

Role of the Interfacial Water Structure on Electrocatalysis: Oxygen Reduction on Pt(111) in Methanesulfonic acid

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Abstract

Most of electrocatalytic reactions occur in an aqueous environment. Understanding the influence of water structure on reaction dynamics is fundamental in electrocatalysis. In this work, the role of liquid water structure on the oxygen reduction at Pt(111) electrode is analyzed in methanesulfonic (MTSA) and perchloric acids. This is because different anions can exert a different influence on liquid water structure. Results reveal a lower electrode activity in MTSA than in HClO₄ solutions and they are discussed in light of anion influence in water structural ordering. From them, the existence of an outer-sphere step in the ORR mechanism is proposed

Keywords: Interfacial water, Pt(111) surface, Oxygen Reduction, Methanesulfonic acid, Hanging meniscus rotating disk voltammetry.

1. Introduction

Oxygen reduction reaction (ORR) is by far the most important cathodic process in energy-related applications. Unfortunately, on platinum, the most active pure metal for this reaction, oxygen reduces to water with a large overpotential, $\eta \sim 0.3$ V [1,2]. Additionally, despite years of intense research, the reaction mechanism is still unknown. This imposes a serious drawback in the development of advanced energy-conversion systems, and an improved molecular understanding of the ORR reaction kinetics is essential for the design of efficient and cheaper catalysts for this reaction.

From electrochemical studies, it is well known that favorable catalytic properties depend sensitively not only on the energetics of bonding interactions at metal–liquid interfaces between key reaction intermediates and the electrode [3], but also on the effect of the water

structure in the interface and the electronic distribution in the metal, which may modify the electronic properties of the substrate [4–8]. However, while several studies on different Pt-based materials have shown that the ORR kinetics and mechanism are strongly affected by the nature and structure of electrodes [1,2,9–12], the influence of interfacial water structure on the reaction is still poorly understood [4–8].

In this work, the role of the interfacial water structure in the rate of the ORR at Pt(111) electrodes is considered. In this sense, the electrode activity in the presence of methanesulfonic acid (MTSA) is evaluated. This organic acid is chosen because despite its promoting effect on the equilibrium that exists at room temperature between ice-like and non ice-like water structure, reflected in noticeable changes in the shape of the characteristic voltammetric profile of Pt(111) in non-adsorbing electrolytes, it does not specifically adsorb on platinum surfaces [13]. Therefore, any change in the ORR dynamic in presence of this acid can be attributed to changes in the water interfacial structure and not to a poisoning of active sites by sulfonic anions. In addition, a comparison of the electrode reactivity in another acidic solution involving non-adsorbing anions [11,12,14,15] is also made. Differences are interpreted in terms of the effect of the anion on the structure of interfacial water.

2. Experimental

Electrodes with (111) surface orientation prepared following standard procedures [16,17] were used as working electrodes. The ORR was measured at the hanging meniscus rotating disk electrode (HMRDE) configuration [18], using a Radiometer, EDI-101. All the experiments were carried out in a two-compartment, three electrode all-glass cell, following an experimental protocol detailed elsewhere [17]. The electrodes were heated in a gas-oxygen flame, cooled down in reductive atmosphere (H_2+Ar) and protected with a droplet of water. Solutions were prepared from suprapure perchloric acid (Merck) and methanesulfonic acid (Merck for synthesis, $\geq 99\%$) in ultrapure water (Purelab Ultra 18.2 $\text{M}\Omega \text{ cm}^{-1}$). H_2 , O_2 and Ar. (N50, Air Liquid) were also employed. All potentials were measured against the Reversible Hydrogen Electrode (RHE).

3. Results and discussion

The cyclic voltammetric profile at Pt single crystals in 0.1 M MTSA and oxygen-free solutions has been recently described and results were compared with the characteristic

cyclic voltammogram (CV) for Pt(111) in 0.1 M HClO₄ [13]. In both solutions, different potential regions can be clearly distinguished, Figure 1. At potentials lower than ~0.50 V, where the hydrogen adsorption/desorption, H_{ads}, and the double layer regions take place, there is an almost perfect coincidence between both CVs, but at higher potentials, when the adsorption of oxygen-containing species occurs, adsorbed hydroxyl (OH_{ads}) from 0.5 to 0.9 and adsorbed oxygen (O_{ads}) between 1.0 to 1.2 V [15,19,20], visible differences between both CVs appear. Changes have been interpreted in terms of the higher promoting effect on the water structure of the MTSA anion than ClO₄⁻, considering its ability to form hydrogen bonds with water molecules in the ice-like network [13].

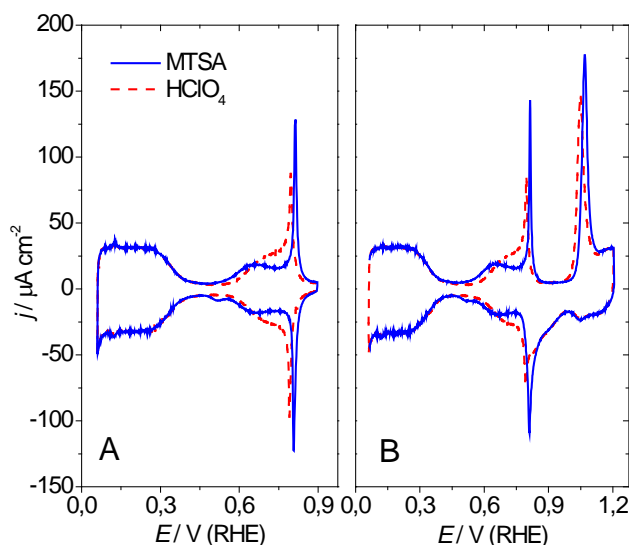


Figure 1: Stable voltammetric profiles of Pt(111) in 0.1 M HClO₄ (dashed) and CH₃SO₃H (solid) at 0.05 Vs⁻¹, from 0.06 to 0.9 V (A) and 1.2 V (B).

The ORR was carried out in oxygen-saturated, 0.1 M MTSA solutions at different rotation rates, ω . Figure 2A collects voltammetric profiles for ORR on Pt(111) surface, between 0 and 1.15 V at 0.05 Vs⁻¹. The upper potential limit was selected to assure the morphological stability of the surface. Because the sweep direction can play an important role on the shape of the CV [12,14], positive (dashed line) and negative (solid line) going scans are shown. In addition, a detailed view of CVs in the high potential region and a plot of the limiting current, j_{lim} , vs. $\omega^{1/2}$ are also shown, Figs. 2B and C. From the last one, it can be appreciated that the hydrodynamic response of the system is well described on the surface by the standard Levich equation, within reasonable experimental error [11,12,14].

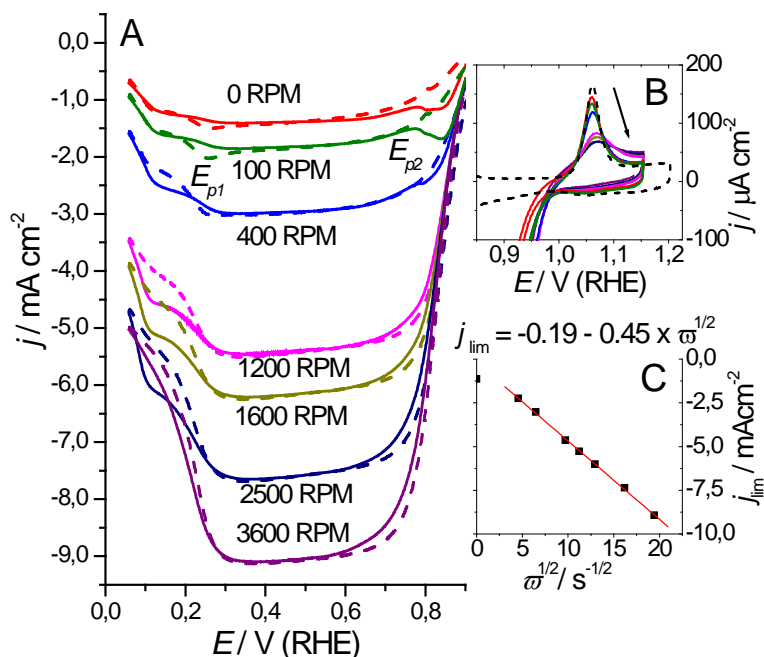


Figure 2: A) Oxygen reduction on a HMRD Pt (111) electrode in O₂-saturated, 0.1 M CH₃SO₃H: Positive (dashed line) and negative-going (solid line) sweeps. Rotation rates are given on the curve. B) Detailed view of CVs in the high potential region. Arrows indicate increasing rotation rates. C) Plots of j_{lim} vs. $\omega^{1/2}$. Scan rate 0.05 Vs⁻¹

Curves in Fig. 2 show similar trends to those already described for Pt(111) in 0.1 M HClO₄ solutions [11,12,14]. The reaction onset is ca. 1.0 V, versus the reversible hydrogen electrode (RHE), and j_{lim} is recorded between ~0.30 and 0.75 V. At $E < 0.3$ V, where H_{ads} is adsorbed, there are two drops in the reduction current and the voltammetric profile depends on the direction of the potential scan and ω . In perchloric acid solutions, hydrogen peroxide, H₂O₂, has been also detected in this potential region [9,10], and experimental findings have been explained considering that H_{ads}, may prevent O–O bond scission or block surface sites [11,12,14]. Consequently, only two electrons would be exchanged in this potential range. Results in Fig. 2A suggest that reaction inhibition by H_{ads} is not affected by changes in the water structure of the solvent.

At high potentials and fast enough rotation rates, $\sim \omega > 400$ rpm, compared to the electrode scan rate, v , CVs display the typical, S-shaped curve (steady state response), theoretically predicted for RDE systems [21]. However, at slow enough rotation rates, $\sim \omega < 400$ rpm, j - E curves exhibit two current peaks: one in the positive direction, E_{p1} , around 0.26 V, and other in the negative-going scan, E_{p2} , at ~0.84 V, Fig. 2A for 100 rpm. In the case of

perchloric acid solutions, while E_{p1} is at 0.27 V and has been assigned to H_2O_2 reduction, accumulated in the interface because of reaction inhibition by H_{ads} , $E_{H_2O_2}$, E_{p2} is at 0.85 V and has been attributed to the reduction of an intermediate soluble species, E_{ORR} [14]. This step would correspond to the rate determining step (RDS) in the ORR mechanism. Additionally, similar as well to 0.1 M $HClO_4$ solutions [14], voltammetric currents during positive going scans between 1.0 to 1.15 V, where O_{ads} appears [15,19,22,23], decrease as ω increases, Fig. 2B, suggesting that in MTSA solutions dissolved O_2 may also act like an extra O_{ads} source and modify oxide growth dynamics.

When studying the ORR kinetics, a common approach, widely used to analyze steady state reaction kinetics, which are first order with respect to the diffusing reactant, is by employing the Levich-Koutecky equation [11,12]:

$$j = j_k + (D C^b \nu)^{1/2} \quad (2)$$

where j_k is the kinetic current density and $B / \text{mA (rev min)}^{-1/2}$ is a constant given by:

$$B = \frac{2.303 F n C^b}{4 \pi D \nu} \quad (3)$$

where F is the faraday constant, n is the number of electrons transferred per molecule of O_2 diffusing through the nerst boundary layer, ν is the kinematic viscosity and D and C^b are respectively the diffusion coefficient and the solubility of O_2 . From Fig. 2C an slope of $0.45 \text{ mAcm}^{-2}(\text{rad})^{-1/2}$ is calculated from the adjusted straight line. This value, somewhat higher than the 0.40 teoretical Levich slope for $HClO_4$ solutions [9,10], suggests a $(2.303 F n C^b / 4 \pi D \nu)$. Nevertheless, it could be said that ORR in MTSA and $HClO_4$ occurs through a similar, four-electron, reaction mechanism.

To analyze the effect of the interfacial water structure in the rate of the ORR at Pt(111) electrodes the ORR activities in MTSA and $HClO_4$ at 1600 rpm are compared, Figure 3. As it can be seen, the activity ORR in MTSA is slightly lower than in $HClO_4$, with a half-height potential, $E_{1/2}$, around 0.851 V vs. 0.865 V. Because the upper limit potential, E_{up} , in this case was 0.9 V, small potential differences are measured between the positive and negative scans: ca. 3 to 6 mV. However, measured Tafel slopes in both solutions are quite similar: 71 and 62 mV in the positive- and negative-going scans, respectively, inset to Fig. 3A. Tafel slopes from 60 to 88 mV have been reported for Pt(111) electrodes [11,12,14]. Therefore, it appears that the presence of anions that promote water structuring reduces to some extent the ORR activity of the electrode, without affecting the ORR mechanism.

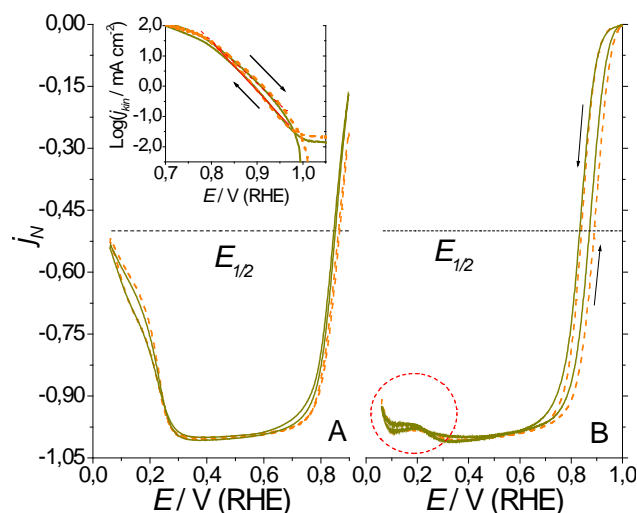


Figure 3: Oxygen reduction at 1600 rpm on a HMRD ordered (A) and disordered (B) Pt (111) electrode in O_2 -saturated, 0.1 M CH_3SO_3H (solid) and 0.1 M $HClO_4$ (dashed) solutions, normalized against limiting currents. Arrows indicate the direction of the scan. Inset to figure A: Tafel slope values obtained for ORR reduction on both solutions. Scan rate 0.05 Vs^{-1} .

The difference in the ORR activity in MTSA and $HClO_4$ solutions during the positive-going scan slightly increases if some surface defects are created onto the electrode surface, while the same activity is measured in both solutions for the negative-going scan, Fig 3B. In this case, a difference of 18 mV in $E_{1/2}$ is measured: 0.872 vs. 0.890 V. Thus, an increase in liquid water structural ordering also decreases to some extent the ORR activity of disordered electrodes, and probably of stepped surfaces too. Contrarily, at oxygen-coated electrodes the effect in the ORR activity is practically negligible. Anyway, ORR activity in disordered electrodes is still higher than in ordered ones, *i.e.* similar to what has been reported for stepped surfaces in acidic solutions [11,12,24,25], steps and defects also increase the ORR activity in MTSA. A small amount of surface defects can be created by cycling the electrode several times until $E_{up} > 1.15 \text{ V}$ [26]. In contrast, in the low potential region ORR activity in MTSA and $HClO_4$ is the same: in ordered electrodes H_{ads} inhibits the reaction, while in disordered electrodes this inhibition decreases [11,12,24].

Changes in the ORR activity with changes in the chemical nature of solution ions have been also reported in alkaline solutions [3]. In this case, ORR activity decreases as the hydration energies of cations increases: $Li^+ > Na^+ > K^+ > Cs^+$. Results were explained in terms of the role of non-covalent interactions between hydrated alkali metal cations

$M^+(H_2O)_x$ and OH_{ads} species. However, these results and results described here can be also suitably explained just considering the different effect that ions exert on the structure of liquid water. In this sense, ions have long been classified as being either kosmotropes (structure makers) or chaotropes (structure breakers) according to their relative abilities to induce the structuring of water [15,27]. In general, it is known that water is ordered by small or multivalent ions and disordered by large monovalent ions [27]. Therefore, in agreement with experiments, the ORR decreases at increasing liquid water ordering, *i.e.* $Cs^+ > K^+ > Na^+ > Li^+$ and $ClO_4^- > SO_3^-$.

From the above results, the natural question is why the structure of liquid water affects the ORR activity. As highlighted before [13,15], liquid water structure modifies the OH_{ads} adsorption dynamics, which in turn changes the adlayer structure and composition [19,22], and the water dipole orientation at the polarized water/electrode interface [6], affecting the structure of the electric double layer (EDL). Supporting the first case, ORR activities, evaluated as current densities at 0.9 V, of Pt single crystals in acidic media have been correlated with the shift in OH-binding energy, $\Delta G_{OH_{ads}}$, on {111} terraces, when a reference charge of $40 \mu C cm^{-2}$ has been transferred, resulting in an volcano type curve [28]. In this framework, Figure 4 depicts the total transferred charge during the positive-going scan in oxygen-free, 0.1 M MTSA and 0.1 M $HClO_4$ solutions at Pt(111), Fig. 4A, as well as the normalized oxygen reduction at 1600 rpm in these solutions, Fig. 4B. For the sake of comparison results at Pt(10 10 9) electrode in 0.1 M $HClO_4$ are also given.

From Fig. 4A, it is clear that a charge of $40 \mu C cm^{-2}$ is first transferred to the electrode in MTSA. Thus, a lower ORR activity would be expected in this electrolyte [28]. It is important to remark, however, that for any dissociative reaction, such as ORR, it has been shown that the reaction rate should always follow a volcano plot as function of the dissociative adsorption energy of the reacting species, regardless the RDS, owing the Brønsted–Evans–Polanyi relation and the linear relationship between the adsorption energy of reactive and intermediate species [29]. Therefore, $\Delta G_{OH_{ads}}$ would be a natural parameter to describe ORR electrode reactivity, following a volcano-type correlation. However, this does not necessarily imply that the potential determining step for ORR is the reduction of OH_{ads} , or O_{ads} [30–35].

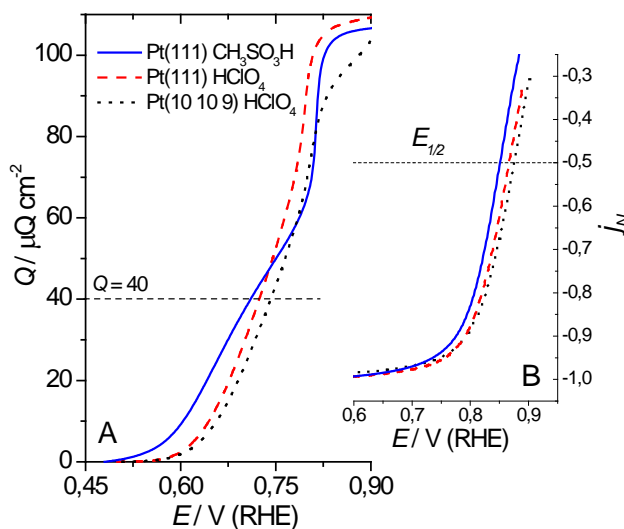


Figure 4: Total transferred charge during the positive-going scan of cyclic voltammograms, integrated from 0.45 to 0.9 V after double-layer charging corrections, in oxygen-free, (A) and normalized oxygen reduction at 1600 rpm, in oxygen saturated, (B) 0.1 M HClO_4 (dashed) and 0.1 M $\text{CH}_3\text{SO}_3\text{H}$ (solid) solutions at Pt(111). Scan rate 0.05 Vs^{-1} . For the sake of comparison results at Pt(10 10 9) electrode in 0.1 HClO_4 are also given.

Indeed, if the availability of Pt surface active sites is considered to be the RDS in ORR, the OH_{ads} coverage at $E > 0.8 \text{ V}$, when the mixed and pure kinetics controlled regions occur, should be higher in those cases when the ORR decreases, *i.e.* there should be less empty Pt sites for the reaction to take place, which clearly is not observed, Fig. 4A. Hence, it is possible that the measured ORR activity change in MTSA, Fig. 4B, it is not a direct consequence of changes in OH_{ads} adsorption dynamics but rather it is related with changes in the EDL structure, due to changes in water dipole orientations. In this sense, theoretical results have shown that because of the weak interaction of water with Pt(111), the electronic structure of the Pt electrode is hardly perturbed by the presence of water and so, processes that occur directly at the electrode surface, such as specific adsorption or the dissociation from a chemisorbed molecular state, are only weakly influenced by water, while processes that occur further away from the electrode can be modified by the water environment through direct molecule–water interactions [4].

In agreement, different experimental results have suggested an outer-sphere step as the RDS in the ORR mechanism [14], such as the approaching of molecular oxygen to the electrode surface [5,7,8] or the reduction of a soluble intermediate species [14,36], instead

of an inner-sphere reaction. In this case, the onset of oxygen reduction would only occur when the degree of oxygen-down saturated water at the interface decreases, as proposed from electrocapillary studies. Consequently, the saturated interface may inhibit the ORR at higher potentials, either by blocking the access to the electrode and/or by the dipole induced potential drop [5]. Therefore, stronger liquid water structuring may decrease ORR activity by increasing water dipole polarization at the EDL, or decreasing mobility or reactivity (changes in entropies of solvation) of participating non-adsorbed species.

4. Conclusions

In this work, the oxygen reduction reaction in methanesulfonic acid (MTSA) on Pt(111) is measured, to examine the role of liquid water structure on the ORR activity. Results show that the ORR activity in MTSA solutions slightly decreases compared to the activity in HClO₄, despite the lower electronic charge transferred to the electrode in the kinetic controlled region in the first case. Results are discussed in light of anion influence in water structural ordering and a possible involvement of an outer-sphere step in the ORR mechanism is suggested.

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