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Dedication ((optional))

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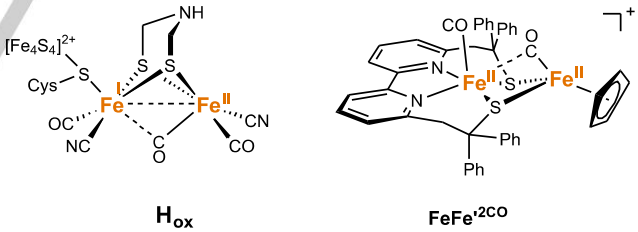
Mimicking hydrogenases with synthetic complexes is a promising strategy for the design of Earth-abundant electrocatalysts for H_2 evolution as alternative to platinum. Here, we describe a bio-inspired FeFe electrocatalyst, with a semi-bridging μ-CO ligand, active and stable for H_2 evolution in acidic aqueous solutions after its physiadsorption onto carbon-based electrodes.

In the current energetic and environmental context, H_2 is a promising fuel to foster the ecological transition.[1] However, the renewable production of H_2 remains challenging and requires stable, efficient, cheap and scalable catalysts for the hydrogen evolution reaction (HER). Nature is a great inspiration through hydrogenase enzymes that produce H_2 with an unrivalled activity.[2, 3] Following this bio-inspired approach, a large number of homogeneous molecular electrocatalysts for H_2 production has been reported, whose structures model either the active site of the [FeFe]- or [NiFe]- hydrogenases.[4-14] Even if these non-noble metal-based catalysts can display high efficiency, they suffer from low stability or/and low solubility in water required for sustainable applications. In order to overcome these drawbacks, the immobilization of molecular catalysts on electrode surfaces is one of the most promising strategies.[15-23]

Here we report electrocatalytic H_2 production in acidic aqueous solutions with a mimic of the [FeFe]-hydrogenase active site (Scheme 1). The previously described complex $[L^{N2S2}(CO)Fe^{II}(CO)Fe^{II}Cp]^+$ (**FeFe′^{2CO}**, Scheme 1, with L^{N2S2} = 2,2'-(2,2'-bipryridine-6,6'-diyl)bis(1,1'-diphenylethane-thiolate) and Cp^- = cyclopentadienyl anion) displays one CO terminally bound to the iron center of the $L^{N2S2}Fe^{II}$ site and a second CO semi-bridging the two centres in favour of the $Fe^{II}Cp$ site.[24] Remarkably, **FeFe′^{2CO}** is a rare example of FeFe model displaying a semi-bridging CO, as observed at the active site of [FeFe]-hydrogenase,[25] where it helps balancing the changes in the oxidation states during catalytic turnover.[2]

We show here that after immobilization of **FeFe′^{2CO}** onto edge-plane graphite (EPG) electrodes, **FeFe′^{2CO}**@EPG behaves as an efficient and robust HER electrocatalyst in acidic water, whereas the HER properties of **FeFe′^{2CO}** could not be studied under homogeneous conditions because of its decomposition upon reduction in CH_2Cl_2 solution.

Scheme 1. Schematic representation of the active site of the H-cluster of



H_{ox} **FeFe′^{2CO}**

[FeFe]-hydrogenases in its H_{ox} state (*left*) and of **FeFe′^{2CO}** (*right*).

Modification of EPG electrodes was achieved by drop casting a solution of **FeFe′^{2CO}** in CH_2Cl_2. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopic characterization (Figure 1) of an **FeFe′^{2CO}**@EPG modified electrode confirms the presence of two Fe-bound CO ligands, with CO vibration stretching frequencies at 1914 and 1961 cm^{-1} vs 1918 and 1959 cm^{-1} (data recorded on a solid-state sample).[24]

A further confirmation that the structure of the heterobinuclear **FeFe′^{2CO}** complex is preserved after physiadsorption comes from X-ray photoelectron (XPS) spectroscopy (Figures 2 and S1). The $2p_{1/2}$ peaks corresponding to two different Fe centres (different ligation) are observed at 708.3 and 710.7 eV, values consistent with those obtained for other reported Fe^{II}-CO species.[18, 22] The 1s peak of the bipyridine nitrogen atoms is observed at

399.3 eV, which also agrees with similar complexes reported in the literature.[26, 27]

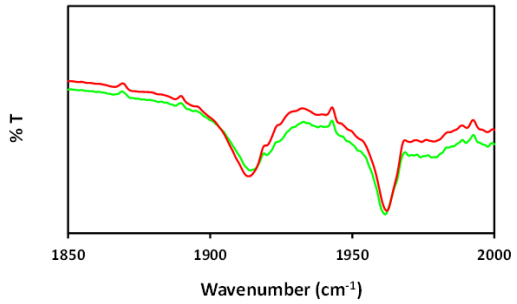


Figure 1. ATR-FTIR spectra of **FeFe′^{2CO}**@EPG electrodes as prepared (*green*) and after 2 hr of bulk electrolysis (*red*) at –0.80 V vs SHE in degassed pH = 4 phosphate buffer.

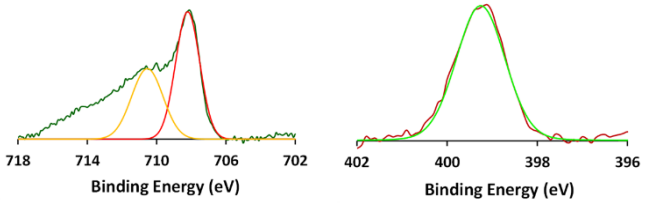


Figure 2. XPS spectra of **FeFe′^{2CO}**@EPG electrode at the (**A**) Fe $2p_{1/2}$ and (**B**) N 1s core level. The XPS spectra were fitted with PeakFit v4.12 software using a combination of Gaussian (70%) and Lorentzian (30%) distributions. Binding energies are referenced with respect to the adventitious carbon (C 1s BE = 284.6 eV).

The cyclic voltammogram (CV) of **FeFe′^{2CO}**@EPG (Figure S2) was recorded in aqueous solutions with 100 mM KPF_6 supporting electrolyte at pH ~5.5. An irreversible cathodic signal is observed at ~ –0.65 V vs SHE, which translates into ~ –1.26 V vs Fc^+/Fc in CH_2Cl_2,[28] and can be assigned to the first one-electron reduction process of **FeFe′^{2CO}**. In CH_2Cl_2 solution, an irreversible reduction is also observed under homogeneous conditions at –1.34 V vs Fc^+/Fc, indicating that the reduced species undergoes rapid evolution over time (Figure S3). A surface loading of 4 x10^{-11} mol·cm^{-2} has been determined based on the integration of the reduction process (*see* the *SI*).

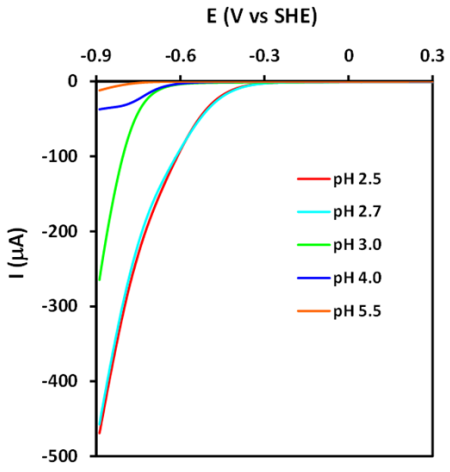


Figure 3. Linear sweep voltammetry of **FeFe′^{2CO}**-modified EPG electrode (3.5 mm diameter) recorded at 50 mV·s^{-1} in aqueous medium with different acid concentrations resulting in different pHs. Conditions: 100 mM KPF_6 as supporting electrolyte, Pt wire as a counter electrode and aq. Ag/AgCl (sat. KCl) as a reference electrode were used.

Linear sweep voltammetry measurements were performed at **FeFe′^{2CO}**@EPG in aqueous solutions of different pH values (Figure 3). Lowering the pH triggers the appearance of a catalytic wave assigned to HER with onset potential corresponding to that of the first one-electron reduction process of **FeFe′^{2CO}**. Lowering of the pH remarkably enhances the catalytic behavior of the material, since the intensity of the catalytic wave continuously increases with decreasing pH values.

Production of H_2 was confirmed based on rotating ring disk electrode (RRDE) measurements at pH = 4 (Figure 4), H_2 being oxidized at the Pt ring poised at 0.4 V vs SHE. By contrast, pristine EPG electrode are inactive for H_2 evolution, to as no H_2 oxidation current is observed at the Pt ring under the same conditions (Figure S4). The overpotential (η) for HER is determined using $E^0_\eta = -0.059 \times pH - E_{onset}$ equation to be ~460 mV for complex **FeFe′^{2CO}** (*see the SI*).

Chronoamperometric measurements run at –0.80 V vs. SHE in pH 4 phosphate buffer displays sustained catalytic current at much higher value (0.42 mA cm^{-2}, Figure S5, *red*) than that shown by unmodified carbon electrode (0.05 mA cm^{-2}, Figure S5, *green*). The sustainability of the electrolysis current is a good indicator of the robustness of the modified electrode. In parallel, the ATR-FTIR spectrum (Figure 1) recorded after an electrolysis of 2 hours is comparable to the as prepared **FeFe′^{2CO}**@EPG material, confirming that the initial molecular structure of the complex, including the two Fe-bound CO ligands, is retained under electrocatalytic conditions. The CVs recorded before and after a bulk electrolysis of 2 hours are also similar in agreement with the absence of degradation of the molecular catalysts at the surface of the EPG electrodes (Figure S8). Controlled potential coulometry experiments (in the 2h and 9h timescale, Figures S5-S6) evidence that the stability of the **FeFe′^{2CO}**@EPG electrode and allow turnover number (TON) and frequency (TOF) to be determined: $TON_{2h} \approx 1.15x10^5 \pm 2.3x10^3$, $TON_{9h} \approx 5x10^5 \pm 2.5x10^3$, $TOF_{2h} \approx TOF_{9h} \approx 15 \pm 0.3$ s^{-1}. Faradaic efficiency of the catalyst has be determined after 9h of controlled potential electrolysis experiment at -0.80 V vs SHE in degassed pH 4 phosphate buffer to be ~89±3%.

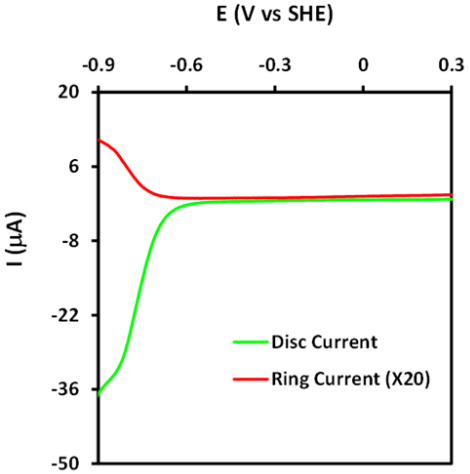


Figure 4. RRDE measurement of **FeFe′^{2CO}**-modified EPG electrodes (3.5 mm diameter) at 300 rpm in aqueous pH = 4 phosphate buffer at 20 mV·s^{-1}, the platinum ring was poised at 0.4 V vs SHE. The corresponding blank sample (pristine EPG) is shown in Figure S4.

We have previously evidenced that when **FeFe′^{2CO}** is solubilized in diluted CH_3CN solutions, one CO is removed leading to the $[L^{N2S2}Fe^{II}\mu\text{-}(CO)Fe^{II}Cp]^+$ complex, **FeFe′^{CO}**, which displays a bridging CO ligand.[24] The **FeFe′^{CO}** complex has revealed to be an efficient homogeneous HER electrocatalyst in CH_3CN, with H_2 being produced through an E[ECEC] mechanism (E = electron transfer; C= proton transfer). Interestingly, it has been evidenced that the one-electron reduction of **FeFe′^{CO}** leads to a fully characterized mixed valence Fe^IFe^{II} species (**FeFe′^{CO,red}**), corresponding to the entry of the electrochemical cycle.[24]

Concerning the electrocatalytic pathway of the present study, we propose that the one-electron reduced state of the immobilized **FeFe′^{2CO}** (i.e. a mixed valence Fe^IFe^{II} complex similar to **FeFe′^{CO,red}**) can be directly protonated at pH 4, since the catalytic wave for the aqueous **FeFe′^{2CO}**@EPG system develops close to the potential of the first one-electron reduction. Conversely, a two-electron reduction process is necessary to induce the first protonation step of the diiron core of **FeFe′^{CO}** under homogeneous conditions in acetonitrile with Et_3NHBF_4 as proton donor. This difference does not infer that the reduced **FeFe′^{CO}** is more basic than reduced **FeFe′^{2CO}** (actually, the presence of a second CO molecule should decrease electron density at the metal because of increased π-back bonding). Rather, the difference in solvent polarity (water for **FeFe′^{2CO}** vs MeCN for **FeFe′^{CO}**) and difference in pH (Et_3NH^+ as a weak acid in MeCN) allow to rationalize this trend.

Such a catalytic pathway becomes more relevant to the cycle of [FeFe]-hydrogenases, since it involves a mixed valence Fe^IFe^{II} species similar to the H_{red} enzymatic intermediate.[29, 30] On the other hand, the majority of the previously described models of the [FeFe]-hydrogenase are active in lower Fe oxidation states ($Fe^{0\text{-}I}$), stabilized by a set of CO, CN^- and P-based ligands,[31] instead of potential bio-relevant states ($Fe^{I\text{-}II}$).[24, 32]

In conclusion, this work describes an efficient and robust HER electrocatalyst active in acidic aqueous solutions after its physiadsorption onto carbon-based electrodes. It also represents a rare catalytic model of the [FeFe]-hydrogenase with the presence of a semi-bridging CO. On modified electrodes, we have proven that its structure is preserved, including the two Fe-bound CO remaining coordinated during catalysis, which is not the case under homogeneous conditions. This is a clear example of how heterogenization of complexes can stabilize structures via specific interaction with the surface, providing access to new catalytic systems.

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Keywords: Electrocatalysis • H_2 evolution • Heterogeneous electrochemistry • Bio-inspired catalysts • Earth-abundant electrocatalysts.

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