MOLECULAR STRUCTURE AS BUILDING BLOCKS OF WELL-DEFINED MATERIALS FOR ELECTROCATALYTIC OXYGEN EVOLUTION

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INTRODUCTION

Water splitting is one of the key processes for many applications related with energy storage and conversion.[1] Water oxidation (WO) or oxygen evolution reaction (OER) is still considered the most challenging step in water splitting since it is a more complex transformation than proton reduction. Cobalt-based water oxidation catalysts (WOC), including molecular complexes[2] and inorganic nanoparticles,[3] have focused on great interest due to their prominent activities and abundance of this metal in the earth.

However, few examples of electrocatalytic WOC based on porous metal-organic frameworks (MOFs) have been reported,[4] despite their large structural features. Among the different secondary building units (SBUs) that form MOFs, the dinuclear $M_2(RCOO)_4$ paddlewheel (M = Cu, Zn, Ni, Fe, Co, Mo, Cr, Ru) is considered a potential core to achieve OER successfully with abundant metallic elements.[5] Herein, we report a new Co-based MOF possessing two distinct dinuclear cobalt SBUs. Upon Nafion coating, **Co_2–MOF** is water-stable, thus allowing its evaluation as an electrocatalyst in the O_2 evolution reaction.[6]

SYNTHESIS AND SINGLE CRYSTAL X-RAY DIFFRACTION OF Co_2-MOF

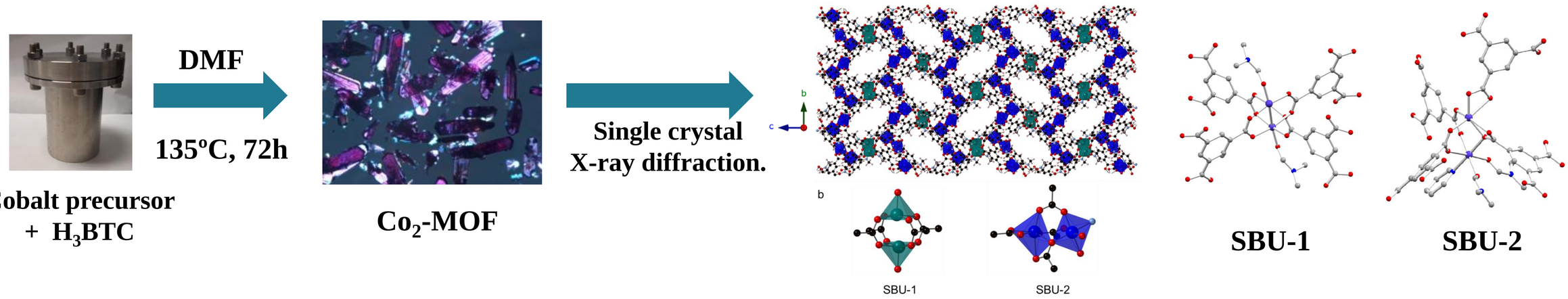


Figure 1. Syntesis and Crystal structure of Co_2-MOF. Representation of the two dimeric SBUs found in Co_2-MOF: SBU1, the characteristic paddlewheel unit, and SBU2, with an unusual coordination of three solvent molecules to one metal centre.

ELECTROCHEMICAL STUDY

The electrochemical behavior of **Co_2-MOF** was investigated by cyclic voltammetry. The voltammogram consists of two well resolved quasi-reversible waves at 1.02V and 1.35V, which can be ascribed to two consecutive monoelectronic redox conversions Co(II)/Co(III) and Co(III)/Co(IV). This is confirmed by the voltammogram of **Co-MOF**, which also displays two well resolved voltammetric waves located at 0.61 V and 1.35 V.

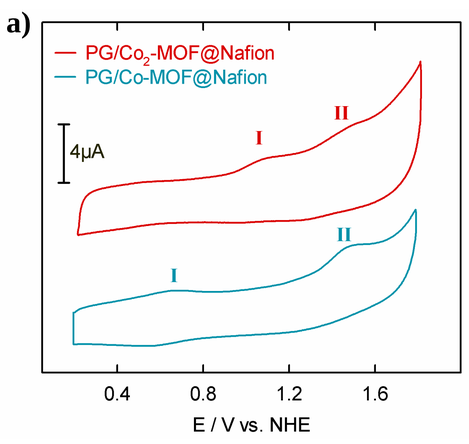
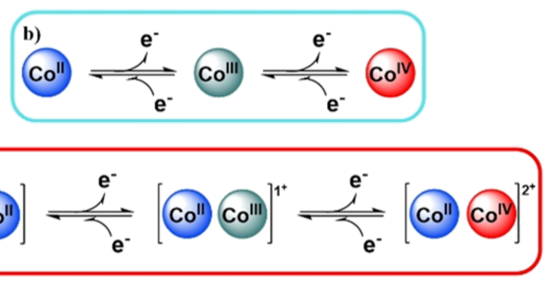


Figure 2. a) Cyclic voltammograms of a pyrolytic graphite electrode modified with **Co_2-MOF**@Nafion (red line) or hydrolyzed **Co-MOF**@Nafion (blue line) recorded at 0.05 Vs^{-1} in a solution containing 0.1 M $[Et_4N]BF_4$ in acetonitrile. b) Redox conversions involved in the voltammetric response of coated **Co-MOF** and (c) **Co_2-MOF**.



ELECTROCHEMIC PERFORMANCE FOR OER

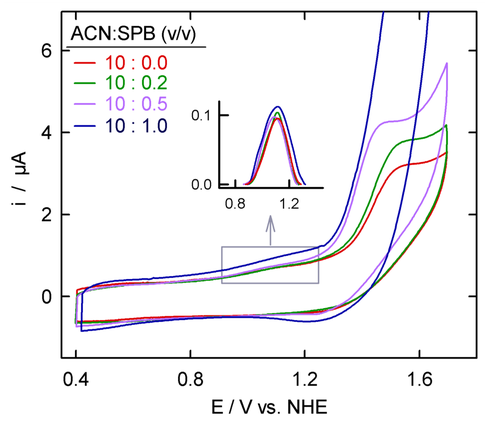


Figure 3. Cyclic voltammograms of **Co_2-MOF**@Nafion-modified pyrolitic graphite electrode for the indicated acetonitrile:aqueous solution (pH 7) ratio.

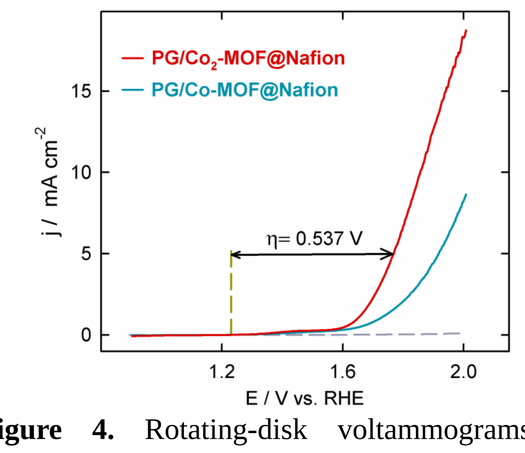


Figure 4. Rotating-disk voltammograms of a pyrolytic graphite electrode modified with **Co_2-MOF**@Nafion or hydrolyzed **Co-MOF**@Nafion in an aqueous solution (pH 7).

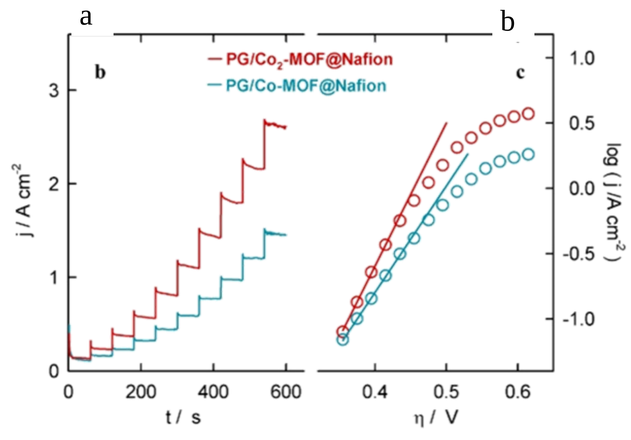


Figure 5 (a) Potentiostatic chronoamperograms of a pyrolytic graphite electrode modified with **Co_2-MOF**@Nafion or **Co-MOF**@Nafion in an aqueous solution (pH 7). (b) Tafel plots of the steady state current density data of a).

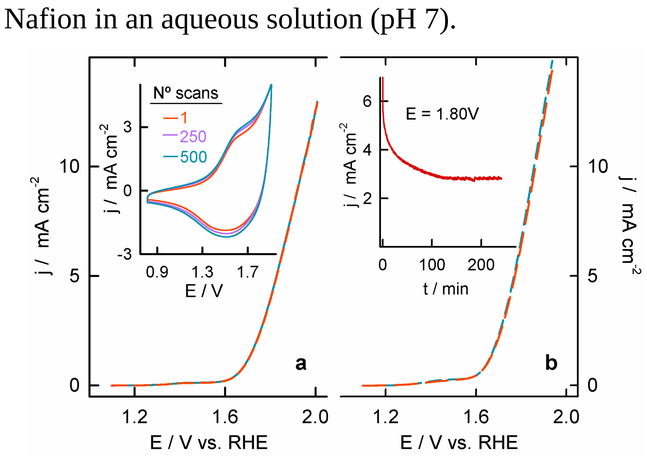


Figure 6. Rotating-disk voltammograms for **Co_2-MOF**@Nafion measured before and after recording (a) 500 consecutive scans. (b) the chronoamperometric current at 1.80V for 4h depicted in the inset plot.

TO SUM UP

We have developed the synthesis of a new microporous MOF based on two SBU with dinuclear cobalt centers. This Co_2-MOF exhibits a high electrocatalytic performance for water oxidation in neutral media, with a TOF value superior to that determined for the mononuclear Co-MOF and to those reported for similar electrocatalysts. Overall, this work has provided a basis for the rational design of new cobalt OER catalysts and related materials employing well-defined metal clusters as directing agents of MOF structure.

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