Role of the interfacial water structure on electrocatalysis: Oxygen reduction on Pt(1 1 1) in methanesulfonic acid

Andrea P. Sandoval-Rojas [a,c], Ana M. Gómez-Marín [a,b], Marco F. Suárez-Herrera [c], Víctor Climent [a,b,c], Juan M. Feliu [a,*]

[a] Instituto de Electroquímica, Universidad de Alicante, Apt 99, E-03080 Alicante, Spain
[b] Eco-Lavka, Cra. 79, #49ª-30, Medellín, Colombia
[c] Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, sede Bogotá, Bogotá, Colombia

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(1 1 1) electrode is analyzed in methanesulfonic (MTSA) and perchloric acids. This is because these different anions can exert a different influence on liquid water structure. Results reveal a lower ORR electrode activity in MTSA than in HClO$_4$ solutions and they are discussed in light of anion's influence on water structural ordering. From them, the existence of an outer-sphere, rate determining, step in the ORR mechanism is suggested.

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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(1 1 1) 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 [13,14], reflected in noticeable changes in the shape of the characteristic voltammetric profile of Pt(1 1 1) in non-adsorbing electrolytes, it is not expected to specifically adsorb on this platinum surface [15]. 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 poisoning of active sites by sulfonic anions. In addition, a comparison of the electrode reactivity in another acidic solution involving non-adsorbing anions [11,12,16,17] is also made. Differences are interpreted in terms of the effect of the anion on the structure of interfacial water.

2. Material and methods

Electrodes with (1 1 1) surface orientation prepared following standard procedures [18,19] were used as working electrodes. The ORR was measured at the hanging meniscus rotating disk electrode
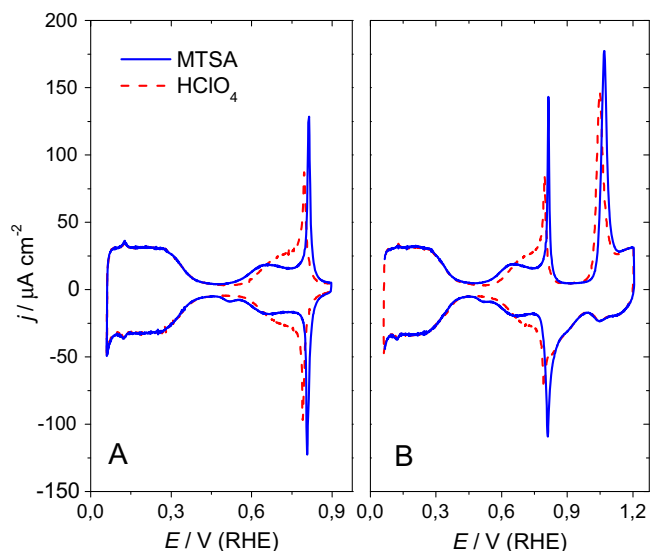

Fig. 1. Stable voltammetric profiles of Pt(1 1 1) in 0.1 M HClO$_4$ (dashed) and CH$_3$SO$_3$H (solid) at 0.05 V s^{-1}, from 0.06 to 0.9 V (A) and 1.2 V (B).

Fig. 2. (A) Oxygen reduction on a HMRD Pt(1 1 1) electrode in O$_2$-saturated, 0.1 M CH$_3$SO$_3$H: 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 V s^{-1}.

(HMRDE) configuration [20], 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 [19]. 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 supra-pure perchloric acid (Merck) and methanesulfonic acid (Merck for synthesis, ≥99%) in ultrapure water (Purelab Ultra 18.2 MΩ cm^{-1}). H$_2$, O$_2$ and Ar. (N50, Air Liquid) were also employed. All potentials were measured against the Reversible Hydrogen Electrode (RHE).

All voltammetric scans were collected at freshly annealed surfaces, cycled first in the low potential region to verify their quality as well as the cleanliness of the surface. The stability of the voltammetric profiles with time was carefully checked to ensure solution cleanliness. As the requirements for HMRDE experiments are stringent owing to forced convection, special care was taken to assure solution cleanliness. IR drop corrections were also made when was necessary to compensate the electrolyte resistance.

3. Results and discussion

Cyclic voltammetric profiles at Pt single crystals in 0.1 M MTSA and oxygen-free solutions have been recently described and results were compared with the characteristic cyclic voltammograms (CV) for these electrodes in 0.1 M HClO$_4$ [15]. For Pt(1 1 1), different potential regions in CVs in both solution scan be clearly distinguished, Fig. 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 curves. However, at higher potentials, when the adsorption of oxygen-containing species occurs visible differences between both CVs appear.

At 0.5 < E < 0.9 V, where adsorption of hydroxyl species (OH$_{ads}$) from water dissociation is expected, OH adsorption starts at slightly lower potentials in MTSA than in HClO$_4$ and this could suggest weak specific adsorption [21]. In contrast, the following sharp peak, the spike of the so-called "butterfly" feature [17], is slightly shifted to higher potentials and this behavior is not characteristic of specific adsorption. Therefore, the dominant effect in the OH adsorption region is the change of the shape of the voltammetric profile, and this suggests deep modifications on the structure of the interfacial water. Correspondingly, between 1.0 and 1.2 V the voltammetric
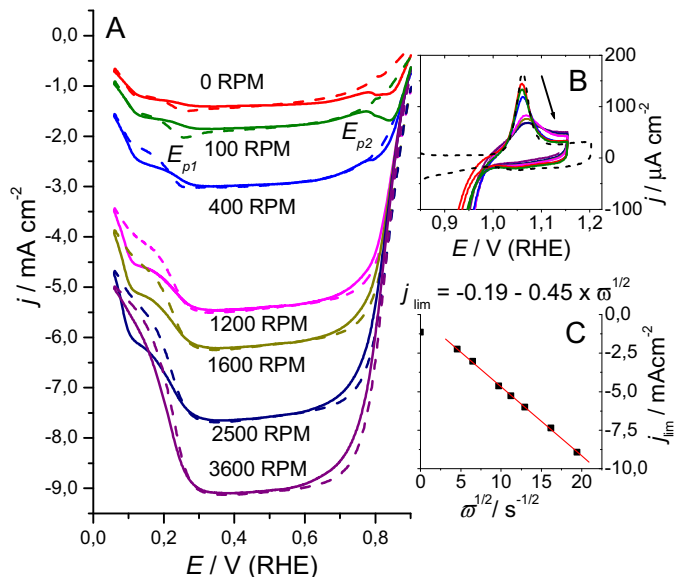
signal attributed to adsorbed oxygen (O$_{ads}$) is also shifted to higher potentials in MTSA than in HClO$_4$ [17,22,23]. Hence, better than to anion specific adsorption, see below, changes in the CV in MTSA have been interpreted in terms of a higher promoting effect on the water structure of the MTSA anion than ClO$_4^-$, considering its ability to form hydrogen bonds with water molecules in the ice-like network [13–15].

The ORR was carried out in oxygen-saturated, 0.1 M MTSA solutions at different rotation rates, ω. Fig. 2A collects voltammetric profiles for ORR on Pt(1 1 1) surface, between 0.06 and 1.15 V at 0.05 V s^{-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 [12,16], both 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 given, Fig. 2B and C, respectively. From the last figure, it can be said that the hydrodynamic response of the system is well described by the standard Levich equation, within reasonable experimental error [11,12,16].

Curves in Fig. 2 show similar trends to those already described for Pt(1 1 1) in 0.1 M HClO$_4$ solutions [11,12,16]. The reaction onset is ca. 1.0 V, vs. 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, H$_2$O$_2$, 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 [11,12,16]. Consequently, only two electrons would be exchanged in this potential range. Results in Fig. 2A suggest that reaction inhibition by H$_{ads}$, as well as the H adsorption process itself, is practically unaffected by changes in the water structure of the solvent.

At high potentials and fast enough rotation rates, ~ω > 400 rpm, compared to the electrode scan rate, v, CVs display the typical, S-shaped curve theoretically predicted for RDE systems (steady state response) [24]. However, at slow enough rotation rates, ~ω < 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