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Additional Information

Cobalt Metal-Organic Framework based on two Dinuclear Secondary Building Units for Electrocatalytic Oxygen Evolution

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Keywords: Cobalt Cluster, Cobalt MOF, Electrocatalysis, Oxygen Evolution Reaction and Gas Storage.

ABSTRACT

It has been developed the synthesis of a new microporous Metal-Organic Framework (MOF) based on two Secondary Building Units (SBU), with dinuclear cobalt centers. The employing of a well-

defined cobalt cluster results in an unusual topology of the **Co₂-MOF**, where one of the cobalt centers has three open coordination positions, which has not precedent in MOF materials based on cobalt. Adsorption isotherms have revealed that **Co₂-MOF** is in the range of best CO₂ adsorbents among the carbon materials, with a very high CO₂/CH₄ selectivity. On the other hand, dispersion of **Co₂-MOF** in an alcoholic solution of Nafion gives rise to a composite (**Co₂-MOF@Nafion**) with a great resistance to hydrolysis in aqueous media and good adherence to graphite electrodes. In fact, it exhibits a high electrocatalytic activity and robustness for the oxygen evolution reaction (OER), with a TOF value superior to those reported for similar electrocatalysts. Overall, this work has provided the basis for the rational design of new cobalt OER catalysts and related materials employing well defined metal clusters as directing agents of MOF structure.

INTRODUCTION

Water splitting is one of the key processes for many applications related with energy storage and conversion.¹⁻³ 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.⁴⁻⁵ In fact, OER is essential to achieve successfully hydrogen production from water⁶⁻⁷ but also in other applications such as regenerating fuel cells⁸ and rechargeable metal-air batteries.⁹ Cobalt-based water oxidation catalysts (WOC), including molecular complexes^{5,10-11} and inorganic nanoparticles,¹²⁻¹⁷ are of great interest due to their prominent activities and abundance of this metal in the earth.¹⁸⁻²¹

However, few examples of electrocatalytic WOC based on porous metal-organic frameworks (MOFs)²² have been reported,²³⁻²⁶ despite their large structural features. In fact, the ample versatility in coordination modes and nuclearity has provided a high structural diversity of MOFs

in barely 25 years, with applications in the fields of gas storage and sensing,²⁷⁻²⁹ catalysis,³⁰⁻³¹ and electroactive materials in devices.³¹⁻³⁶ In addition, MOFs are also emerging as potential electrocatalysts for CO₂ reduction, hydrogen and oxygen evolution reactions.³⁷⁻³⁹

Among the different secondary building units (SBUs) that form MOFs, the dinuclear M₂(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.⁴⁰ However, cobalt MOF materials based on this SBU have shown poor stability in water.⁴¹ Different approaches have been used to augment the water stability of MOFs mainly based on the employment of bulky, hydrophobic and/or irremovable ligands.^{40,42-43} Herein, we report a new Co-based MOF of formula {[Co₂(BTC)_{1,3}(DMF)₂][Co₂(BTC)_{1,3}(DMF)₂py]}, denoted as **Co₂-MOF**, possessing two distinct dinuclear cobalt SBUs. Upon Nafion coating, **Co₂-MOF** is water-stable, thus allowing its evaluation as an electrocatalyst in the O₂ evolution reaction (OER) with high activity under mild conditions.

DISCUSSION AND RESULTS

Synthesis and characterization of Co₂-MOF. The solvothermal reaction of the cubane cluster [Co₄O₄(OAc)₄(py)₄]⁴⁴ and benzene tricarboxylic acid (H₃BTC) in DMF results in the formation of violet plates of **Co₂-MOF** after 72h. The use of the cubane cluster as starting material is key for the formation of **Co₂-MOF**, unachievable with other common cobalt reagents (Figures S1 and S2). Single crystal X-ray diffraction reveals that **Co₂-MOF** crystallizes in the monoclinic P2₁/n space group (Table S1). Two different dinuclear secondary building units (SBU), denoted SBU1 and SBU2, are found in this structure (Figure 1). The SBU1 unit is the archetypal paddlewheel structure, formed by two crystallographically related Co²⁺ atoms (via an inversion center, more details in SI). The SBU2 unit is more atypical, formed by two crystallographically independent

Co²⁺ atoms, each of them with a different connectivity. One Co center is coordinated by six oxygen atoms from four BTC³⁻ ligands, with Co–O distances in the range of other reported cobalt MOFs (Figure S3).⁴⁵⁻⁵⁰ Specifically, there are two ligands that chelate the metal center, whereas the two ligands coordinate in the classical way of a paddlewheel structure. The other Co center of the SBU2 unit is coordinated by three O atoms from three shared BTC³⁻ ligands and three solvent molecules (one pyridine molecule and two DMF molecules), with distances in the range of other reported cobalt MOFs (Figure S1b).

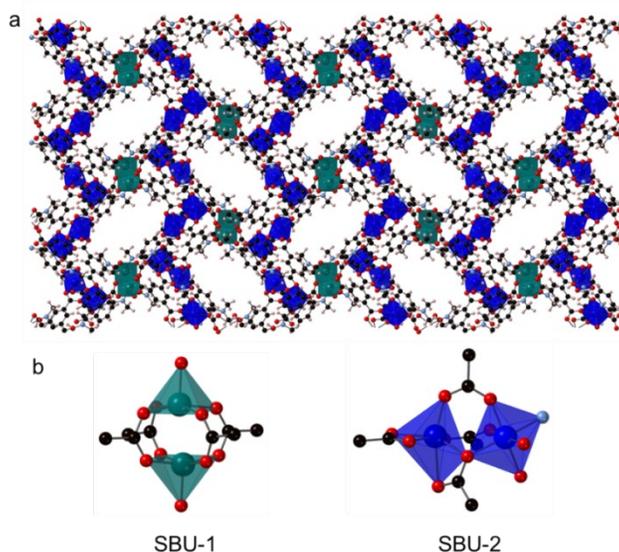


Figure 1. (a) Crystal structure of Co₂-MOF; (b) Representation of the two dimeric SBUs found in compound 1: SBU1, the characteristic paddlewheel unit, and SBU2, with an unusual coordination of three solvent molecules to one metal center. Hydrogen atoms are omitted for clarity.

The connection of these two different SBUs yield a 3D network with 1D channels parallel to the crystallographic a axis (Figure S4), which are filled with DMF molecules, as confirmed by thermogravimetric analysis (Figure S5). The microporosity of the material has been demonstrated upon activation at 100 °C under vacuum, with a high CO₂ adsorption capacity of 1.1 mmol/g at

0°C and 100 kPa (Figure S6a-b), which corresponds with an apparent surface area of 233 m²/g. The value of isosteric heat of adsorption of CO₂ at zero coverage ($q_{st,0}$) calculated from the Henry constants is 30 kJ/mol (Figure S6c), being comparable to the one of a LTA zeolite of Si/Al ratio of 5.⁵¹ This value was set as a good compromise between adsorption capacity and regenerability for a CO₂ adsorbent, due to the strength of the gas-solid interactions. The high pressure CO₂ and CH₄ isotherms (up to 10 bar) obtained at different temperatures (Figures S6d) supports that **Co₂-MOF** is a promising material for CO₂/CH₄ separation (Figure S6e) with very similar values to those of zeolitic molecular sieves.⁵² Although the selectivity decreases with the increase of pressure, it remains very high, even at 298 K and 500 kPa. Magnetic measurements of **Co₂-MOF** (Figure S7) were also employed to characterize this new material. Finally, **Co₂-MOF** was studied by FESEM (Field Emission Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray spectroscopy) analysis (Figure S8), to provide further composition characterization and by XPS (X-ray photoelectron spectroscopy), in order to know more about the electronic structure. The photoelectron spectra of the Co 2p line for the **Co₂-MOF** (Figure S9) and the fitting results are shown in Table S2. From this analysis, it could be confirmed that cobalt centers are exclusively in Co(II) oxidation state.

Chemical stability of Co₂-MOF. Despite the high thermal stability of **Co₂-MOF**, a structural reorganization takes place in the presence of protic solvents such as ethanol, water and their mixtures (Figures S10, S11). Thus, **Co₂-MOF** is transformed into a previously described mononuclear cobalt material of formula Co₃(BTC)₂(H₂O)₃, denoted as **Co-MOF**.⁵³ This material forms a hydrogen-bonded 3D structure based of zig-zag chains in which coordinated water molecules interact with carboxylate groups of adjacent chains. In an effort to overcome this drawback, we have found that its dispersion in an alcoholic Nafion solution provides a composite

(**Co₂-MOF@Nafion**) that is stable in water, as evidenced by the absence of significant changes in the X-ray power diffraction patterns measured for **Co₂-MOF@Nafion** before and after being treated with water (Figures S12 and S13). According to recent studies with HKUST-1/Nafion and Zn(II) based MOF/Nafion composites,^{54,55} the enhancement of the MOF chemical stability can be ascribed to a lower water content in the composite compared to that in the absence of Nafion. These studies reported on a decrease of the water uptake by the composite upon increasing the amount of MOF, which was ascribed to the reduction of the number and size of the available pores. Apart from its protective role, Nafion also improves the adherence of **Co₂-MOF** to graphite electrodes, enabling the study of its electrocatalytic performance for the water oxidation (*vide infra*).

Electrochemical study over Co₂-MOF and Co-MOF. The electrochemical behavior of **Co₂-MOF** was investigated by cyclic voltammetry employing a pyrolytic graphite electrode coated with a **Co₂-MOF@Nafion** film in a solution containing 0.1 M [Et₄N]BF₄ in acetonitrile (Figure 2a). The voltammogram consists of two well resolved quasi reversible waves at 1.02V (wave I) and 1.35V (wave II), superimposed on a rising background current. To get some clues of the redox conversion involved in each voltammetric wave, the voltammetric response of the mononuclear **Co-MOF** has been measured (Figure 2a). It also shows two well resolved voltammetric waves located at 0.61 V and 1.35 V, that correspond to the two consecutive monoelectronic redox conversions Co(II)/Co(III) (wave I) and Co(III)/Co(IV) (wave II), respectively (Scheme in Figure 2b). The similarity on the charge under the baseline of the corrected voltammetric waves for both MOFs suggests that monoelectronic charge transfers are also taking place in the **Co₂-MOF**, the first being ascribed to the Co(II)/Co(III) redox conversion. For the second wave, however, there are two plausible scenarios, namely, i) the Co(II)/Co(III) redox conversion of the second cobalt

center or ii) the Co(III)/Co(IV) redox conversion of the Co(III) center formed in the first anodic wave (Scheme in Figure 2c). Although we cannot discriminate among these two possibilities, the similarity in the peak potentials for the second anodic wave of both **Co-MOF** and **Co₂-MOF** suggests that it may also correspond to the Co(III)/Co(IV) redox conversion for the dinuclear **Co₂-MOF**. Nevertheless, it cannot be discarded that both species Co(II)-Co(IV) and Co(III)-Co(III) could coexist in equilibrium as Nocera et al. have proposed recently for other dinuclear cobalt OER catalyst based on its specific electronic features.^{56, 57}

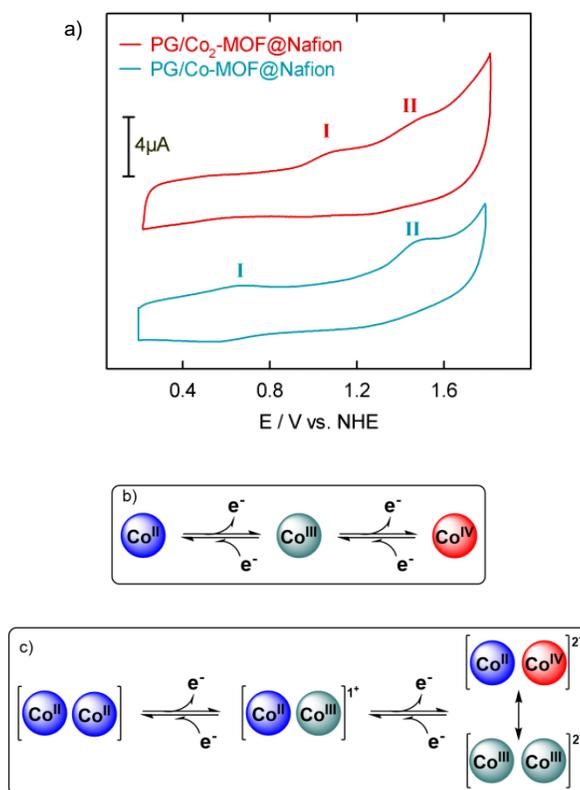


Figure 2. a) Cyclic voltammograms of a pyrolytic graphite electrode modified with **Co₂-MOF@Nafion** (red line) or hydrolyzed **Co-MOF@Nafion** (cyan line) recorded at 0.05 Vs⁻¹ in a solution containing 0.1 M [Et₄N]BF₄ in acetonitrile at 25 °C. b) and c) Redox conversions involved in the voltammetric response of coated (b) **Co-MOF** and (c) **Co₂-MOF**.

Additionally, it has been found that increasing the scan rate from 0.002 to 0.2Vs⁻¹ results in a decrease of the faradaic voltammetric charge from ~7.5 to ~0.6 μC (Figures S14 and S15). This finding is consistent with a progressive limitation of the redox conversion by charge transport across a multilayered film.⁵⁸⁻⁵⁹ In addition, the small variation of the anodic peak potentials with the scan rate (Figures S14 and S15) is indicative of different local environments for the cobalt center along the film. Moreover, it should be noted that upon extending the potential scan to more negative values, two additional cathodic voltammetric waves at -0.450 and -0.870 V (vs. NHE), with their corresponding anodic waves at -0.317 and -0.080V (vs. NHE), appear (Figure S16). The fact that the more negative cathodic wave also appears in the Co₂-MOF-free Nafion-coated graphite electrode reveals that only the first cathodic wave at -0.450 V can be ascribed to the reduction of the cobalt centers. The similarity of its baseline-corrected charge with the total charge exchanged in the two anodic waves preceding the OER signal suggests that it corresponds to the two monoelectronic Co(II)-Co(II)/Co(I)-Co(I) redox conversions.

On the other hand, as shown in Figure 2a, the second redox conversion of cobalt MOFs is accompanied by a significant increase of the background current. The fact that this component of the overall current increases upon addition of variable volumes of an aqueous sodium phosphate buffer solution of pH 7 (Figure 3a) indicates that it corresponds to the **Co₂-MOF** mediated electrocatalytic oxidation of water, commonly known as the oxygen evolution reaction (OER). The insensitivity of the voltammetric wave I to the presence of increasing amounts of water reveals that Nafion not only serves to anchor **Co₂-MOF** to the electrode surface, but also to preclude its hydrolysis, since otherwise a shift of this voltammetric wave towards the one observed for the hydrolyzed **Co-MOF** would be expected.

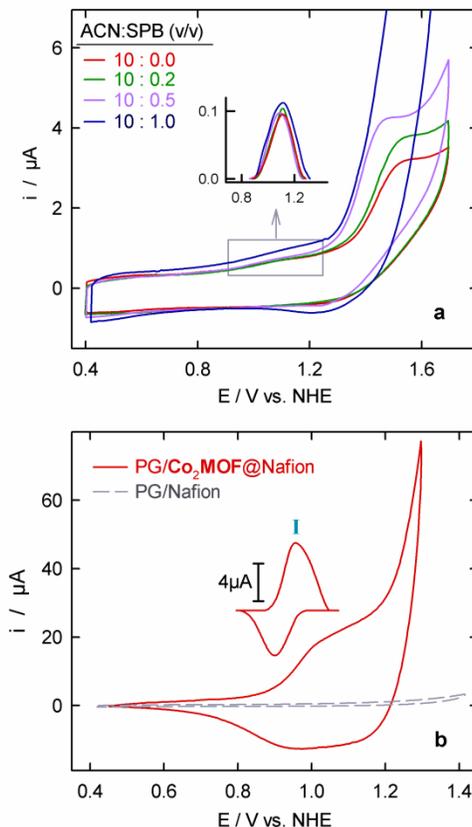


Figure 3. a) Cyclic voltammograms of the $\text{Co}_2\text{-MOF@Nafion}$ modified pyrolytic graphite electrode recorded at 10 mVs^{-1} for the indicated acetonitrile:aqueous sodium phosphate buffer solution (pH 7) ratio. b) Cyclic voltammograms of a pyrolytic graphite electrode modified with Nafion (dashed grey line) or $\text{Co}_2\text{-MOF@Nafion}$ (red line) recorded at 10 mVs^{-1} in an aqueous solution containing 0.1 M sodium phosphate buffer pH 7 at $25 \text{ }^\circ\text{C}$.

Figure 3b illustrates the voltammetric response of $\text{Co}_2\text{-MOF}$ deposited onto a graphite electrode measured in a deaerated 0.1M sodium phosphate buffer solution (SPB) of pH 7. Only one voltammetric wave (wave I) is observed at 0.98 V vs. NHE due to the broad overlapping of the exponentially increasing OER electrocatalytic current with the voltammetric wave involving the Co(III)/Co(IV) redox conversion. Under these conditions, the scan rate dependence of the voltammetric peak parameters of wave I is similar to the ones found in acetonitrile (Figure S17),

so that the rate of the redox conversion is limited by charge transport across the film, and different local environments exist for the cobalt centers along the film.⁵⁸⁻⁵⁹

Electrocatalytic Performance for the Oxygen Evolution Reaction. To explore the electrocatalytic activity of **Co₂-MOF** toward the OER in neutral media, rotating disk voltammetry was employed to obtain nearly steady state polarization curves. All measurements were carried out with a scan rate of 5 mVs⁻¹ and a rotation rate of 4000 rpm, to preserve a uniform concentration profile around the working electrode and to prevent the accumulation of O₂ bubbles. A typical polarization curve is depicted in Figure 4a, which shows a sharp rise of the anodic current at 1.68V vs. RHE that is associated with the onset of the electrocatalytic OER, while there is no appreciable current signal in the absence of the catalyst. In the same experimental conditions, the hydrolyzed mononuclear **Co-MOF** produces smaller electrocatalytic currents, with almost the same onset potential, than its dinuclear counterpart **Co₂-MOF**. The similarity between their electrocatalytic onset potentials and their redox potential for the Co(III)/Co(IV) conversion suggests that the electrocatalytic oxidation of water being driven by Co(IV). An important operating parameter for the OER performance evaluation is the overpotential at a fixed current. Taking the thermodynamic OER potential value of 1.23 V vs. RHE as reference, the PG/**Co₂-MOF**@Nafion electrode shows overpotential values of 460 and 537 mV at 2 and 5 mAcm⁻², respectively. These overpotential values are lower than those determined for the mononuclear **Co-MOF** (565 and 687 mV at 2 and 5mAcm⁻², respectively) and those previously reported for MOF based catalysts operating in neutral media, with the exception of the hybrid MOF MCF-49⁶⁰ (Table S3 in SI). Moreover, a comparison of the polarization curves of **Co₂-MOF** with those obtained for the well known IrO₂ and RuO₂ OER electrocatalysts reveals the excellent OER performance of the herein constructed cobalt based MOF (Figure S18 in SI).

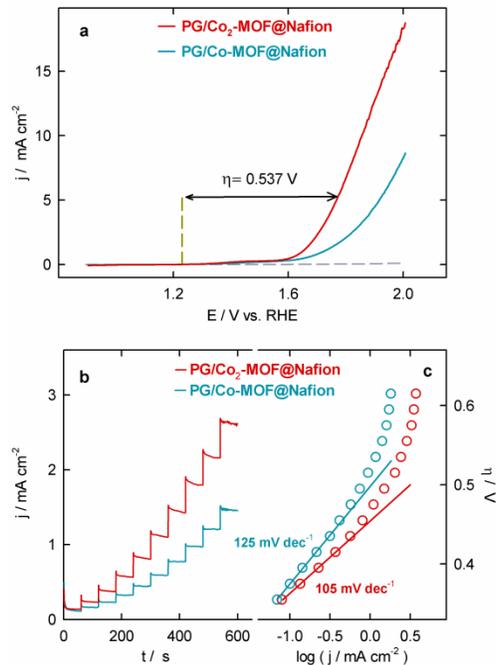


Figure 4. (a) Rotating disk voltammograms of a pyrolytic graphite electrode modified with **Co₂-MOF@Nafion** (red line) or hydrolyzed **Co-MOF@Nafion** (cyan line) recorded at 5 mVs⁻¹ and 4000 rpm in an aqueous solution containing 0.1 M sodium phosphate buffer pH 7 at 25 °C. Dashed grey line is the corresponding cyclic voltammogram of a pyrolytic graphite electrode modified with Nafion. (b) Potentiostatic chronoamperograms of a pyrolytic graphite electrode modified with **Co₂-MOF@Nafion** (red line) or **Co-MOF@Nafion** (cyan line) recorded at 4000 rpm for incremental potential steps of 0.02 V, from 1.59 V to 1.85 V, in an aqueous solution containing 0.1 M sodium phosphate buffer pH 7 at 25 °C. (c) Tafel plots of the steady state current density data of b).

The electrocatalytic kinetics of the OER were estimated from the corresponding Tafel plot obtained from the steady state current density data recorded in the 1.59-1.85V vs. RHE potential range by means of potentiostatic chronoamperometry, with a potential step of 0.02V (Figure 4b). At least three **Co₂-MOF@Nafion** electrode replicates were used in the chronoamperometric

measurements for the determination of Tafel slope, with an electroactive cobalt surface concentration (Γ) in the $15 < \Gamma < 30$ nmol cm⁻² range. **Co₂-MOF** exhibits a Tafel slope of 105 ± 5 mV decade⁻¹ in 0.1M SPB pH 7, being, to our knowledge, the best value among known cobalt MOFs catalysts⁶⁰ (Table S3 in SI). In the same experimental conditions, the Tafel slope for the mononuclear **Co-MOF** is 125 ± 5 mV decade⁻¹.

The turnover frequency number (TOF) was determined from the expression $TOF = jA/(4Fm)$, where j is the current density at a given overpotential, A is the geometrical surface area of the graphite electrode, F is the Faraday constant and m is the mole number of electroactive cobalt participating in the catalytic process. The amount of electroactive cobalt was determined from $m = Q/(nF)$, where Q is the faradaic charge under the baseline-corrected voltammetric peak preceding the electrocatalytic wave, and n is the number of electrons transferred per cobalt center. A value of 0.026 ± 0.005 s⁻¹ was obtained for the TOF number of **Co₂-MOF** at an overpotential of 400 mV with $m = 1.70 \cdot 10^{-9}$ moles and $n = 1$ (Figure 4c). This value is superior to the one determined for the mononuclear **Co-MOF** (0.014 ± 0.005 s⁻¹ with $m = 1.75 \cdot 10^{-9}$ moles and $n = 1$) and to those values reported for similar electrocatalysts (Table S3 in SI).

The influence of the redox electroactive surface concentration of **Co₂-MOF** on the electrocatalytic water oxidation was also evaluated. Figure 5a shows how the current density increases and the corresponding overpotential at a given current density decreases upon rising the redox electroactive surface concentration. As shown in Figure 5b, the estimate TOF number for **Co₂-MOF** at an overpotential of 400mV decreases upon growing the catalyst loading, until it levels off at ~ 0.045 s⁻¹ for a surface concentration of redox active cobalt of $1.7 \cdot 10^{-8}$ moles cm⁻². This leveling off effect may result from agglomeration of the catalyst grains upon increasing their

surface concentration that may limit the solvent exposed catalytic surface area and change the surface mass transport regime from cylindrical to planar symmetry.

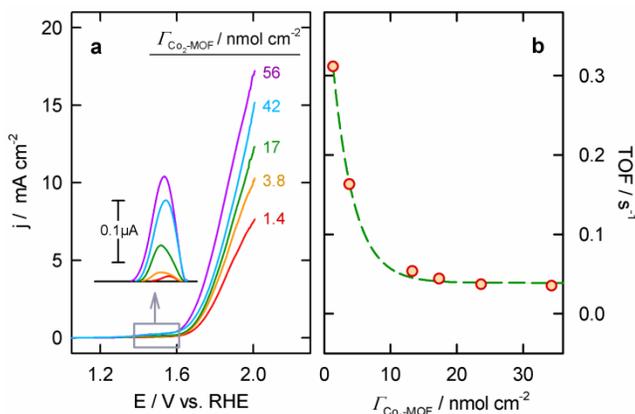


Figure 5. (a) Rotating-disk voltammograms of a pyrolytic graphite electrode modified with different electroactive amounts of **Co₂-MOF@Nafion** in the $0.1\text{-}3.9\cdot 10^{-9}$ mole number range, recorded at 5 mVs^{-1} and 4000 rpm in an aqueous solution containing 0.1 M sodium phosphate buffer pH 7 at 25 °C. Inset plot: baseline-corrected voltammetric wave I. (b) Estimated TOF number at an overpotential of 400mV as a function of electroactive cobalt surface concentration. The green dashed line is just an eye guide.

To assess the stability of the electrocatalyst during the OER, we have compared the polarization curves measured before and after performing 500 consecutive cyclic voltammograms in the 0.8-1.9 V (vs. RHE) potential window, at a sweep rate of 0.2 Vs^{-1} . As shown in Figure 6a the polarization curves shape barely changes after this extensive cycling. Moreover, the robustness and long-term durability of the catalyst have been evaluated under operating conditions by recording the chronoamperometric current at 1.80V for 4 hours (inset of Figure 6b). As shown in the inset of Figure 6b, the chronoamperogram is characterized by an initial decrease of the current until it approaches a steady state value of $\sim 55\%$ of the initial current at long times. The invariance of the voltammograms recorded before and after the chronoamperometric experiment (Figure 6b)

reveals that the decrease of the chronoamperometric current is not due to a loss of **Co₂-MOF**, but to mass transport limitation within the multilayered film. Formation of oxygen microbubbles at the electrode surface may affect water transport inside the film. Nevertheless, the preservation of the voltammetric features after such long term electrolytic experiment proves the good stability of the catalyst. In order to estimate the Faraday efficiency of **Co₂-MOF** for OER, the oxygen production during the water electrolysis Δm_{O_2} has been measured with a polarographic oxygen sensor. A Faraday efficiency of 87% was determined from the slope of the plot of Δm_{O_2} against the charge consumed during the electrolysis Q as illustrated in Figure S19, indicating that the current intensity mostly originates from water oxidation as evidenced by the formation of oxygen bubbles on the electrode surface (Figure S20 in SI).

Finally, it should be noted that the present **Co₂-MOF** retains its electrocatalytic activity and stability toward the OER in aerated conditions (Figure S21), which is demanded for practical applications. Moreover, the stability of **Co₂-MOF@Nafion** after water electrolysis has been proved employing XPS and EDX analysis (Figure S22 and S23, respectively). EDX (Figure S23) shows that cobalt is well distributed on the composite as happened in **Co₂-MOF**, and metal aggregations are not detected. In addition, XPS data of the composite (Figure S22, table S4) supports that cobalt remains in the same oxidation state and the small shift appreciated (1.4 eV) in E_b Co 2p is associated with the presence of fluorine in the composite. It is well known that fluorine tends to induce large chemical shifts in other elements.

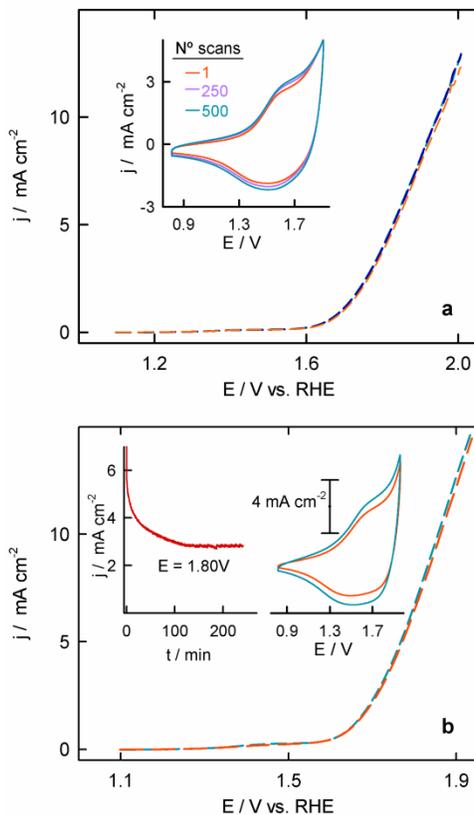


Figure 6. (a) Rotating disk voltammograms for a $\text{Co}_2\text{-MOF@Nafion}$ modified graphite electrode measured at 5 mVs^{-1} after recording 1 scan (dashed orange line), 20 consecutive scans (dashed blue line) and 500 consecutive scans (dashed cyan line) at 0.2 Vs^{-1} in an aqueous solution containing 0.1 M sodium phosphate buffer pH 7 at $25\text{ }^\circ\text{C}$. Inset plot: voltammograms recorded at the indicated number of scans with 0.2 Vs^{-1} . (b) Rotating disk voltammograms for a $\text{Co}_2\text{-MOF@Nafion}$ modified graphite electrode measured at 5 mVs^{-1} before (dashed orange line) and after (dashed cyan line) recording the chronoamperometric current at 1.80V vs. RHE for 4h are depicted in the inset plot. The corresponding cyclic voltammograms at 0.2 Vs^{-1} before (orange line) and after (cyan line) electrolysis experiment are depicted in the inset plot.

CONCLUSIONS

In summary, we have developed the synthesis of a new microporous MOF based on two SBU with dinuclear cobalt centers. In this sense, the employing of a well-defined cobalt cluster drives force an unusual topology for Co-MOFs, where one of the cobalt has three open coordination positions, which has not precedent in MOF materials based on cobalt. In addition, the largest channel size is in the range of 10 to 12Å. Adsorption isotherms have revealed that **Co₂-MOF** is selective for CO₂ adsorption versus CH₄ with similar values to those of zeolitic molecular sieves. Dispersion of **Co₂-MOF** in an alcoholic solution of Nafion gives rise to a composite (**Co₂-MOF@Nafion**) with a high resistance to hydrolysis in aqueous media. The obtained composite shows good adherence to graphite electrodes, where it exhibits a high electrocatalytic performance for water oxidation in neutral media, with a TOF value superior to the one 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.

EXPERIMENTAL SECTION.

All chemicals were purchased from the Sigma Aldrich Chemical Co. and used as received. $[(Co_4O_4)(OAc)_4(Py)_4]$ was synthesized according to published procedures.⁴⁴

Synthesis of Co₂-MOF. Solvothermal conditions were employed to generate **Co₂-MOF** using $[(Co_4O_4)(OAc)_4(Py)_4]$ ⁴⁴ as building block of the final materials. It was synthesized from 2.7 equivalents of H₃BTC (2.38 mmol) per each equivalent of $[Co_4O_4(OAc)_4(py)_4]$ (0.89 mmol) which were dissolved in two different solutions with 25 mL DMF each one. The two solutions were mixed and 8 equivalents of trifluoroacetic acid were added to reaction mixture. The resulting

solution was introduced into a stainless steel autoclave, being heated at 135°C for 72 hours under autogeneous pressure and static conditions. Once cooled to room temperature, the solution was filtered and the collected purple crystals were washed with acetone in order to remove the remaining DMF solvent molecules. Finally, the material was isolated and dried under vacuum at room temperature. Anal. Calcd for C₃₅H₃₉Co₃N₅O₁₆: C, 43.676; H, 4.084; N, 7.276; Co, 18.369. Found: C, 43.947; H, 4.005; N, 7.593; Co, 18.570.

Chemical analysis: Elemental analysis of nitrogen, carbon and hydrogen (N, C, H) contents of isolated solid materials were determined with a Carlo Erba 1106 elemental analyzer using sulfanilamide as reference. Also, a Varian 715-ES inductively coupled plasma atomic emission spectrometer (ICP-AES) was used in order to determine the content of Co. (More information in SI).

Thermogravimetric analysis (TGA). It was carried out in a Netzsch TGA/STA 449 F2 Jupiter apparatus; using a heating rate of 10 °C/min in an air stream of 100 mL/min until a temperature of 600 °C was reached.

X-ray Powder Diffraction. The X-ray Diffraction measurements were acquired according to the powder method, in Bragg-Bretano geometry using a CUBIX diffractometer from PANalytical equipped with a PANalytical X'Celerator detector. X-ray radiation of Cu K α was used and the measurement range was from 2.0° to 40° (2 θ) with a step of 0.020° (2 θ).

Single-crystal X-ray diffraction. A single crystal of Co₂-MOF was mounted on a cryoloop using a viscous hydrocarbon oil to coat the crystal. X-ray data were collected at 120 K on a Supernova diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray Source ($\lambda = 0.71073 \text{ \AA}$). (More information in SI).

Scanning electron microscopy of field emission. FESEM images of **CO₂-MOF** were acquired using a Ultra 55 (Zeiss), operating at 2.0 KV, using powder samples prepared on a sample holder with a double-sided adhesive tape for the dispersion of the sample. Samples were coated with platinum in order to avoid charging effect.

Magnetic measurements. Magnetic susceptibility measurements were carried out on a polycrystalline sample with a Quantum Design MPMS-XL-5 SQUID susceptometer. The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables.

X-ray photoelectron spectra. X-ray photoelectron spectra of the catalysts were recorded with a SPECS spectrometer equipped with a Phoibos 150MCD-9 multichannel analyzer using non monochromatic MgK α (1253.6 eV) irradiation. Spectra were recorded using an analyzer pass energy of 30 eV and an X-ray power of 100W under an operating pressure of 10⁻⁹ mbar. (More information in SI).

Adsorption Measurements. High resolution adsorption isotherms up to 1 bar were measured in a Micromeritics ASAP 2010. Approximately 150 mg of solid were immersed in a liquid circulation thermostatic bath within a glass sample holder. The samples were degassed overnight at 333 K under high vacuum before each isotherm. Then, CO₂ adsorption isotherms were acquired at 273, 283, 298, 313 and 333 K.

High pressure adsorption isotherms were evaluated in an IGA-3 gravimetric analyzer (Hiden Isochema). About 50 mg of sample were loaded into the hanging pan and degassed at 333K under high vacuum during 4 hours. No weight loss was recorded at the end of the degasification process. The sample was then cooled down to the adsorption temperature under vacuum prior the isotherms

acquisition. Pure CO₂ and CH₄ isotherms were measured up to 1 MPa (10 bar) at 283, 298, 313 and 333 K. (More information in SI).

Electrochemical Measurements. Linear scan voltammetric measurements were performed with an AUTOLAB PGSTAT 30, from Eco Chemie B.V, in a three electrode undivided glass cell, equipped with a gas inlet and thermostated with a water jacket. The counter and reference electrodes were a Pt bar and an Ag|AgCl|NaCl saturated electrode, respectively. The reference electrode was connected to the cell solution via a salt bridge, and kept at room temperature ($25 \pm 1^\circ\text{C}$) in a non-isothermal configuration. The working electrode was a homemade pyrolytic graphite electrode constructed by fitting a rod of highly oriented pyrolytic graphite from Mineral Technologies into a PEEK casing, so that it exposed the edge of the graphite planes with a circular geometric area of 0.07 cm^2 . Prior to cobalt MOFs coating, graphite electrodes were polished with abrasive P2400 sandpaper, then they were rinsed with Millipore water and dried. To modify the electrode, suspensions of 5 mg mL⁻¹ of **Co₂-MOF**, hydrolyzed **Co-MOF**, **IrO₂** or **RuO₂** electrocatalyst in a Nafion solution (5 wt. % in lower aliphatic alcohols and 15 20% water solution, from Sigma Aldrich) were prepared by ultrasonication for 15 minutes. Then, a volume of $\sim 5 \mu\text{L}$ of this suspension was dropped cast onto the graphite electrode and dried at room temperature overnight.

Before electrochemical measurements, cyclic voltammetry (CV) was performed in the potential range of 0.2 1.3 V at a sweep rate of 50 mVs⁻¹ to obtain a stable CV profile. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument. The current density was referred to the geometrical electrode area. (More information in SI).

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Experimental procedures employed during this study, chemical analysis of **Co₂-MOF**, PXRD, TG, FESEM, EDX and XPS results, magnetic, adsorption and electrochemical measurements, and crystallographic data are described in the Supporting Information (PDF). Crystallographic data for **Co₂-MOF** (CIF).

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