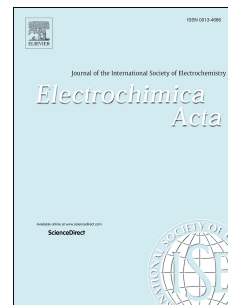


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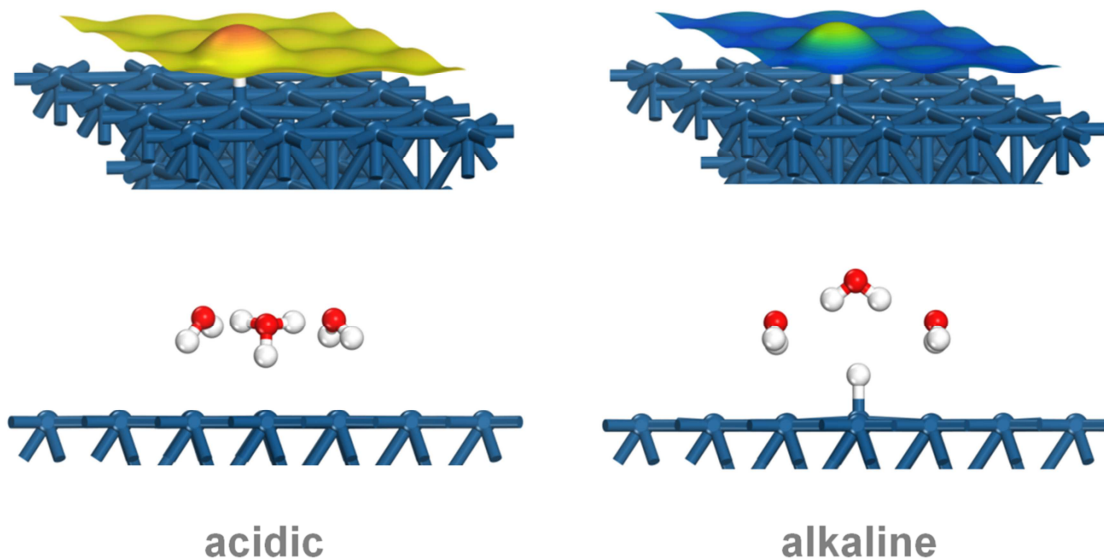
Why the activity of the hydrogen oxidation reaction on platinum decreases as pH increases

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Abstract

Platinum is a very effective electrode for the hydrogen evolution and oxidation reactions (HER/HOR) in acidic media. However, the activity for the HOR on platinum falls two orders of magnitude from acidic to alkaline media, which has not been completely understood yet. Here, we provide an explanation for that. Both the HER and the HOR were investigated on the three basal planes of platinum in a pH range near neutral pH conditions in buffered solutions in the absence of anion specific adsorption for guaranteeing the protons availability. Whereas changes in the pH from acid to neutral values produced negligible effects on the HER, the HOR was found to be pH sensitive, even under near neutral pH conditions. From these results, it can be consistently reasoned that the drastic fall in the activity of the HOR on platinum from acidic to alkaline media is an effect of the charge on the electrode, which is more negative as the pH increases. With the aid of density functional theory calculations, kinetic arguments explaining the unfavorable effect that negative charge on the electrode has on the HOR are provided.

Keywords

Hydrogen oxidation reaction; hydrogen evolution reaction; HOR; HER; platinum single crystal electrodes; neutral pH; DFT calculations

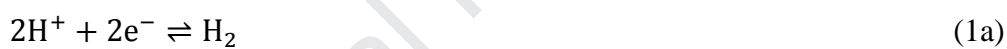
1. Introduction

Hydrogen as a flexible energy carrier, produced in electrolyzers and used in fuel cells, could become in the core of an advanced energy conversion and storage technology driven by renewable sources. To materialize this view, the hydrogen and the oxygen evolution reactions (HER and OER), in electrolyzers, and the oxygen reduction and hydrogen oxidation reactions (ORR and HOR), in fuel cells, require suitable catalysts. Platinum as catalyst for the HOR on anodes under acidic conditions is so effective that a small load of this noble-metal produces the desired performance. Platinum is also the reference catalyst for the ORR on cathodes in acidic media. However, the sluggish kinetics of the ORR on platinum under acidic conditions implies that large loads of the metal are required to satisfy the performance goals, which compromise the cost/effectivity of the whole of the device. Platinum as cathode for the ORR can be advantageously substituted by other materials under alkaline conditions. The problem is that the high activity exhibited by platinum as anode for the HOR falls even two orders of magnitude from acidic to alkaline media [1, 2]. This behavior has not yet been completely understood, which prevents optimizations.

To rationalize HER/HOR activity differences among pH values [2-4] and metals [2, 4, 5], the hydrogen binding energy (HBE) to the surface has been extensively used as a descriptor [2, 6, 7]. However, since they are protons and not hydrogen atoms that are extracted from the surface during the HOR, HBE by itself cannot completely explain the drastic fall in the activity of the HOR on platinum from acidic to alkaline media, given that the eventual presence of charge on the electrode would have a very different effect on neutral hydrogen atoms than on protons. In addition, it has been pointed out that the slower HOR kinetics in alkaline media should be explained by fundamental changes to the reaction mechanisms and not only due to changes in the HBE [8]. It has

been suggested that adsorbed OH or solution OH⁻ species could be involved in the mechanism. In fact, Davydova et al. proposed using the OH binding energy (OHBE) as an additional descriptor [9, 10]. However, Zheng et al. provided evidences against the promoting effect of adsorbed OH on the HER/HOR [4]. And, Lu and Zhuang considered that HOR activity in alkaline electrolyte is not controlled by the OH adsorption [7]. Finally, Durst et al. concluded that there is no evidence of the direct participation of the OH⁻ in the proton extraction during the HOR [2]. Thus, new insights on the mechanism are required. For that, a careful comparative investigation of the HER/HOR on platinum is needed.

The HER and the HOR are, actually, the two possible directions of the same reversible process depending on the applied potential. The equation for the HER (and the inverse for the HOR) in acidic media is:



while in alkaline media it can be expressed as:



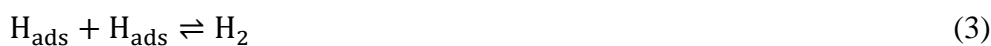
The general mechanism for the HER [11-13] starts with a discharge reaction (Volmer step),



and



in acidic and alkaline media, respectively. This step can be followed by a chemical recombination step (Tafel step)



or an electrochemical desorption (Heyrovský step):



and



The reaction mechanism for the HOR can consist in either Tafel/Volmer or Heyrovský/Volmer pathways.

First studies of the HER on platinum suggested that this reaction is not surface structure sensitive in acidic media [14-18]. However, later investigations by Conway et al. [19] and Markovic et al. [20] reported different electrocatalytic activities among basal planes for the HER on platinum under acidic conditions, which were observed to increase in the order Pt(100) < Pt(111) < Pt(110) by Conway et al. [19] and Pt(111) < Pt(100) < Pt(110) by Markovic et al. [20]. A recent work by He et al. [21] on Pt(111) agrees well with the results presented in ref. [20]. Additionally, Hoshi et al. [22, 23] and Pohl et al. [24] also pointed to the surface structure sensitivity of the HER on platinum stepped surfaces in acidic media, which is explained by the lower coordination of the atoms at the steps acting as the active sites. On the other hand, the HER was found to be more clearly surface structure sensitive on platinum under alkaline conditions from the beginning, though there were discrepancies regarding the activity order, reported as Pt(111) < Pt(100) < Pt(110) by Markovic et al. [9, 25, 26] and as Pt(100) < Pt(111) < Pt(110) by Conway et al. [27, 28]. Finally, it is generally accepted that the activity of the HOR on platinum is surface structure sensitive under acidic conditions following the order Pt(111) < Pt(100) < Pt(110) [20], while in alkaline media Pt(100) is significantly less active than Pt(111) [26].

On polycrystalline platinum electrodes, a better activity has been always observed under acidic than under alkaline conditions both for the HER and for the HOR [2, 29, 30]. More recently, Auinger et al. have investigated pH effects near the electrode surface during the HER/HOR on polycrystalline platinum electrodes in the presence of

different buffer species [31, 32], and Ramaswamy et al. have reported on the HOR on polycrystalline Pt, Ru, Nb, PtRu and PtNb [8]. However, due to the surface structure sensitivity of the considered reactions, conclusions obtained on polycrystalline electrodes have a limited scope. On single crystal platinum, though not on well-defined surfaces, these reactions have been studied along a wide pH range by using different buffer solutions, observing that HER/HOR activities decrease always with pH [3, 4, 33, 34]. Finally, on well-defined surfaces, Markovic et al. and Conway et al. studied the HER/HOR on the three basal planes of platinum under extreme acidic and alkaline conditions, respectively, measuring activities that were always lower in alkaline than in acidic media [20, 26, 27, 35]. However, it is not clear whether the differences between extreme acidic and alkaline conditions can be extrapolated to the intermediate pH values [36], which are the focus of our research strategy. Strmcnik et al. studied the HER/HOR on Pt(111), Au(111) and polycrystalline Ir in non-buffered solutions from pH 1 to 13 [10, 37], but the use of unbuffered solutions invalidates the results for the HER at pH values from 4 to neutral, given that the proton is the reactive species [37]. In any case, beyond observing the performance degradation of the HER/HOR on platinum from acidic to alkaline media, a definitive explanation for that has not been provided yet.

Searching for pH derived fundamental effects and trends consistent with both the HER and the HOR observations, these two reactions have been here investigated on the three basal planes of platinum under static and dynamic (hanging meniscus rotating disk electrode (HMRDE)) conditions along a pH range near neutral conditions ($3 < \text{pH} < 5.4$) in buffered solutions (NaF/HClO₄ mixtures), which avoid anion specific adsorption while guaranteeing the proton availability [36, 38]. From these results, the pH effect on the charge of the electrode can be confidently determined and extrapolated to alkaline conditions. It should be noted that, given that the onset for specific adsorption of the

anions present in the typical buffer solutions for neutral pH values (i.e., phosphate) can be as low as 0.1 V, buffer solutions have to be chosen with care. In fact, the lack of suitable buffered solutions for pH from 7 to 12 prevents the investigation of the HOR on platinum electrodes in the whole pH range. Finally, with the aid of DFT calculations, an explanation for the experimentally observed performance degradation of the HOR on platinum from acidic to neutral-pH media is provided, which can be extrapolated to justify the traditionally observed lower activity in alkaline media.

2. Methods

2.1. Experimental methods

Experiments were performed according to the general procedure described in ref. [39]. The working electrodes were Pt(111), Pt(100) and Pt(110) single crystals prepared from small Pt beads ca. 2 mm in diameter, following the method described by Clavilier et al. [40, 41]. Before every measurement, the working electrode was flame annealed in a propane-oxygen flame, cooled in an Ar/H₂ (3:1) atmosphere and protected with an ultrapure water drop saturated with these gases before being transferred to the glass electrochemical cell. This preparation procedure assures that the obtained experimental surfaces are in agreement with the nominal topographies [42]. Due to the reconstruction phenomena undergone by the Pt(110) surfaces, which are strongly affected by the treatment, the surfaces presented here correspond to (1×1) surfaces or (1×1)/(1×2) with major (1×1) contribution [43, 44]. The counter electrode was a Pt coiled wire cleaned by flame annealing and quenched with ultrapure water. The reference electrode was a Ag/AgCl, KCl (saturated) electrode (CH Instruments, Inc.).

The supporting electrolytes were prepared using 60% HClO₄ (Merck, for analysis), NaF (99.99%, trace metal basis, Aldrich) and KClO₄ (Merck, Suprapur).

Ultrapure water (Elga PureLab Ultra, 18.2 M Ω cm) was employed for glassware cleaning and the preparation of the solutions. NaF/HClO₄ mixtures were prepared in such a way that the concentration of the generated hydrofluoric acid is between 4×10^{-3} M and 10^{-2} M, which, as it will be checked, are enough to buffer the HOR and HER within the studied potential ranges [45]. The concentrations of the different solutions are given in table S1. The composition of the different working solutions is presented in table S1. KClO₄ was used in some cases in order to have enough ionic strength and therefore avoid conductivity problems. Ar and H₂ (N50, Air Liquide) were used for deoxygenating the solution and for studying the HOR, respectively. In the latter case the solution was bubbled with hydrogen during at least 10 minutes in order to achieve saturation.

Electrochemical measurements were carried out by using a signal generator EG&G PARC and eDAQ EA161 potentiostat with an Edaq e-corder ED401 recording system. Experiments in hydrodynamic conditions were performed with the HMRDE configuration using an EDI101 rotating electrode and a Radiometer CTV 101 for controlling the rotation rate (both Radiometer Analytical). All experiments were carried out at room temperature.

2.2. Computational methods

Periodic DFT calculations under neutral and negative charge (one electron) conditions were carried out using numerical basis sets [46], semi core pseudopotentials [47] (which include scalar relativistic effects) and the RPBE [48] functional (specifically developed for catalysis) as implemented in the Dmol³ code. Moreover, the insights derived from these calculations were also verified using PBE [49] (a much more general purpose functional) with and without correction for dispersion forces by

the Tkatchemko and Scheffler method [50]. Continuous solvation effects were taken into account by the COSMO model [51]. Additionally, the solvation effect treatment was improved including explicit water molecules in the model. Negative charge on the model was equilibrated by means of a positive jellium as implemented in Dmol³. The effects of non-zero dipole moments, in the supercells, were cancelled by means of external fields [52].

To model ionization processes involving the surface, and to compare results under neutral and negative charge conditions, the Pt(111) surface was represented by a periodic supercell comprising 54 Pt atoms (six layers of metal atoms) and a vacuum slab of 20 Å. The most internal 18 Pt atoms of the surface (two layers) were frozen in their bulk crystal locations, meanwhile the remaining 36 Pt atoms were completely relaxed joint to the adsorbates. The shortest distance between periodic images was in the order of 8.50 Å.

Hydrogen chemisorbed states and pseudo-states (obtained from elongation constraints) were optimized using numerical basis sets of double-numerical quality. For this phase of the calculations, the optimization convergence thresholds were set to 2.0×10^{-5} Ha for the energy, 0.004 Ha/Å for the force and 0.005 Å for the displacement. The SCF convergence criterion was set to 1.0×10^{-5} Ha for the energy. Assuming the previously optimized configurations, energies were estimated using numerical basis sets of double-numerical quality plus polarization. In this phase, the SCF convergence criterion was set to 1.0×10^{-6} Ha for the energy.

Orbital cutoffs radius of 3.1, 3.3 and 4.5 Å were always used in the numerical basis set for H, O and Pt atoms, respectively. Brillouin zones were always sampled, under the Monkhorst-Pack method [53], using grids corresponding to distances in the reciprocal space of the order of 0.04 1/Å. Convergence was always facilitated

introducing 0.002 Ha of thermal smearing, though total energies were extrapolated to 0 K. The value 78.54 was taken, as dielectric constant for water, in the continuous solvation model.

3. Results and discussion

3.1. Electrode/solution interface characterization

The voltammetric profiles in NaF/HClO₄ mixtures in absence of H₂ for each basal plane of platinum within a potential region in which the HER is not taking place are displayed as Figure 1. These profiles are in agreement with previous results [36, 38, 54, 55]. Both the H and OH adsorption/desorption regions for Pt(111) are symmetrical and lie in the same potential region (in the RHE scale) for the different pH values, which indicates that the local pH is maintained during each test. Changes in the shape of the OH region evidence the influence of the interfacial charge on the water structure involved in the OH adsorption. An additional feature at ca. 0.55 V vs. RHE can be observed for pH = 3. The maximum of this reversible broad peak appears at ca. 0.36 V vs. SHE for all pH values, very close to the potential of zero charge for Pt(111) (0.28 V vs. SHE) [54], which has been attributed to a change in the interfacial water orientation [56-59]. The H and OH regions for Pt(100) overlap and evolve to the characteristic shape in alkaline media as the pH is increased [60], while the two peaks which appear for Pt(110) at low potentials shift to higher potentials and become less resolved [36]. These changes are related to complex variations in the adsorption isotherm of OH when changing the pH. However, they will not affect the following analysis of HER and HOR reactions since they occur at potentials much positive than those in which the HER/HOR are discussed.

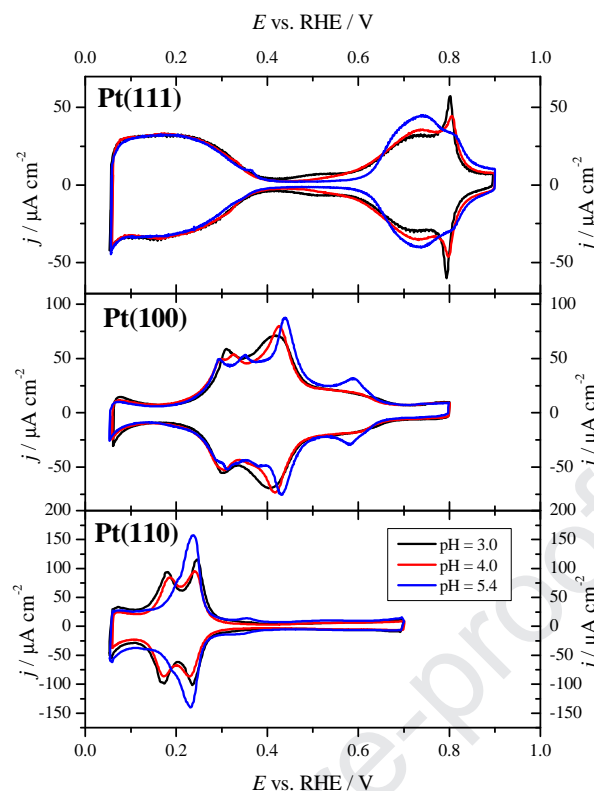


Figure 1. Voltammetric profiles for the three Pt basal planes in Ar-saturated solutions at different pH values prepared using NaF/HClO₄ mixtures. Exact solution compositions are given in table S1. Scan rate: 50 mV s⁻¹.

3.2. HER experimental results

Although major changes in the activity with the pH are observed only for the HOR, the HER is here also studied because the behavior comparison between both reactions will enable to understand the origin and nature of the observed differences. Also, our HER results will serve to verify our experimental protocol, so that confident experimental data, under the considered conditions, are not available for the HOR. The HER voltammetric profiles obtained at different pH values on the three basal planes of platinum under static conditions are displayed as Figure 2. It can be observed that the hydrogen reduction peak for each electrode is accompanied by the corresponding hydrogen oxidation peak from the H₂ generated during the HER, which has the usual shape for a quasi-reversible process since the reaction product remains close to the

surface in the absence of rotation. From these profiles, two significant qualitative conclusions can be drawn. First, the influence of pH on the peak-to-peak separation for each electrode is practically negligible. Second, this separation is very sensitive to the electrode surface structure, being 59, 109 and 165 mV for Pt(110), Pt(100) and Pt(111), respectively, implying that the reactivity order is Pt(111) < Pt(100) < Pt(110), in agreement with reference [20].

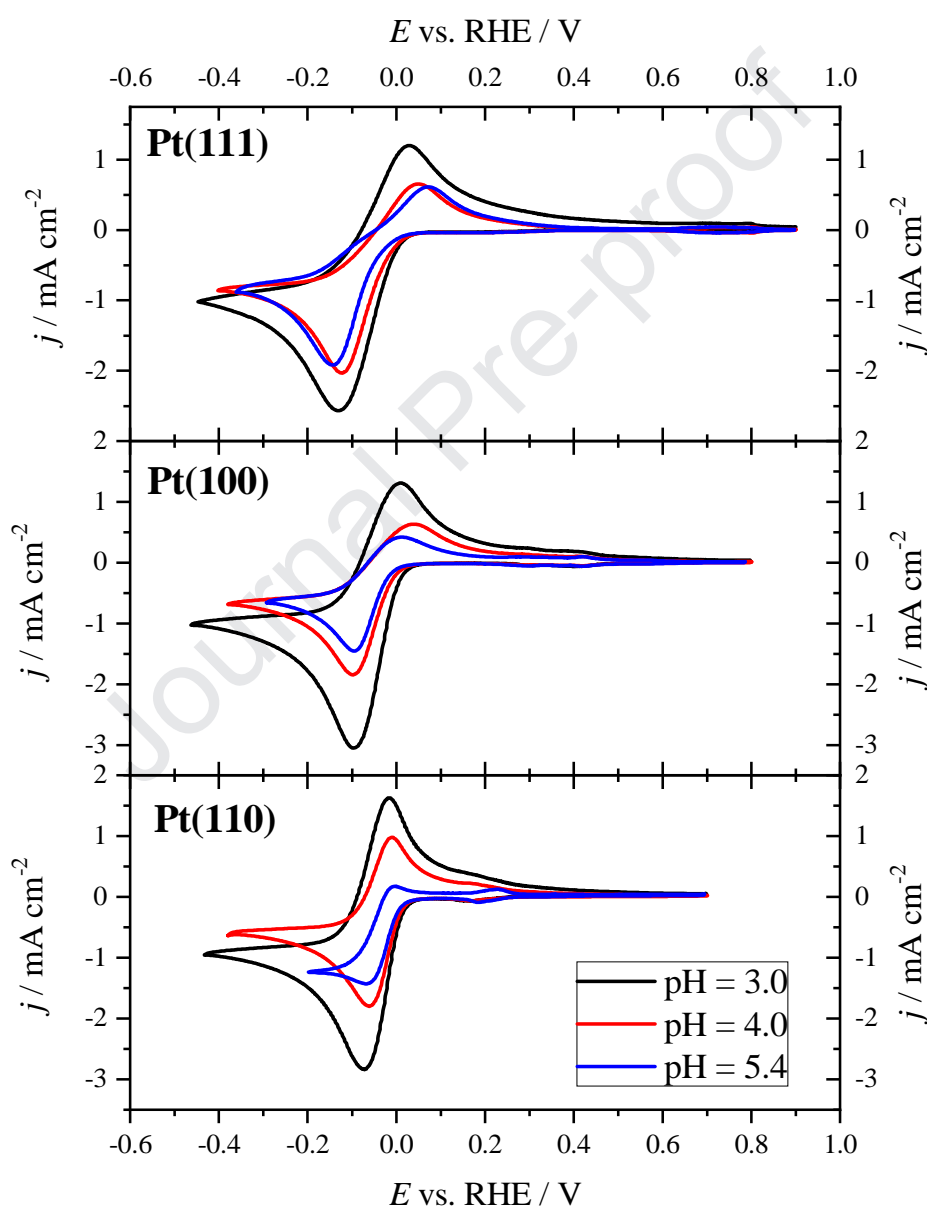


Figure 2. HER (and HOR) voltammetric profiles in Ar-saturated solutions at different pH values prepared using NaF/HClO₄ mixtures under static conditions for the three basal planes of platinum. Exact solution compositions are given in table S1. Scan rate: 50 mV s^{-1} .

To quantitatively analyze the reaction, the diffusion processes must be controlled, which is usually achieved using hydrodynamic techniques that control the flux of reactant species towards the surface. As an example, the polarization curves for the HER on Pt(111) obtained using the HMRDE configuration under hydrodynamic conditions are displayed at pH = 3 for different rotation rates in Figure 3A and at 2500 rpm for different pH values in Figure 3B. The results for the other pH values at different rotation rates and for the other basal planes are presented in Figures S1 and S2. Under these conditions, the limiting current density is determined by two contributions: the diffusion of protons, and the diffusion of hydrofluoric acid, which can release a proton near the surface to be reduced [32]. The differences in the limiting current densities for the different pH values observed in Figure 3B arise mainly from different proton concentrations, though possibly also from small differences in HF concentration because of the experimental error in the solution preparation. No oxidation currents are observed under rotation since the generated H₂ readily diffuses away from the electrode surface before it can be oxidized.

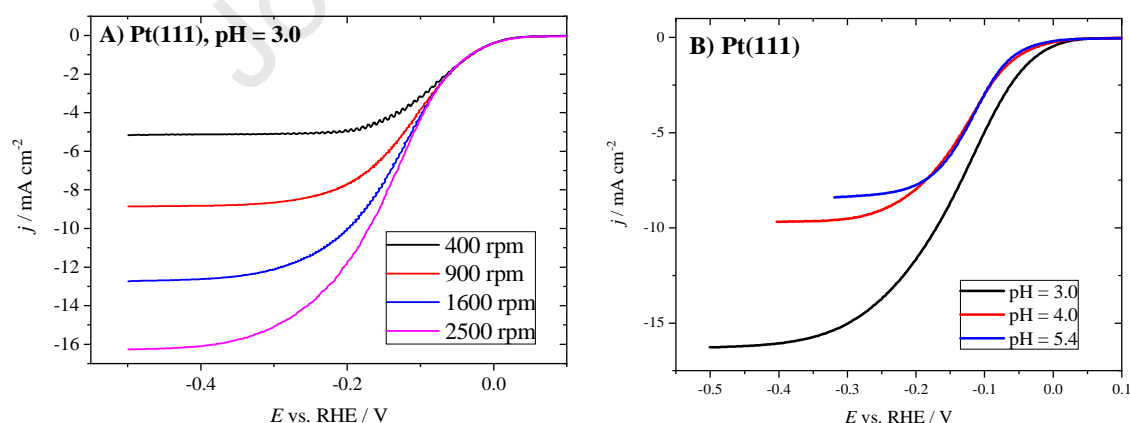


Figure 3. Polarization curves for the HER on Pt(111) in solutions prepared with NaF/HClO₄ mixtures at pH = 3.0 for different rotation rates (A) and at 2500 rpm for different pH values (B). Exact solution compositions are given in table S1. Scan rate: 50 mV s^{-1} .

As mentioned in the Methods section, the concentrations of generated HF, which acts as the buffer of the reaction, are between 4×10^{-3} M and 10^{-2} M. These buffer concentrations are not very high. However, higher concentrations than 2×10^{-2} M cannot be used, due to the corrosive action of HF towards the glass. The presence of a plateau from ca. -0.2 V vs. RHE to more negative values in Figure 3 indicates that the diffusion of proton (or the proton donor species, in this case, HF) becomes the rate determining step of the process [32]. At these potentials, the pH near the surface is significantly higher than that in the bulk. Therefore, in order to carry out a kinetic analysis as a function of pH, one should choose a potential region in which the interfacial pH is maintained equal to the bulk pH. Katsounaros et al. [31] pointed out that, for total buffer concentrations of 10 mM, the interfacial pH is maintained, at least, for current densities of ca. 1 mA cm^{-2} . Moreover, the comparison of the currents measured depending on the rotation rate of the electrode allows determining the region where pH is maintained. Currents which are independent of the rotation rate imply that the bulk and surface concentration of electroactive species is the same, so that the surface and the bulk pHs are essentially equal. Figures 3A and S1 show that at potentials more positive than ca. -0.1 V vs. RHE for Pt(111), ca. -0.07 V vs. RHE for Pt(100) and ca. -0.05 V vs. RHE for Pt(110) currents are independent of the rotation rate. Dependence with the rotation rate is observed above 1 mA cm^{-2} , which is in agreement with ref. 31. Therefore, we will compare the results within these potential regions in order to extract the corresponding conclusions. It should be mentioned that at potentials more negative than those presented in the polarization curves of Figure 3B, the HER from H_2O (eq. 1b) starts taking place (full curves are displayed in Figure S3). At these potential values the surface pH is extremely alkaline and similar in all cases, although it is difficult to determine exactly. As a result, the onset potential for this reaction in the SHE is similar

in all cases, and this is the reason why the lower potential limits in the RHE scale are different when comparing the different polarization curves in Figures 3B and S2.

The current density at each pH value depends not only on the electrode potential and surface structure, but also on the concentration of the reactants, that is, proton and HF. According to the previous discussions, it is clear, that for each studied pH value, the proton concentration is intrinsically different, and that there can be also experimental variations in the concentration of generated HF buffer, so that the measured current densities are not directly comparable. Therefore, it is necessary to establish a methodology to study the effect of surface charge on the HER which is not affected by the proton and HF concentration values. In this sense, the HF concentration effect was analyzed. The HER polarization curves on Pt(111) at pH = 4 and 2500 rpm for two different solutions in which one has twice the buffer concentration in comparison with the other are displayed in Figure 4 (the initial concentration of NaF and HClO₄ was doubled for the second solution, see table S1). As expected, the limiting current density for the solution with twice the buffer concentration in Figure 4A is doubled, since the current signals have a contribution from the buffer species and in this case the contribution from protons is almost negligible [32, 37]. When current density vs. potential is normalized (Fig. 4B), the current density curves overlap almost perfectly for both concentrations, especially at low potential values. Since the limiting currents are very dependent on the solution pH (Fig. 3B), it can be concluded that, to compare the electrocatalytic activity at different pH values, it is necessary to normalize the obtained polarization curves. From these observations, and in order to avoid changes in the interfacial pH (as discussed above), we chose to compare the normalized current density values at potentials more positive than -0.1 V vs. RHE.

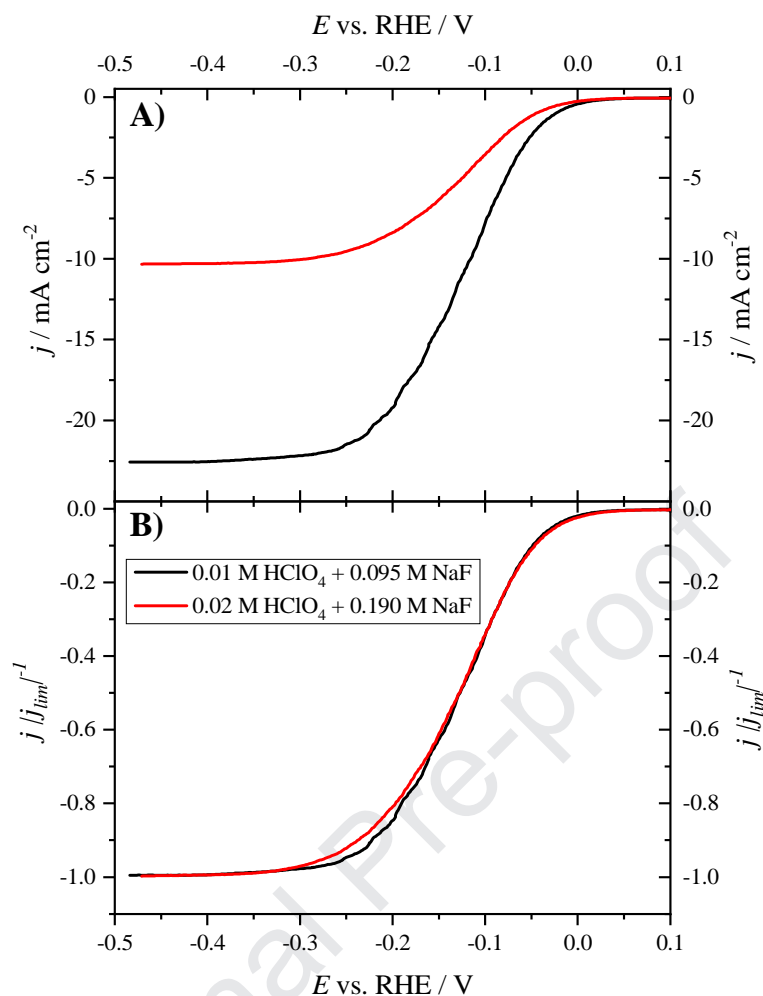


Figure 4. Polarization curves for the HER on Pt(111) in Ar-saturated solutions at pH = 4 prepared with NaF/HClO₄ mixtures and 2500 rpm for different buffer concentrations as current density (A) and normalized current (B). Exact solution compositions are given in table S1. Scan rate: 50 mV s⁻¹.

The polarization curves for the HER on platinum normalized by j_{lim} are displayed grouped by plane, for comparison among pH values, in Figure 5, and grouped by pH value, for comparison among planes, in Figure S4. In Figure 5, it can be observed that the differences among the pH values at potentials near the onset potential value for each plane are very small, and therefore the activity for each orientation is practically the same along the studied pH range. This result is in agreement with the idea that the difference in electrocatalytic activity between acidic and alkaline media for the HER is mainly due to the sluggish water dissociation process since in alkaline media water is

the proton donor [61]. Sheng et al. also reported very similar activities at $\text{pH} < 6$ for polycrystalline Pt in acetate buffer solutions [3]. Therefore, below $\text{pH} = 6$, when the proton donor is H_3O^+ , the electrocatalytic activity is the same as can be seen in the present results. On the other hand, it can be concluded from Figures 5, S1, S2 and S4 that the HER is clearly structure sensitive along the studied pH range, following the activity order $\text{Pt}(111) < \text{Pt}(100) < \text{Pt}(110)$, in agreement with the results of Markovic et al. [20].

To further validate these conclusions, the kinetic currents (j_k) at -0.1 V for the different pH values and electrodes were calculated using the typical Koutecky-Levich analysis (Figure S5). To eliminate the effect of the reactant concentration in the values of j_k , these values should be divided by the total acid concentration, that is, to the sum of $[\text{H}^+] + [\text{HF}]$. As can be seen in Figure S6, these values are nearly independent of the pH, and follow the order $\text{Pt}(111) < \text{Pt}(100) < \text{Pt}(110)$, corroborating the conclusions obtained in the analysis of the normalized j_{lim} .

Additional measurements were performed in the presence of H_2 using H_2 -saturated working solutions. The curves for $E < 0$ V vs. RHE in the presence and absence of H_2 overlap (Figure S7), implying that in this case the kinetics in the presence and absence of H_2 are the same. This is because the measurements were carried out using the HMRDE configuration, which assure the homogeneity of the concentrations over the surface. The kinetic analyses for the HER are here carried out in the absence of H_2 , but the same conclusions arise in the presence of H_2 .

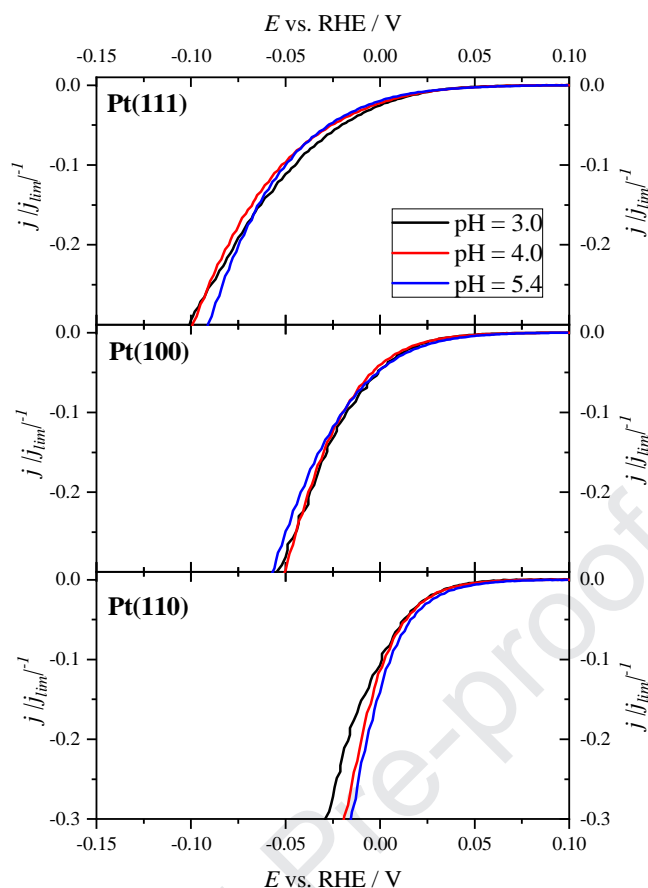


Figure 5. Polarization curves for the HER on platinum in Ar-saturated solutions at 2500 rpm normalized by j_{lim} grouped by plane for comparison among pH values. Exact solution compositions are given in table S1. Scan rate: 50 mV s^{-1} .

Tafel slopes at a potential region near the onset potential (between 0 and -0.05 V vs. RHE), where the interfacial and bulk pHs are the same, were also calculated and are displayed as Figure 6. For each surface, similar results for the different pH values are obtained, being the mean values ca. 73 mV, 55 mV and 46 mV for Pt(111), Pt(100) and Pt(110), respectively. Therefore, the mechanism of the HER remains unchanged within the studied pH range. Tafel slopes follow the trend $\text{Pt}(110) < \text{Pt}(100) < \text{Pt}(111)$, indicating surface structure sensitivity for this reaction.

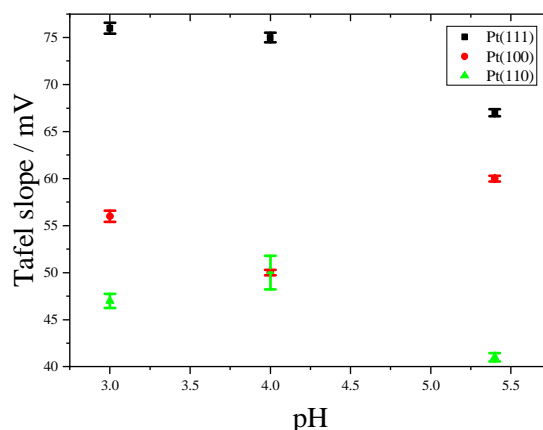


Figure 6. Tafel slope values calculated between 0 and -0.05 V vs. RHE for the HER on the three basal planes of platinum in Ar-saturated solutions. Scan rate: 50 mV s⁻¹.

In short, the HER activity on platinum is structure sensitive and virtually pH independent (and hence surface charge independent) in the pH range 3 to 5.4, that is, no noticeable effects of pH can be drawn from the experimental results, which suggest that the slower rates observed in alkaline media for this reactions may be due to other reasons than pH, such as, for instance, the different nature of the proton donor, as has been already proposed [7].

3.3. HOR experimental results

Analyzed the HER, the HOR experimental results are here presented and analyzed for comparison. The polarization curves for the HOR on platinum in H₂-saturated solutions obtained using the HMRDE configuration under hydrodynamic conditions are displayed grouped by plane, for comparison among different pH values (Figure 7), and grouped by pH value, for comparison among planes (Figure 8). From these figures it can be concluded that, whereas the HOR and HER are structure sensitive, only the HOR is pH sensitive, unlike the HER. For Pt(100) and Pt(111) electrodes, the HOR activity decreases clearly as the pH is increased, especially near the onset potential, whereas for the Pt(110) this variation is very small. Additionally, Pt(110) is always the most active surface, achieving the diffusion control at very low

potentials. Pt(111) and Pt(100) exhibit a similar activity, though the potentials at which the reaction is controlled by the mass transfer are higher for Pt(100). These results are in agreement with previous ones obtained under extreme acidic and alkaline conditions [20, 26]. Additional measurements at different scan rates were also performed, showing that the polarization curves are independent of the scan rate (figure S8).

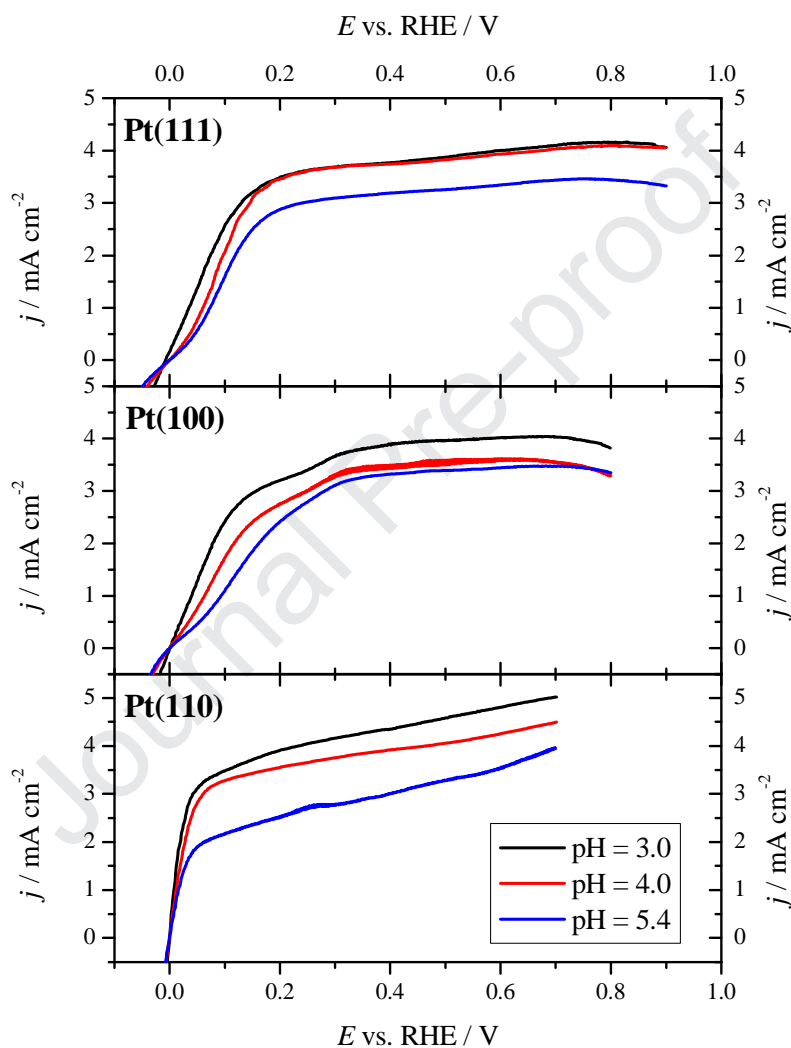


Figure 7. Polarization curves for the HOR on platinum in H₂-saturated solutions at 2500 rpm grouped by plane for comparison among pH values. Exact solution compositions are given in table S1. Scan rate: 50 mV s⁻¹.

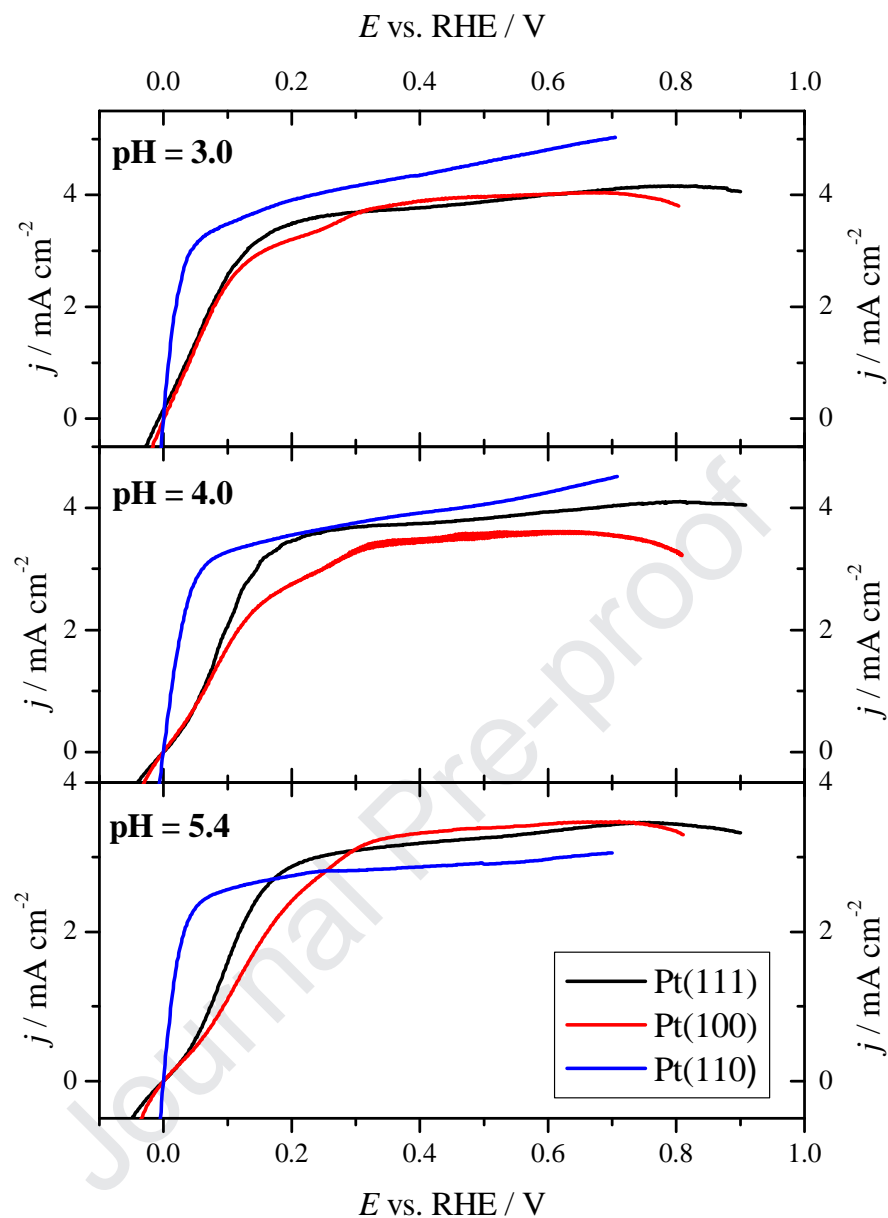


Figure 8. Polarization curves for the HOR on platinum in H₂-saturated solutions at 2500 rpm grouped by pH value for comparison among planes. Exact solution compositions are given in table S1. Scan rate: 50 mV s⁻¹.

3.4. *pH effect on the electrode charge during the HOR*

The pH sensitivity of the HOR on platinum could be related to the presence of charge on the electrode surface. However, determining the charge that is present on electrodes during a given electrocatalytic reaction is not an easy task. In the absence of redox processes, the charge flowing through the circuit as a result of a change in the potential is that corresponding to the electrode charge difference under the two potentials, according to the Stern model of the double layer. The potential at which the surface charge is zero is known as the potentials of zero charge (pzc). Thus, the values of the pzc for metals such as gold and silver can be easily determined from capacitance curves. However, in the presence of adsorption processes involving charge transfer (i.e., hydrogen adsorption on Pt electrodes) the scenery is more complex. Under a change in the potential, the total charge flowing through the circuit can have two origins: the one corresponding to the change of the electrode charge, which is known as the free charge of the electrode, and that involved in changes in the adsorption coverage. Thus, two different pzc can be defined: the potential of zero total charge (pztc) and the potential of zero free charge (pzfc). The pzfc is the potential where the excess of electrons (free charge) in the metal is zero, whereas the pztc is the potential at which the free charge plus the charge involved in the adsorption processes are zero (schematized in figure S9). The relevant potential here is the pzfc, though this quantity cannot be directly measured for platinum. By contrast, the pztc can be directly measured by different probes [62-65]. Moreover, an additional potential closely related to the pzfc can be measured. This is the potential of maximum entropy (pme) of double layer formation, which is the potential at which the entropy of formation of the interphase is maximized (schematized in figure S10) [66-68]. This potential is close to the pzfc, since the dipoles of interfacial water are sensitive to the electric field, that is, to the free charge, so that, when the free

charge is close to zero, they show random orientation. From pztc results, the pzfc can be inferred by extrapolation under specific conditions [69], taking into account that pztc's are pH sensitive in the SHE scale.

García-Aráez et al. [66] obtained, by laser-induced temperature jump experiments in 0.1 M HClO₄, 0.37, 0.33 and 0.14 V vs. RHE as pmes for Pt(111), Pt(100) and Pt(110), respectively. Moreover, for the most studied surface, the Pt(111) electrode, the pzfc (and the pme) is constant with pH in the SHE scale [54, 66-68], as expected from the observed behavior on gold electrodes [70]. By contrast, the pztc shifts to more negative values with a slope considerably smaller than -60 mV per pH unit [54, 66-68]. At acidic pH values close to 1, the pztc lies at the end of the hydrogen adsorption/desorption region, whereas at neutral pH values close to 5, it lies at the beginning of the OH adsorption/desorption region, respectively [54]. Interestingly, at pH values around 3, the pztc is located exactly in the double layer region, and it coincides with the pfzc. In short, within the considered pH range, the pztc for Pt(111) is not strongly dominated by OH and H adsorption processes, and hence it shifts with a much smaller slope than -60 mV per pH unit in the SHE scale, which is the pH shift for the OH and H adsorption processes. For the other two basal planes, the observed behavior is different. In these cases, the pztc values remain essentially unaffected by pH in the RHE scale, that is, they shift -60 mV per pH unit in the SHE scale [66]. This is in contrast with the Pt(111) electrode, and it is because for Pt(100) and Pt(110) the pztcs are located near the center of the potential region where hydrogen and OH coadsorption take place, and therefore they are strongly affected by the latter. Since these adsorption processes are expected to be little affected by pH variations on a RHE scale (see figure 1), one can expect that pztc values also remain essentially constant. On the other hand, the pme shifts 30 mV and 15 mV per pH unit in the RHE scale for Pt(100) and Pt(110),

respectively, meanwhile the pzfc values should follow a similar dependence with pH [66]. This unexpected shift in comparison with Pt(111), which shifts -60 mV per pH unit in the RHE scale, is because the extent of H and OH adsorption dominates the magnitude of the free charge density, and as a result, free charge density values remain little affected by pH on the RHE scale [66]. The pztc and pzfc variations with the pH for the three basal planes of platinum under both the RHE and SHE scales are schematized as figure S11.

From the measured values, the extrapolated value of the pzfc for the Pt(111) electrode in 0.1 M HClO₄ is ca. 0.28 V vs. SHE, which remains constant with pH [54]. When this value is transformed to RHE scale and compared to the corresponding experiment reported in 3.3, the obtained value is higher than the equilibrium potential for the HOR (see figure S11), which implies that a negative charge is present on the electrode during the HOR. For the other two basal planes, the determination of the electrode charge is more complicated because the pzfc cannot be obtained by extrapolation. However, from the relationship among the pzfc, the pme, and the work function of different surfaces [71], it can be expected that the pzfc of platinum surfaces follows the order Pt(110) < Pt(100) < Pt(111). This would imply that the equilibrium potential for the HOR on Pt(110) in 0.1 M HClO₄ would be closer to the pzfc than on Pt(111) and thus the charge on Pt(110) would be less negative. Finally, the charge on Pt(100) would be between those of Pt(110) and Pt(111). In any case, as the pH increases, separation between the pzfc and the equilibrium potential increases for the three planes. In short, the study of the HOR under near neutral pH conditions points to charge on the electrode playing a key role in the HOR kinetics, in contrast to the HER, for which the pH effect (and hence charge on electrode surface) is insignificant.

3.5. Electrode charge effect on the HOR

To explore the effect that negative charge on the electrode has on the HOR, different DFT calculations were carried out on an appropriated Pt(111) model to compare results under neutral and negative charge (one electron for the whole of the model) conditions (see Computational methods section). The Tafel slope measured for the hydrogen reactions on Pt electrodes in alkaline media is ca. 120 mV per decade, suggesting that the Volmer step is the rate determining step in these conditions [33, 72, 73]. Therefore, in order to obtain information about the effect of surface charge on the HOR in alkaline media for explaining the decrease in electrocatalytic activity from acidic to alkaline solutions, the computational studies are performed for the Volmer step. Given that the Volmer step of the HOR involves the transfer of an electron coupled to each proton extraction, the barrier for this step cannot be estimated from DFT by only modeling the anode side of the cell under constant charge conditions, due to the different number of electrons between the initial and final states. To circumvent this drawback, the energetic difference between a chemisorbed hydrogen pseudo-state (obtained by means of Pt-H bond elongation, maintained as a constrained distance during the optimization process) and that of the true hydrogen chemisorbed state (completely relaxed) was used as a descriptor for comparison. Assuming that this elongated pseudo-state is on the ascending side of the barrier toward the deprotonation, the neutralizing electron of the proton is still on the electrode, allowing comparing trends for the reaction under constant charge conditions. The values calculated for this descriptor at 16% of elongation under different solvation effect treatments for neutral and negative charge conditions are summarized in Table 1.

	neutral	charged
vacuum	0.39	0.38
csm	0.39	0.37
csm + H ₂ O	0.23	0.32
csm + 3 H ₂ O	-	0.32

Table 1. Energetic difference in eV between the Pt-H elongated by 16% chemisorbed hydrogen pseudo-state and the true chemisorbed hydrogen state under different solvation effect treatments (vacuum, continuous solvation model (csm), continuous solvation model plus one explicit water molecule and continuous solvation model plus three explicit water molecules) and charge conditions (neutral and one electron).

In the vacuum, but also when only the continuous solvation model was used as solvation effect treatment, similar values (ca. 0.40 eV) for the descriptor under neutral and negative charge conditions were obtained, which suggests that the hydrogen HBE to the Pt(111) surface under neutral and negative charge conditions would be similar. However, both under acidic and alkaline conditions, it is a proton, and not a hydrogen atom, what is extracted from the surface during the Volmer step of the HOR, being the electron simultaneously extracted to the circuit. Under acidic conditions, a solvated hydronium would be immediately formed by combining the proton and water near the surface. Under alkaline conditions (in the presence of negative charge on the electrode), water is finally formed when a solvated hydroxide anion is eventually reached by the proton. However, in any case, from the point of view of the Volmer step mechanism, both under acidic and alkaline conditions, the proton would be always extracted to water, forming solvated hydronium near the surface.

To better understand the nature of the hydrogen/surface interaction, the electrostatic potentials of the found hydrogen chemisorbed states mapped on density isosurfaces, obtained under neutral and negative charge conditions (one electron) in continuous solvation model, are visualized as Figures 9A and B. As can be observed in

these figures, as a result of the adsorption processes, adsorbed hydrogen rests positively polarized under neutral charge conditions, whereas this positive polarization is clearly lower as the charge on the electrode becomes more negative. However, it can be also observed that the difference in the electrostatic potential between hydrogen and the surface remains almost constant independently of the charge, as the calculated partial charges according to the Mulliken and Hirshfeld analysis (figure S12) shown. These electrostatic potentials can be explained as the result of three combined effects: i) The relative difference between hydrogen and platinum is first controlled by their electronegativity difference, ii) which is then intensified as a result of the solvation effect, iii) the absolute value of the electrostatic potential being determined by the value of the charge on the surface.

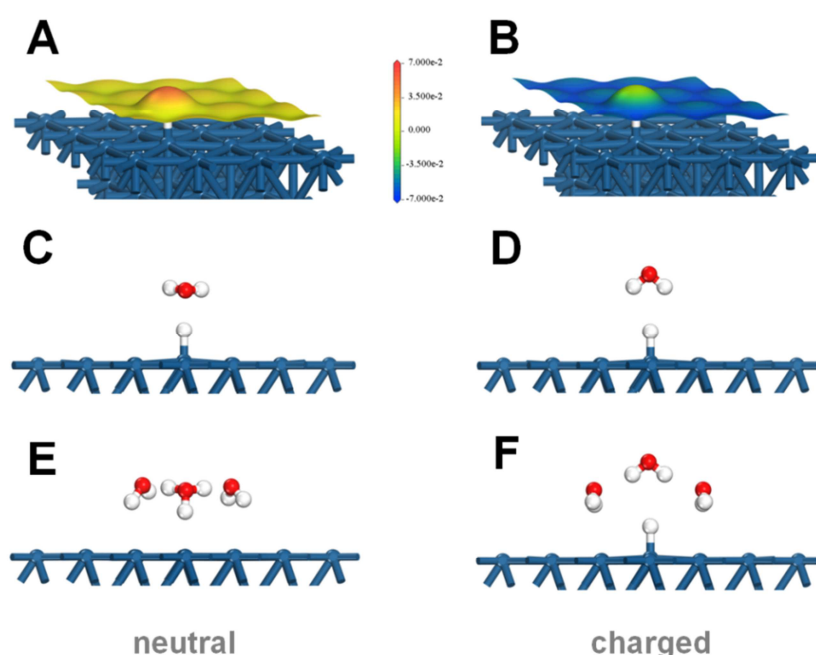


Figure 9. Electrostatic potential mapped on the density isosurface $\rho=0.02 \text{ e } \text{\AA}^{-3}$ in Ha per e and hydrogen adsorption configurations under different solvation effect treatments (continuous solvation A and B, continuous solvation plus one explicit water molecule C and D and continuous solvation plus three explicit water molecules E and F) and charge conditions (neutral A, C and D and one electron B, D and F).

Since both under acidic and alkaline conditions protons by the Volmer step would be extracted to water, an adequate solvation effect treatment is essential. So, knowing that hydrogen bonds are not captured by the continuous solvation model, a water molecule was explicitly introduced in the calculations, in addition to the continuous solvation model, as solvation effect treatment. Under the latter, the previously estimated descriptor values go from c.a. 0.40 to 0.23 and 0.32 eV under neutral and negative charge conditions, respectively. Curiously, the calculated values are much more sensitive to the solvation effect treatment under neutral than under negative charge conditions. From the adsorbed hydrogen atom to oxygen atom distances observed in Figures 9C and D, which display the geometries of the found chemisorbed states, it can be inferred that water interacts much more favorably with adsorbed hydrogen under neutral than under negative charge conditions. This effect can be easily rationalized with the aid of the polarized surfaces shown in Figures 9A and B. The partial positive charge on the adsorbed hydrogen atom is higher under neutral charge conditions, which favors the dipole coupling with the oxygen side of the water molecule. The Pt-H distance elongates beyond that is typically obtained for an adsorbed H and the distance between the H atom and the O atom of the water molecule is consistent with the formation of a bond. Thus, the water molecules move away from the surface when the charge is made more negative, as has been also observed from Quantum Mechanics Molecular Dynamics [74]. Obviously, the water molecule could be forced to move toward the adsorbed hydrogen, though from a larger distance, having an effect on the kinetics. In any case, only when oxygen is close enough to adsorbed hydrogen the proton can be extracted from the surface. Then, the more negative (less positive) the charge on the electrode is, the more trapped the proton on the surface becomes.

To explore the sensitivity of the proton extraction process to the solvation effect treatment, a more complete first solvation shell of explicit water (comprising three water molecules) in addition to the continuous solvation model was considered in the calculations. The hydrogen adsorption states on Pt(111) obtained under this last solvation effect treatment for neutral and negative charge are displayed as Figures 9E and F, respectively. Surprisingly, it can be observed in Figure 9E that, when the solvation effect is sufficiently captured, adsorbed hydrogen on Pt(111) spontaneously deprotonates towards the solution without barrier, which is consistent with the experimental evidence obtained from hydrogen adsorbed on platinum in the presence of adsorbed water in UHV [75]. By contrast, Figure 9F shows that a solvation shell favorable enough to the proton extraction from the surface cannot be orchestrated around adsorbed hydrogen under negative charge conditions. That is, the negative charge on the electrode hinders the favorable solvation of the proton on the surface, which is essential for its extraction. In fact, the more negative (less positive) the charge on the electrode is, the more unfavorable the proton solvation on the surface becomes. As a result of the poor solvation, the energy for the calculated descriptor under negative charge conditions cannot be significantly reduced by the improved solvation effect treatment. Considering that 0.32 eV is only the energy difference used as a descriptor, a very significant barrier to deprotonation toward the solution can be anticipated under negative charge conditions.

Moreover, in the presence of negative charge on the electrode, the key reactant species under alkaline conditions, the hydroxide anion, would be repelled away from the surface as an effect of the charge repulsion between the anion and the negative charge on the surface. In fact, the higher the negative charge on the electrode is, the longer the path from the surface to hydroxide becomes. A recent work by Huang et al.

using a microscopic Hamiltonian model for the Volmer step also pointed out that there is larger activation energy for the hydrogen reactions at more negatively charged interfaces because it consumes more work in bringing the hydroxide anion from the solution bulk to the double layer since hydroxide anion is more desolvated in these conditions [76]. To make things worse, the proton would have to advance towards hydroxide retained away by the negative charge on the electrode. Thus, the final formation of water would be not a fast process. Meanwhile, the presence of the solvated proton between the negatively charged surface and the solvated hydroxide would hinder the extraction of other protons.

In short, the more negative (less positive) the charge on the electrode is, the more unfavorable the proton solvation on the surface becomes, the more trapped the proton on the surface is, and the longer the path from the surface to hydroxide is. Given the nature of the identified effects, they would operate not only on Pt(111), but also on the other two basal planes of platinum.

3.6. Discussion

The HBE has been extensively used as a descriptor of the HER/HOR activity [2, 6, 7]. However, since protons, and not hydrogen atoms, are extracted from the surface during the HOR, HBE cannot completely explain the drastic fall in the activity of the HOR on platinum from acidic to alkaline media. The most obvious difference between acidic and alkaline conditions would be the ionic composition of the media. As the solution pH increases, the hydroxide anion increases. However, evidence against the promoting effect of adsorbed OH on the HER/HOR has been provided [4]. It has been also concluded that the HOR activity in alkaline electrolyte is not mainly controlled by the OH adsorption [7]. Furthermore, pieces of evidence for the direct participation of

the OH^- in the proton extraction during the HOR could not be obtained [2]. In addition, no significant effect of the proton concentration should be expected on the HER/HOR under near neutral pH conditions in buffer solutions because the high diffusivity of the protons. Protons are the product of the HOR, while they are the reactant in the HER. Thus, the effect of pH should be even more important for the HER than for the HOR. However, as expected, noticeable pH effects were not clearly observed from the experimental results for the HER under near neutral pH conditions. These results suggest that the specific ionic composition of the media would have not a significant effect on the HER/HOR activity under near neutral pH conditions. However, in spite of that, the HOR was found to be pH sensitive on platinum even under near neutral pH conditions. Thus, the reasons for the observed pH sensitivity must be different from the ionic composition and diffusivity in the media.

It has been shown that at the potentials where HOR takes place in acidic solutions, a small negative charge is present on the Pt(111) electrode and that this charge become more negative as pH increases for the three basal planes of platinum. Moreover, it has been argued that, the more negative (less positive) the charge on the electrode is, the more unfavorable the proton solvation on the surface becomes, the more trapped the proton on the surface is, and the longer the path from the surface to hydroxide is, for the three basal planes of platinum. Thus, it can be reasonably understood that, combined, these effects can seriously disrupt the mechanism of the proton extraction from the surface during the HOR, drastically slowing down the kinetics of the reaction under alkaline conditions. So, we propose here charge on the electrode as the explanation for the observed pH sensitivity of the HOR on platinum.

The described effects of charge on the electrode would be consistent with the laser induced temperature jump experiments used to determine the pme. The recorded

transient potential for 0.1 HClO₄ solutions contains contributions from both the double layer and the hydrogen desorption processes. However, at pH = 3 these processes are decoupled, because the hydrogen desorption is slower [57]. Similarly, impedance measurements indicate that the rate for hydrogen desorption is significantly slower in alkaline solutions [77]. In any case, charge on the electrode has been already pointed out as having an effect on other electrocatalytic processes. For the oxygen reduction reaction (ORR), it was observed from a kinetic analysis at different pH values that the maximum of activity would be obtained at pH ca. 9, because at this value the equilibrium potential for the ORR is near to the pzfc of the metal surface [36].

According to these results and mechanisms, the activity of the HOR should decrease as pH increases on the three basal planes of platinum. However, the pH sensitivity of the HOR on Pt(110) was found to be almost negligible. Three causes can be pointed out for this unexpected behavior. First, the kinetic activity for this electrode is higher than that can be measured during the time window of the technique, so that the curves are very close to the thermodynamic limit. Note that the peak-to-peak separation measured in Figure 2 for the HER/HOR on Pt(110) is very close to the reversible limit, which supports this hypothesis. Second, the specific adsorption energies and lateral interactions on each surface may play a role in the mechanism. It should be noted that the sceneries in terms of adsorbed H and OH near the HOR onset potential on the three basal planes are different (see figure 1). Third, the specific pH dependence of the pme in the RHE scale observed for the Pt(110) electrode could imply specific changes in the interfacial structure.

Given that the HER on platinum would take place always at potentials negative to the pzfc, negative charge would be also present on the surface during the HER. However, the effect of the pH on the HER was found to be negligible under near neutral

pH conditions. Nevertheless, the negative charge on the electrode has a very different effect on the HER than on the HOR. During the HER, a positively charged reactant (the proton) approaches the surface, whereas a neutral product (H_2) leaves the same. By contrast, during the HOR, a neutral reactant (H_2) approaches the surface, whereas a positively charged product (the proton) leaves the same. Thus, the HER would be favored whereas the HOR disfavored as an effect of the negative charge on the surface. In any case, the favorable effect of negative charge on the HER under alkaline conditions would be not observed because the sluggish kinetics of the water dissociation would limit the rate of the whole of the reaction. The larger effect of surface charge for the HOR in contrast to the HER at near neutral pH values could be due to the fact that for the HOR the potentials at which the reaction takes place are closer to the pzc, while for the HER they move away from the pzc. Thus, not only HBE, but also other factors, such as the nature of the proton source, or the presence of surface spectators [61, 78], could also play a role in the HER/HOR rate [61, 78]. Moreover, we point out here charge on the electrode as a factor to be taken into account when predicting activity of the HER/HOR on surfaces. It has been pointed out recently by theoretical calculations with a microkinetic model that the ionic strength could modulate the effect of the surface charge on the electrocatalytic reactions[79], and therefore systematic investigations about the effect of pH on the HOR at different ionic strengths will be carried out in future studies.

Conclusions

Hydrogen evolution and oxidation reactions on Pt(111), Pt(100) and Pt(110) were studied under near neutral pH conditions in the absence of anion specific adsorption. The HER was found to be virtually pH insensitive, for each plane, at these

pH values. This result suggests that the ionic composition of the media has not a significant effect on the HER, and that the availability of protons does not limit this reaction under near neutral pH conditions. By contrast, the HOR was found to be markedly pH sensitive even under near neutral pH conditions, mainly on Pt(111) and Pt(100). It has been reasoned that, as pH increases, the electrode charge becomes increasingly negative, both for the HER and for the HOR. However, this charge has a very different effect on the HER than on the HOR, favoring the HER and disfavoring the HOR. Moreover, it has been argued by DFT calculations that, the more negative (less positive) the charge on the electrode is, the more unfavorable the proton solvation on the surface becomes and the more trapped the proton on the surface is. Thus, it can be reasonably understood that, these combined effects can seriously disrupt the mechanism favoring the proton extraction from the surface during the HOR, drastically slowing down the kinetics of the reaction under alkaline conditions. So, we proposed here charge on the electrode as the explanation for the observed pH sensitivity of the HOR on platinum. This mechanism would operate also on other metals, though modulated by the corresponding specific work function, pztc, pzfc and H/OH adsorption behavior.

Authors contribution

V. Briega-Martos has carried out the experimental work. A. Ferre-Vilaplana has carried the theoretical calculations. E. Herrero and J. M. Feliu have devised and guided the experimental work. E. Herrero and A. Ferre-Vilaplana have devised the theoretical calculations. All authors have contributed in the analysis and writing of the manuscript.

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V. Briega-Martos has carried out the experimental work. A. Ferre-Vilaplana has carried the theoretical calculations. E. Herrero and J. M. Feliu have devised and guided the experimental work. E. Herrero and A. Ferre-Vilaplana have devised the theoretical calculations. All authors have contributed in the analysis and writing of the manuscript.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: