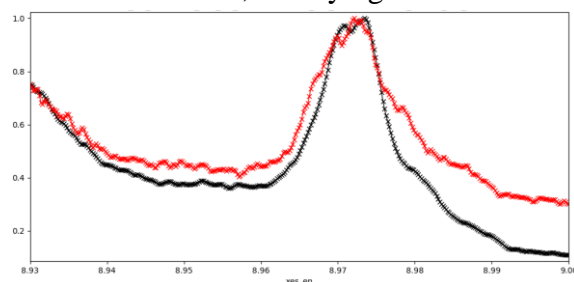


Fig.4: Cu VtC-XES spectrums showing in increasing intensity of Oxygen ligand peak and shoulder peaks. (red: @ 1.65 V, black: without potential)