

# Water Oxidation at Neutral pH using a Highly Active Copper-Based Electrocatalyst

## Summary

The sluggish kinetics of the oxygen evolution reaction (OER) at the anode severely limit hydrogen production at the cathode in water splitting systems. Although electrocatalytic systems based on cheap and earth-abundant copper catalysts have shown promise for water oxidation under basic conditions, only very few examples with high overpotential can be operated under acidic or neutral conditions, even though hydrogen evolution in the latter case is much easier. This work presents an efficient and robust Cu-based molecular catalyst, which self-assembles as a periodic film from its precursors under aqueous conditions on the surface of a glassy carbon electrode. This film catalyzes the OER under neutral conditions with impressively low overpotential. In controlled potential electrolysis, a stable catalytic current of  $1.0 \text{ mA cm}^{-2}$  can be achieved at only 2.0 V (vs. RHE) and no significant decrease in the catalytic current is observed even after prolonged bulk electrolysis. The catalyst displays first-order kinetics and a single site mechanism for water oxidation with a TOF ( $k_{\text{cat}}$ ) of  $0.6 \text{ s}^{-1}$ . DFT calculations on of the periodic  $\text{Cu}(\text{TCA})_2$  (HTCA=1-mesityl-1H-1,2,3-triazole-4-carboxylic acid) film reveal that TCA defects within the film create  $\text{Cu}^{\text{I}}$  active sites that provide a low overpotential route for OER, which involves  $\text{Cu}^{\text{I}}$ ,  $\text{Cu}^{\text{II}}\text{-OH}$ ,  $\text{Cu}^{\text{III}}\text{=O}$  and  $\text{Cu}^{\text{II}}\text{-OOH}$  intermediates and is enabled at a potential of 1.54 V (vs. RHE), requiring an overpotential of 0.31 V. This corresponds well with an overpotential of approximately 0.29 V obtained experimentally for the grown catalytic film after 100 CV cycles at pH 6. However, to reach a higher current density of  $1 \text{ mA cm}^{-2}$ , an overpotential of 0.72 V is required.

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