Supporting Information

Investigation of Protective Properties of Organic Layers Towards Reactive Oxygen Species (ROS).

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1. SECM methodology.

We follow a foot-printing strategy based on the use of SECM in feedback mode when the substrate under investigation is not electrically connected (unbiased conditions). This foot-printing strategy can be described by three main steps:

- (i) Positioning of the SECM tip at 5 μm from the substrate. The tip UME is placed in the close proximity of the organic layer by registering approach curves with the aid of a redox probe in solution; from the approach curves, the distance tip-substrate is derived.
- (ii) Oxygen reduction on the surface of the SECM tip. Once the SECM tip is in position, the solution with the redox probe is replaced with the target solution (10⁻² mol L⁻¹ KPF₆ or 10⁻² mol L⁻¹ KOH in this study) for oxygen reduction. During this replacement, the electrochemical cell is thoroughly rinsed to remove possible pollutants that could affect the experiment. The potential to reduce oxygen is applied to the SECM tip; this potential is previously established by recording the cyclic voltammogram of oxygen reduction in the medium under investigation.

(iii) Probing local modifications of the organic layer after ORR. To evidence the local transformations, the organic layer is probe with an indifferent redox mediator. The impact of the reactive oxygen species on the organic layer can be assert either moving the tip in the solution to register an image of the area in the x-y plane (the image should be registered before and after exposure by comparison); or registering the approach curves before and after ROS interaction. Different types of approach curves are obtained (from positive to negative feedback) that sense the ability of the probe to pass through the layer, providing a view of the modifications.

2. Control experiments.

A set of control experiments have been performed during this study. First, a common feature is that no modification occurs when the applied potential is around 0 V vs Ag/AgCl in both alkaline and neutral media and on both organic films.

2.1. Effect of H_2O_2 .

Platinum is widely used as component in the cathode of fuel cells to speed up the ORR and promote the direct 4-electron pathway to water.¹ However, the catalysis of ORR on platinum surfaces also depends on the state of the surface (platinum single crystal, facets, alloys with other metals, pre-treatments of the surface, adsorption of anions from the electrolyte among others).^{2,3,4,5} Not all platinum surfaces have the same catalytic activity. The amount of H₂O₂ produced, as well as the overall reaction kinetics, is sensitive to the platinum surface structure. For example, a larger proportion of H₂O₂ is formed during ORR on polycristalline platinum, than when the preferential surface orientation is (100) or (111) (See reference [6] and references therein). In this context, to assess the role of H₂O₂ in the modification observed on the *p*-(methyl)phenyl films at potentials corresponding to the plateau of the ORR, we performed an experiment where *p*-(ethynyl)phenyl and the p-(methyl)phenyl films were kept during 30 seconds in a 30 % H₂O₂ solution. Approach curves were registered before and after H₂O₂ treatment. As shown in Figure S1, any degradation effect due to H₂O₂ can be observed for both organic films, as approach curves recorded before and after treatment in H₂O₂ are similar and display a negative feedback character (note that plots registered before and after are overlayed). These findings suggest that H₂O₂ may not be directly involved in the damage of the *p*-(methyl)phenyl films during the ORR on Platinum UME.



Figure S1. SECM approach curves registered with a Pt UME (5μ m-radius) in 10^{-3} mol L⁻¹ Fc(MeOH)₂ solution + 0.1 mol L⁻¹ H₂SO₄ on PPF surfaces modified with (a) p-(ethynyl)phenyl multilayer and (b) p-(methyl)phenyl multilayer before (black) and after (blue) the treatment with a 30 % H₂O₂ solution.

2.2. Fenton-like reactions.

It has been previously proposed in the literature that H_2O_2 can undergo reduction at metals such as platinum or be catalytically decomposed to HO[•] in presence of transition metals such as iron (II).^{7,8,9} As it is known, H_2O_2 is a weak oxidant, while HO[•] is one of the most active oxidants known.**Error! Bookmark not defined.** An open question arising from the reactivity observed is whether traces of Fc(MeOH)₂ possibly present in the target solution (10⁻² mol L⁻¹ KPF₆) during the ORR were able to mediate the decomposition of H_2O_2 to HO[•] by Fenton-like reactions, and in turn damage the *p*-methyl(phenyl) films. The electro-Fenton reactions have been widely studied in the framework of the electrochemical advanced oxidation processes (EAOPs) for waste water remediation, and there is a consensus in the literature on the role of HO[•] as the primary oxidizing agent involved in the destruction of the organic matter.^{10,11,12} The *in-situ* electro-generation of HO[•] from H_2O_2 in presence of metals by electro-Fenton reactions at the cathode is very well established (Equations S1 and S2).^{13,14}

$$O_2 + 2 H^+ + 2 e^- \rightleftharpoons H_2O_2$$
 (S1)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO \bullet + HO^-$$
 (S2)

The most favorable experimental conditions for an efficient electro-Fenton process are: noncatalytic cathodic materials such as carbon derivatives, graphite or mercury, where the production of hydrogen peroxide is maximized, ambient temperature, acidic medium (pH 2 - 4), and the presence of metal catalysts such as salts of iron (II) and (III), copper (I), cobalt (III) among others. Although, the salts of iron (II) and (III) are the best catalysts since they act efficiently at lower concentrations, typically 10⁻⁴ mol L⁻¹.¹³ In our case, the experimental conditions are not the most favorable for an electro-Fenton process, with a pH close to 6 in the KPF₆ solution, where platinum can be considered catalytic for a direct conversion of oxygen to water following a 4-electron pathway, and with no metals in solution, only possible traces of Fc(MeOH)₂ from the redox mediator used to approach the tip to the surface. Other sources of metal ions such as iron, copper, cobalt, chromium and nickel were previously discarded by ICP-MS analysis of the electrolytes (*n*Bu₄NPF₆ and KPF₆), reagents (4-(methyl)benzenediazonium tetrauoroborate) and water used for the modification of PPF surfaces and during the SECM experiments. Traces of iron, copper and nickel were only found in concentrations below 0.02 ppm in KPF₆. In any case, production of H_2O_2 by the reduction of oxygen develops in most cathodes materials, but even so, a source of metal ions is required for its decomposition.

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