

Galán-Mascarós Research Group



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Abstract

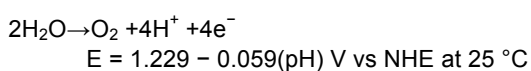
Our research team is devoted to the development of new molecule-based materials for applications in the fields of Renewable Energies and Materials Sciences. On the former, we are developing efficient and stable redox catalysts from Earth abundant metals, with

special interest in water oxidation catalysis for the production of solar fuels. On the later, we target the design of novel multifunctional hybrid materials with co-existence of properties of interest (magnetic, catalytic, electrical, optical,...) with control of the synergy between physical properties in the search for new phenomena..

Catalytic water oxidation

Water oxidation catalysis is one of the biggest challenges that inorganic chemistry is facing today. The discovery of a fast, robust, and cost-effective catalyst would be key for the realization of artificial photosynthesis, an achievement that could probably solve the energy problem worldwide in the near future.

Oxygen evolution from water is a complex redox process. It occurs at high oxidation potentials, and it involves four electrons. An active water oxidation catalyst (WOC) for such a high-energy, multielectron process will probably need the participation of metal ions, as occurs in natural photosynthesis. And it should meet many important requirements to be technologically relevant: inexpensive, readily available, produced in bulk, and stable to air, light, water, heat and oxidative deactivation



We are working in two different types of catalysts that exhibit very promising features: cobalt-containing polyoxometalates (POMs) and Prussian blue (PB) derivatives.

Polyoxometalate WOC

Polyoxometalates (POMs) are a versatile family of inorganic molecular clusters. In these complexes, a transition-metal core can be stabilized by discrete metal oxide frameworks, usually tungstate or molybdate. These inorganic polyanionic ligands are perfectly stable towards oxidative degradation, and their oxo-bridged structure also allows for reversible proton exchange with the solvent, a feature usually combined with the subsequent oxidation steps in the reaction mechanism of WOCs.

After discovering the excellent catalytic activity of $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ (**Co₉**, Fig. 1) in homogeneous conditions, we have processed this POM into carbon paste electrodes, to determine if it remains active in the solid state.

The **Co₉** modified electrodes exhibited a strong catalytic activity, reaching over 1 mA/cm^2 at low overpotentials, at neutral pH, and with catalyst loadings below 15 %. The performance of these electrodes is remarkable. Benchmarking studies demonstrate that small **Co₉** contents ($< 2 \mu\text{mol}$) yield higher current densities than equivalent electrodes with large excess of other known catalysts, such as Co_3O_4 (Fig. 2). Furthermore, these **Co₉**-modified anodes showed very robust performance, maintaining identical currents for hours, without any apparition of fatigue.

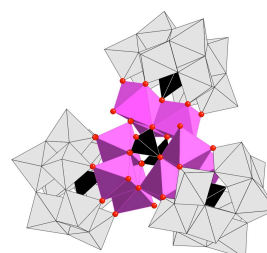


Fig. 1 - Structure of the polyanion $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ (**Co₉**).

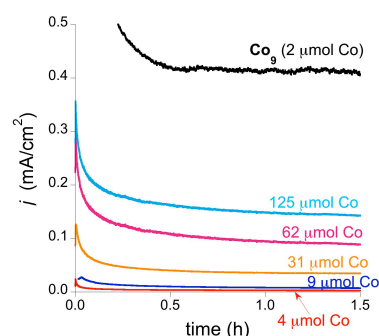


Fig. 2 - Current density at +1.3 V (vs NHE) in a pH 7 solution with a **Co₉**-modified carbon paste working electrode (black line) and with Co_3O_4 working electrodes at different catalyst contents (color lines). Numbers related to the total amount of Co atoms in the blend.

An additional advantage of **Co₉** is its stability and activity in acidic media. Our POM-modified electrodes exhibited significant catalytic current even at pH 1, where most metal oxides just dissolve. Until now, only noble metal oxides had been shown such capability. Thus, **Co₉** is the first oxide-based WOC from Earth-abundant metals that is stable and active in acidic media, and even faster than extended solid state analogs at neutral pH.

Prussian blue WOCs

Transition metal hexacyanometallates (PBs) are isostructural to the original Prussian blue, the all-iron $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ derivative discovered over 300 years ago as a pigment. In the crystal structure, two octahedral metal centers are bound through cyanide bridges to construct a face-centered cubic unit cell (Fig. 3a). PBs are known for many combinations of transition metal ions in multiple oxidation states. Despite of their rigid structure, these coordination polymers are usually non-stoichiometric because different non-integer ratios can be accommodated. This chemical variety makes of them a versatile type of molecule-based materials.

We have investigated the catalytic activity in water oxidation conditions of the PB derivative $\text{K}_{2x}\text{Co}_{(2-x)}[\text{Fe}(\text{CN})_6]$ ($0.85 < x < 0.95$) (PBCoFe).

PBCoFe was prepared on fluoride doped tin oxide (FTO) coated glass electrodes. The modified electrodes are highly transparent, with a transmittance over 70 % in the 400-900 nm region without significant absorption bands. The morphology of the electrodes surface consists of an agglomerate of cubic-shaped crystallites with maximum edges up to 0.25 μm (Fig. 3b). These electrodes show significant catalytic current was detected just above 1.10 V (NHE) at pH 7, corresponding to a 300 mV overpotential (η). Taking into account the surface coverage on the electrode ($\Gamma_0 = 1.4 \pm 0.2 \text{ nmol cm}^{-2}$), we can estimate turnover frequency numbers between $2 \times 10^{-3} \text{ s}^{-1}$ at $\eta = 300 \text{ mV}$ and 0.5 s^{-1} at 550 mV.

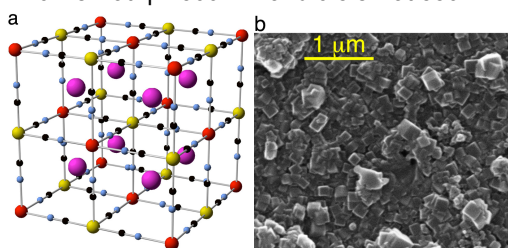


Fig. 3. (a) Representation of a cubic Prussian blue type structure. (b) SEM image of a PBCoFe modified FTO electrode.

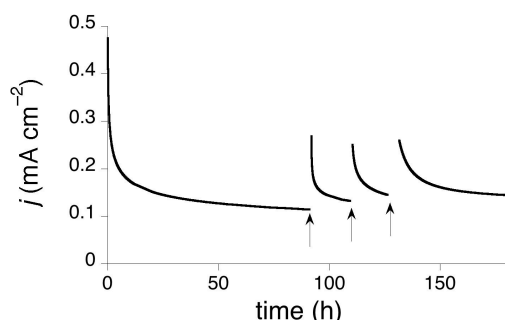


Fig. 4 Current profile during water electrolysis at 1.41 V (NHE) at pH 7.0 with a PBCoFe modified working electrode. Black arrow indicates change of buffer solution.

Figure 4 shows the current density (j) data for a bulk water electrolysis in the same experimental conditions. After a short induction period due to capacitance, j decreases slowly to reach a stable regime at 35-40% of the initial catalytic current after one day. Successive electrolyses in new buffer solutions reach consistent stable currents for weeks, at a nominal rate of 60000 cycles per day (Fig. 5) This would account for a production of 5000 L of O_2 per day, per gram of PBCoFe catalyst, at neutral pH and ambient conditions. Such catalytic performance is unparalleled in the field, where PBCoFe represents the first non-oxide heterogeneous WOC.

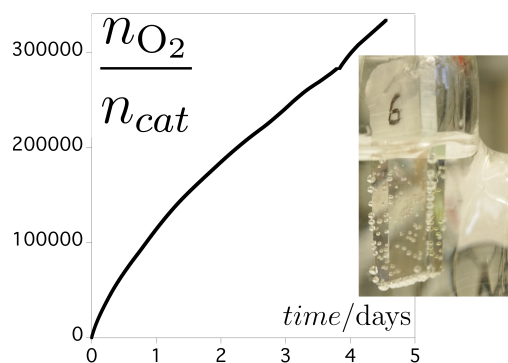


Fig. 5 Oxygen evolution profile during water electrolysis at 1.41 V (NHE) at pH 7.0 with a PBCoFe modified working electrode.

Novel building blocks for multifunctional materials: Sulfonate functionalized 1,2,4-triazoles

One of our interests in molecule-based materials is the functionalization of 1,2,4-triazole (trz) molecules with sulfonate groups. These multidentate anionic ligands are expected to promote the formation of novel metal-organic frameworks, since its charge would avoid the need for additional counterions.

We have developed a new synthetic method for the preparation of functionalized trz, since they are typically obtained from organic solvents, incompatible with highly polar groups. Our water-based synthetic protocol consists of a transamination of N,N-dimethylformamide azine with primary amines. The procedure is general, and it allows for the synthesis of 4-substituted trz with highly polar functional groups, as sulfonates, but also carboxylic acids or amino acids, where chirality is conserved (Fig. 6).

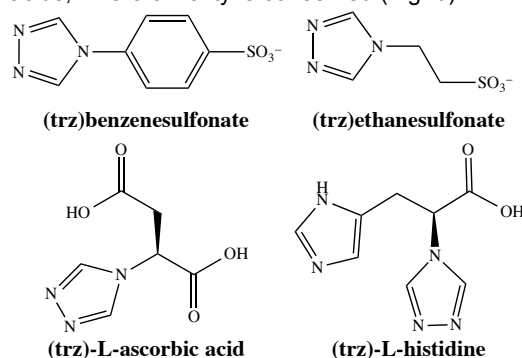


Fig. 6 Some example of the 4-substituted trz molecules with highly polar functional groups obtained following a water-based synthesis.

With sulfonate-functionalized trz we have obtained new 2D cadmium coordination polymers, constructed by neutral layers. Regarding physical properties, the luminescence of the ligand (trz)benzenesulfonate (Fig. 6) shows a remarkable blue-shift as part of the

metal-organic framework, with respect to the free molecule that arises from the coordination to Cd^{2+} cations. No luminescence from the Cd^{2+} centers was detected in this case. It is worth mentioning that (trz)benzenesulfonate shows a

very energetic excitation and emission when compared to similar compounds/ligands, where they appear typically over 400 nm. This is due to the strong electron-withdrawing effect of the sulfonate group.

Articles

“Nonelectrochemical Synthesis, Crystal Structure, and Physical Properties of the Radical Salt $[\text{ET}]_2[\text{CuCl}_4]$ (ET = Bis(ethylenedithio)tetrathiafulvalene)”
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