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The role of water in hydrogen electrocatalysis

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5. Summary

This thesis discusses the role of the solvent in the hydrogen oxidation and evolution reactions on platinum and gold. This novel approach contributes to the understanding of the molecular origins affecting the kinetics of the hydrogen evolution reaction, which is a model electrochemical reaction as well as a promising source of energy, in the era of sustainable energy production and storage.

Since the traditional approach focuses on the nature of the catalyst and the catalytic activity, an exploration of the electrolyte and, specifically, the role of the solvent in the electrocatalysis of hydrogen is much needed. The experimental work presented here was carried out using linear sweep voltammetry and cyclic voltammetry, *in situ* Fourier-Transform InfraRed spectroscopy and Surface-Enhanced Raman spectroscopy, Electrochemical Impedance spectroscopy and the Laser-Induced Temperature Jump method. These techniques were key to elucidate the molecular nature of the solvent-proton, solvent-electrolyte and solvent-electrode interactions taking place at the electrode-electrolyte interface.

In Chapter 2 we studied the hydrogen oxidation and evolution reactions on a polycrystalline platinum electrode in acetonitrile. We started the study by comparing systems in presence of two different cations; namely, a metallic, hydrophilic cation and a lipophilic, organic cation. With this comparison we tried to establish the sensitivity of the reaction to the nature of the cation and we found no direct correlation. However, the kinetics happened to be sensitive to the presence of water in the organic-based electrolytes, since the interaction of the cation with water-traces was found to be different for each system. We used *in situ* FTIR to monitor these interactions and we observed that protons and small cations are preferentially solvated by water. On the other hand, the SERS measurements showed that platinum oxides are not involved in the catalysis of hydrogen evolution and oxidation in acetonitrile. Furthermore, these experiments confirmed that under hydrogen oxidation conditions, water solvates the protons preferentially and together they migrate from the electrode surface towards the bulk. These findings

impact on the hydrogen evolution and oxidation reaction, as we found out that these reactions are mediated by water. Hence, it is difficult to establish a reference electrode for organic solvents due to the sensitivity of the reaction to trace amounts of water. Our conclusions can be extended to several non-protic electrolytes used as test systems for molecular catalysts. Additionally, the sensitivity of these systems to trace amounts of water hinders the possibility of establishing consistent comparisons between systems with a different solvent, leading to an inaccurate comparison of the catalytic activity for the different (molecular) catalysts.

For the sake of completeness, we present a study on the influence of water on the hydrogen evolution reaction on a polycrystalline gold electrode in acetonitrile, which is found in Chapter 3. In this chapter we used *in situ* FTIR as spectroelectrochemical technique which allowed us to follow the migration of ions and water in and out of the interface. Our study reveals that water accumulates at the interface in presence of protons, exhibiting preferential solvation, in agreement with the observations discussed in Chapter 2. These findings endorse the relevance of the electrolyte conditions in the hydrogen electrocatalysis in non-protic solvents, as well as the importance of water in the hydrogen oxidation and evolution reactions. A Tafel plot analysis on polycrystalline gold and platinum in acetonitrile electrolytes shows that the hydrogen evolution presents the same rate-determining step for both metals; i.e. the first electron transfer along with the adsorption of atomic hydrogen on the electrode surface. This mechanism resembles the observations reported for hydrogen evolution in alkaline solutions, reinforcing the hypothesis that the solvent has a significant influence in the hydrogen electrocatalysis.

In Chapter 4 we present a thorough spectroelectrochemical study of the kinetics of hydrogen evolution and H-UPD formation in aqueous electrolytes. The study covers a wide pH range, and the electrode used is a Pt(111) single crystal. We start by measuring the charge transfer resistance in the H-UPD region, and our experiments show that not only the hydrogen evolution in alkaline solutions is

slower, but also the H-UPD formation is. Tafel slopes in the wide pH region (from pH 1 to pH 13) showed how the mechanism for hydrogen evolution changes, implying a major contribution of the solvent as we moved towards higher pH values. Next, we decorated the Pt(111) surface with submonolayer amounts of nickel and generated nickel hydroxide on the surface to monitor the improvement of the hydrogen kinetics in presence of this electropositive metal as a promoter. Once again, impedance spectroscopy and Tafel plot analysis were used. Our observations suggest that the presence of $\text{Ni}(\text{OH})_2$ lowers the hydrogen adsorption reaction barriers, since it was found that not only the HER kinetics change, but also the charge transfer resistance kinetics for the UPD region happens to be faster in presence of the promoter. From these observations we propose a new kinetic model based on the energetic penalty paid for the reorganization of the interfacial water, since the rate of hydrogen adsorption has a pH dependent barrier because the interfacial water structure at the Pt(111) electrode is pH dependent. Therefore, the kinetics of charge transfer would be faster if water were easily reorganized (low pH values), and slower if the water network is rigid (high pH values), as determined by the potential of maximum entropy, which is closely related to the potential of zero free charge (pzfc). The latter is determined by the charge separation between the metal electrode and the electrolyte solution, which in turn, is dependent on the position of the pzfc. The temperature jump technique experiments showed how a submonolayer amount of nickel hydroxide shifts the pzfc closer to the equilibrium potential of the hydrogen evolution, impacting on the energy penalty associated to the movement of charges through the double layer. In consequence, the study elucidates the molecular origin of the slow reaction rates for the hydrogen evolution reaction in alkaline solutions.

In brief, this thesis showed the importance of the solvent in the hydrogen electrocatalysis, specifically, water, by settling its role as a solvent, as a proton donor, and by preferential proton solvation, ultimately clarifying a long-existing debate regarding the pH dependence of the hydrogen evolution, setting a path for

future exploration of solvent-electrode interfaces for tailoring electrocatalytic reactions.

