

Molecular Mechanism of Copper-based Catalytic Reaction of Water Oxidation. In-situ Electrochemical Liquid Phase Transmission Electron Microscopy Study.

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The understanding of molecular mechanisms of water oxidation reactions is very important for development of renewable energy storage solutions [1]. Inspired by a naturally occurring water splitting catalyst, the Mn_4CaO_5 particles [2], many first-row transition metal compounds are being synthesized and studied as catalysts in oxygen-evolution reactions (OER) at various conditions [3, 4]. For that purpose, copper(II) complexes are considered to be very promising, with the $[\text{Cu}(\text{TMC})(\text{H}_2\text{O})](\text{NO}_3)_2$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) compound (further, the **Cu(II)-complex**) reported among the most efficient copper-based catalyst for electrocatalytic OER in neutral aqueous solutions [5, 6, 7]. However, the control over the stability and catalytic activity of the compound during OER is handicapped by a complicated reaction path, and general lack of understanding of the molecular mechanism of the reaction [7].

In our study, we followed the OER in the presence of the **Cu(II)-complex** at the same conditions as in [7], but employing the most advanced analytical and computational techniques, including *in-situ* vis-spectroelectrochemistry, *in-situ* electrochemical liquid-phase transmission electron microscopy (EC-LPTM) and extended X-ray absorption fine structure (EXAFS) studies.

Our *in-situ* EC-LPTM studies including post-reaction analytical and electron diffraction analyses revealed that already in the first anodic scan, small CuO nanoparticles formed at the surface of working electrode at a significantly lower potential than required for OER (Figure). This indicates that these can be the true catalysts rather than the **Cu(II)-complex**. Further, during the OER, the small CuO particles dissolved to form larger ones. Moreover, during cyclic voltammetry (CV) runs, we observed the formation of a very thin, nearly continuous Cu-oxide film at the working electrode of the reactor cell of the TEM holder. These data accord very well with the electrochemical impedance spectroscopy (EIS) curves acquired in a separate experiment.

In conclusion. Our findings demonstrate that even at the very beginning of the OER, the active compound can undergo decomposition or transformation. We also show that the actual OER mechanism in the presence of the **Cu(II)-complex** is more complicated than a mere molecular mechanism. All these results signal the fact that the metal catalyst cannot be presumed to stay intact during the OER, unless the reaction path is known and fully controlled. Dedicated, in-depth studies of the particular reaction path using the advanced morphological and analytical methods are therefore crucially important for the catalyst design.

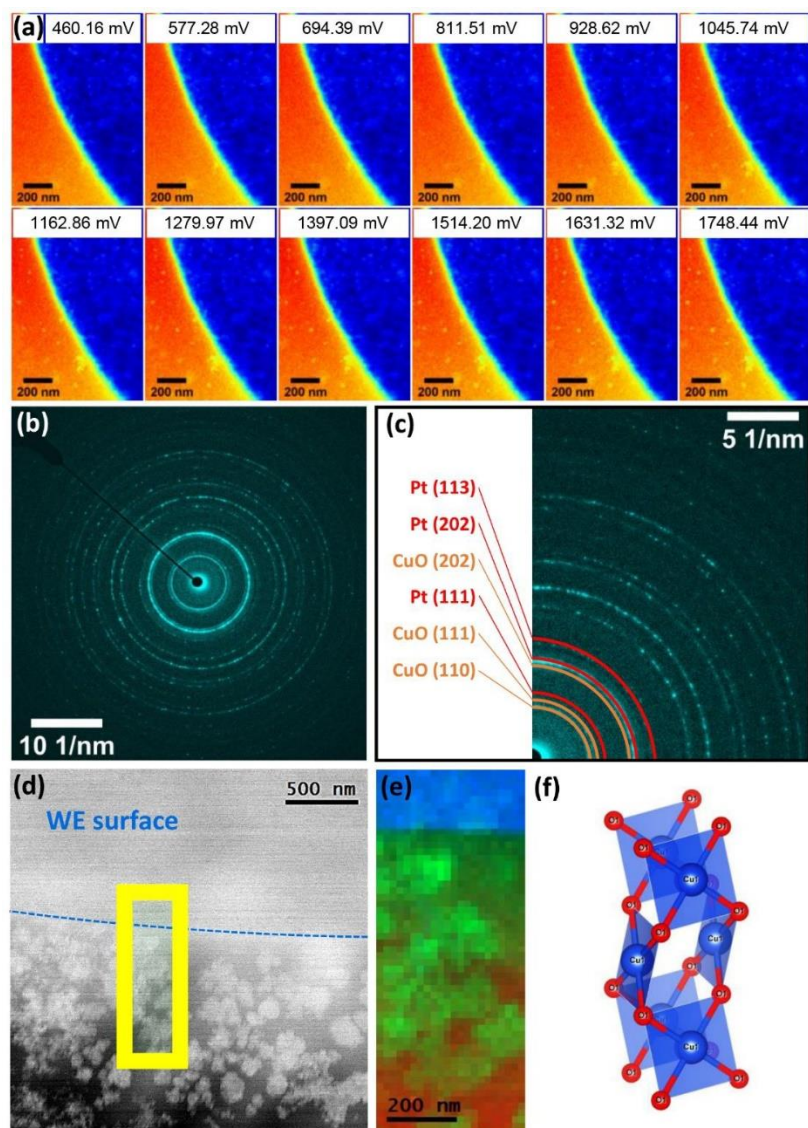


Figure 1. Electro-chemical LPTM studies of the Cu-complexes mediated OER.

(a) Degradation of the Cu-complexes during an anodic scan during cyclic voltammetry versus Ag/AgCl reference electrode. The sequence of TEM micrographs presents the snap-shots of the early stages of the nucleation of the copper oxide particles (bright yellow) at the surface of the working electrode (blue). The phase state change of the liquid phase at the electrolyte is verified by electron diffraction pattern (eDP) analyses: (b) shows the eDP from the Pt-working electrode, whereas (c) demonstrates the presence of the CuO-phase particles. The elemental content analyses by of the electrode adjacent region were carried out using the energy-dispersive X-ray spectroscopy (EDS) in a spectrum image (SI) mode (d, e). The EDS SI confirms the formation of CuO phase in the electrolyte. The schematic of the CuO unit cell is shown in (f). The schematic of the electro-chemical in-situ TEM set-up in operation.

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