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The role of water in hydrogen electrocatalysis

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1. Introduction

1.1. Motivation

This work is part of a larger project from our research group, focused on a better understanding of the role of the solvent in electrocatalytic reactions. The main project is subdivided in the following three different approaches: the first project involves the use of ultra-high vacuum techniques (UHV) for the study of H₂ and O₂ dissociation on stepped platinum surfaces covered with water. The research is carried by MSc. Cansin Badan, as his PhD project in the UHV section of the group, under the supervision of Dr. Ludo Juurklink. The second project comprises a detailed computational study, to be found in the PhD thesis entitled: "Water Related Adsorbates on Stepped Platinum Surfaces", by MSc. Manuel Kolb. The third project is presented in this thesis, and pertains to the study of the role of the solvent in the electrocatalysis of hydrogen evolution and oxidation in a "wet" non-aqueous solvent and in alkaline solutions, joining the efforts for a future sustainable hydrogen production and conversion.

Currently, we produce H₂ primarily from the steam-reforming process¹, and from water electrolysis² in a less prominent way. The hydrogen produced is mainly used for processes such as oil refining and in the Haber-Bosch reaction for ammonia synthesis. The ideal picture contemplates a far-reaching use: a hydrogen-based economy³, where electrolyzers driven by renewable energy (solar and wind) are used for splitting water into hydrogen and oxygen with low energy losses. These fuels would be piped to the industry, cities and fuel stations as feedstock for chemical reactors, and for the built-in fuel cells for domestic appliances and cars^{3b}, replacing the use of fossil fuels in a large sector of human activities. The excess could be stored when the supply exceeds the demand. As an extra positive outcome, we would have attained environmental progress by diminishing the greenhouse gas emissions.

The truth is that the sustainable water splitting technologies are still far from scalable and affordable. The electrolyser technologies use rather expensive

catalysts for the anodic oxygen evolution, based on rare metal oxides such as IrO₂ and RuO₂ in acidic environment, which also yield a good turnover for hydrogen production whenever the cathode is made out of platinum. On the other hand, several theoretical⁴ and experimental⁵ efforts have been put forward for the scalability of the oxygen evolution in alkaline media, allowing the use of anodes made from perovskites or earth-abundant metal oxides, such as Ni, Mn and Fe, lowering the cost of production and improving reaction rates, since these metal oxides and perovskites are proven to be stable and cost-efficient. However, the hydrogen evolution in alkaline solutions presents slow reaction rates⁶, leading to an overpotential at the cathode, which translates into energy losses.

Although the hydrogen evolution reaction has been intensely studied, the efforts have been consistently focused on the design of good catalysts, overlooking the role of the solvent. Consequently, a systematic study of the electrolyte interactions in the hydrogen electrocatalysis seems appropriate. We strongly believe that a better understanding of the solvent-intermediates, solvent-electrolyte and solvent-catalyst interactions is fundamental for improving the hydrogen electrocatalysis, and could be extended to several other electrocatalytic reactions involving water, contributing to a more realistic description of the processes occurring at the electrode-electrolyte interface.

1.2. Hydrogen electrocatalysis on platinum

In 1928, Bowden⁷ described an adsorbed layer of hydrogen near the equilibrium potential for H₂/H⁺, deposited on the surface of a thin layer of Pt on a Hg electrode. Later, in 1934, Frumkin and Shalygin⁸ gave evidence of the adsorption of hydrogen on a platinum electrode before the equilibrium potential, i.e. at potentials positive to the H₂/H⁺ equilibrium potential. It was until 1956 when Breiter *et al.*⁹ identified two different forms of hydrogen adsorbed on platinum, coming back seven years after with a well-defined model for the strongly and

weakly adsorbed hydrogen on platinum electrodes¹⁰. The model was based on Langmuir and Frumkin isotherms. The species identified were the hydrogen deposited positive of the equilibrium potential, known as underpotential deposited hydrogen, or H-UPD, and another type of hydrogen deposited negative of the equilibrium potential, commonly called overpotential deposited hydrogen or H-OPD.

Once these adsorbed forms of hydrogen on platinum were identified, questions were redirected towards their kinetics of formation and their role in the hydrogen oxidation and evolution reactions. From the early studies, we pay special attention to those reported by Conway on kinetics^{6a}, followed by the structure sensitivity of the reaction¹¹, the kinetics of H-UPD/H-OPD in alkaline media¹² and the consequences of the coadsorption of anionic species¹³. More recently, Yan *et al.* reported¹⁴ that the binding energy of hydrogen atoms to the polycrystalline platinum surface is the sole descriptor for the hydrogen oxidation and evolution in aqueous media. These studies refuelled the discussion on the origin of the pH dependence of the hydrogen evolution, for which a plausible explanation is still missing.

In acid media, the overall electrochemical hydrogen reaction is



Whereas for alkaline media we write



The key step for the hydrogen evolution reaction is the adsorption of atomic hydrogen on the electrode surface (Volmer step), with one electron transfer:



It is known that from (Eq. 3) to hydrogen evolution, two routes should be considered; i) the combination of two H_{ADS} on the electrode surface to produce H_2 , known as the Tafel step, or ii) the combination of H_{ADS} with one proton and one electron transfer to give H_2 , known as the Heyrovsky step¹⁵.

In the overall mechanism for hydrogen evolution, there will be one step with the least favourable reduction potential, or the least favourable thermodynamics (in case of a chemical step), and this step is usually identified as the rate-determining step (or rather potential-determining step) for the hydrogen evolution to proceed. In the simplest model, the thermodynamics of these steps depends on only a single parameter, or “descriptor”, namely the free binding energy of hydrogen to the catalyst, ΔG_H° .

In Figure 1 we illustrate the relationship between the thermodynamic overpotential, η , which corresponds to the potential difference between the equilibrium potential of the H_2/H^+ redox couple and the extra driving force (potential) necessary for the reaction to proceed; and the binding energy of the atomic hydrogen to the metal, ΔG_H° . The plot is based on the Sabatier principle¹⁶, which predicts that the ideal catalyst binds the intermediate in a balanced way; neither too strongly nor too weakly. In an ideal catalyst, the zero overpotential is achieved when each reaction step is thermodynamically neutral, because the reaction does not need to overcome energetic barriers (the optimal binding energy at the top of the volcano). So far, this relationship is the most accepted descriptor for the hydrogen electrocatalysis, and ΔG_H° is considered as the sole descriptor of the hydrogen evolution rate. However, the question remains how the solvent influences the rate-determining step; in other words, the impact of the solvent interactions on the already established descriptor, or if solvent effects should be considered as an additional separate descriptor.

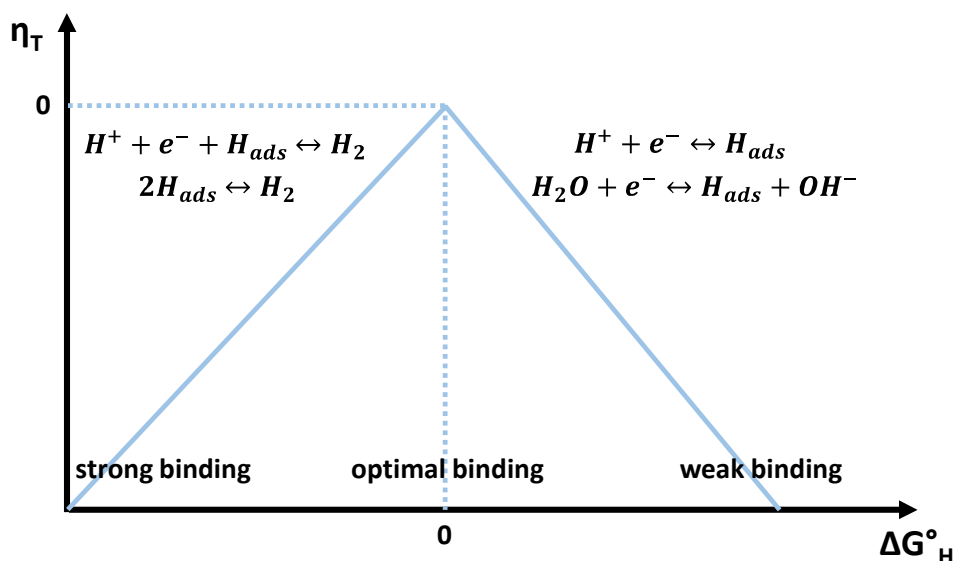


Figure 1. Volcano plot depicting the thermodynamic overpotential, η , versus the binding energy, ΔG_H° . Adapted from Ref.¹⁷ The top of the volcano indicates an optimal binding energy of the intermediates with zero overpotential.

It has been reported¹⁸ that from the Sabatier principle one cannot extract a sole descriptor for the hydrogen evolution because the reaction chooses the pathway with the lowest activation energy, and it does not always depend on stability. Therefore, the transition states should also be considered. It is clear that the potential at which Eq. 3 takes place will strongly depend on the binding energy associated to the adsorbed atomic hydrogen. What is not clear yet is how other molecules in the interface such as solvent molecules and electrolyte could influence the energetic requirements and the activation energies for the separate steps in the hydrogen evolution mechanism. From transient measurements, Conway and co-workers^{6a} have discussed the difference in reactivity between H-UPD and H-OPD; the former being strongly adsorbed on the electrode surface as an spectator for the HER, whereas the latter has been ascribed as the real intermediate in the hydrogen evolution. It has also been stated¹⁹ that the H-UPD is

also sitting in the platinum subsurface, in order to leave some surface available for the H-OPD to react. From these observations we understand that H-UPD does not intervene in the hydrogen evolution/oxidation reaction, although the interplay between the kinetics of both types of hydrogen and the solvent present at the interface has not been discussed.

Since there is little agreement about the molecular nature of reaction descriptors in the hydrogen evolution other than ΔG_H° , in this work we study the contribution of the solvent to the kinetics of hydrogen adsorption and evolution on platinum and gold, by means of electrochemical and spectroelectrochemical studies in a non-aqueous and aqueous solvents. We focus on the solvation of protons and the solvent-proton, solvent-electrode interactions at the electrode interface.

1.3. Acetonitrile as a solvent

Acetonitrile is one of the preferred solvents in electrochemistry due to some of its physicochemical properties: high dielectric constant (37.5), miscibility with water and amphoteric properties. The free electron pair in the nitrogen interacts strongly with cations and electrode surfaces²⁰, whereas the anions seem to interact, although not specifically, with the methyl groups of the solvent. Since acetonitrile is both a weak acid and base, acids tend to be weaker in acetonitrile than in water²¹. For instance, perchloric acid has been reported as the strongest acid in acetonitrile, although the measured $\text{p}K_a=1.57$ ²² indicates that it does not dissociate completely²³. Most acids are weak in acetonitrile, meaning that they only dissociate partially. When this is the case, the base formed from the partial deprotonation associates with the conjugated acid. The process is called homoconjugation and is observed in many aprotic solvents^{23b}. It is due to the fact that the solvent molecules do not confer enough stability to the anions, instead, these anions prefer to go for

the partially shared charge of the proton with another molecule of acid, seeking a better stability.

1.4. Proton solvation

It is obvious that the proton solvation depends on the nature of the solvent and the acid itself. In addition to the capability of the solvent to stabilize the proton, homoconjugation and partial dissociation may depend on how stable the configuration of the solvated proton and the corresponding anion is. On the other hand, aprotic solvents like acetonitrile solvate protons in a different way than protic solvents. For instance, the absolute free energy of solvation of a proton in acetonitrile is $-1089 \text{ kJ.mol}^{-1}$ ²⁴, whereas for water it is $-1104.5 \text{ kJ.mol}^{-1}$ ²⁵. Given these solvation energies, it is not surprising that for the solvation of protons in acetonitrile/water mixtures it has been found that, even at trace levels of water, the preferred solvation spheres are attributed to protons surrounded by water²⁶. Furthermore, it has been shown²⁶⁻²⁷ that water tends to form clusters in the mixture²⁸. Other works suggest²⁹ that, in mixtures of water and aprotic solvents, both electrostatic and steric interactions play an important role in whether the proton is solvated by water or by the aprotic solvent molecules. Steric effects would contribute to the preferential solvation of protons in water, since water molecules are smaller than those of organic nature. While these studies are directed to the understanding of solvation processes, our main interest here focuses on the impact of proton solvation from the electrocatalytic perspective, which has not been evaluated in great detail in the literature.

1.5. Outline of the thesis

This work aims at gathering fundamental insight in the role of the solvent in the electrocatalysis of hydrogen, by revisiting the benchmarking systems; i.e. hydrogen evolution and oxidation on platinum and gold electrodes. Since the study is focused on solvation processes and the interactions between solvent, electrolyte and reaction intermediates at the electrolyte-electrode interface, the techniques used span from *in situ* Fourier-Transform InfraRed Spectroscopy (FTIR) and Surface Enhanced Raman Spectroscopy (SERS) to Electrochemical Impedance Spectroscopy (EIS) and Laser-Induced Temperature Jump method, as well as the classic cyclic voltammetry. Our findings highlight the role of water in the hydrogen electrochemistry, and opens a new perspective towards electrocatalytic processes oriented to the production of alternative energy sources by means of electrocatalytic reactions.

We make our first exploration in Chapter 2, where we studied the hydrogen oxidation and evolution reactions on a polycrystalline platinum electrode in acetonitrile. In this work we compare the voltammetric response of the system in presence of a metallic, hydrophilic cation and a lipophilic, organic cation, to show the sensitivity of the reaction kinetics to the presence of water in the organic-based electrolytes. In this first approach, we used *in situ* FTIR and SERS to demonstrate that the hydrogen oxidation and evolution is mediated by water, as protons and small cations are preferentially solvated by water. The importance of our findings impacts on the difficulty to establish a reference electrode for organic solvents due to the high sensitivity of the reaction to trace amounts of water, reflecting on several studies on molecular catalysts which use a non-protic solvent as test systems. Furthermore, these limitations make us realize the difficulty to establish reliable comparisons between catalytic activities of these different compounds in different solvents, especially if they contain different trace amounts of water.

In the same vein, Chapter 3 presents a study on the influence of water on the hydrogen evolution reaction on a polycrystalline gold electrode in acetonitrile, since it is a non-ideal system due to the fact that gold does not catalyse the hydrogen oxidation. In this chapter we follow the migration of ions and water using *in situ* FTIR spectroscopy, revealing that water accumulates at the interface in presence of protons, which again exhibit preferential solvation, as proposed in Chapter 2. Remarkably, the Tafel plot analysis shows that the hydrogen evolution on polycrystalline gold and platinum present the same rate-determining step, which consists of the first electron transfer and the consequent adsorption of hydrogen.

Since the role of water as a solvent has proved to be crucial for the electrocatalysis of hydrogen, we present a study in aqueous electrolytes in Chapter 4. The study covers a thorough spectroelectrochemical study of the kinetics of H-UPD and hydrogen evolution in a wide pH range, on a Pt(111) single crystal. The study elucidates the molecular origin of the slow reaction rates for the hydrogen evolution reaction in alkaline solutions. We show that the kinetic limitations are linked to the energetic penalty associated to the reorganization of water and the migration of charges through the water networks at the electrode-electrolyte interface. We also present a model based on the displacement of the potential of zero charge closer to the equilibrium potential of the H^+/H_2 redox couple by using submonolayer amounts of Ni deposited on the electrode surface.

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