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Peroxodisulfate reduction as a probe to interfacial charge

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ABSTRACT

Peroxodisulfate reduction has been investigated on Pt(111) on a broad range of pH values as a way to test interfacial charge. The reaction always proceeds in a potential window that is almost pH independent, regardless of changes in the presence of adsorbed species. Comparison with other available information for these interphases allows to conclude that this reaction is very sensitive to the free charge on the metal, being inhibited when the latter is negative. This explains the complete current inhibition when the potential is lower than the potential of zero free charge. Most remarkably, the inhibition at high potentials can be related to the existence of a second potential of zero charge, above which the surface becomes again negatively charged. This conclusion agrees with classical results for polycrystalline platinum (which has been reexamined), results from laser induced T-jump experiments and recent theoretical models of the interphase. In this way, this reaction is postulated as a new probe to locate the values of the potential of zero free charge.

1. Introduction

The potential of zero charge (pzc) is a pivotal parameter in interfacial electrochemistry [1]. For liquid or coinage metal electrodes (ideally polarizable interphases), the determination of the pzc is carried out by means of electrocapillary curves or by looking for the minimum differential capacity as predicted by Gouy-Chapman theory [2], respectively. In metals that adsorb hydrogen, or under the presence of other charge transfer processes, the later methods are precluded. Moreover, in the platinum/electrolyte interphase, two different potentials of zero charge should be defined: the potential of zero total charge (pztc) and the potential of zero free charge (pzfc), each one related to total (q) or free charge (σ), respectively. The pzfc is equivalent to the pzc in metals that do not experience adsorption processes with charge transfer [3].

The CO charge displacement experiment [4] can be used to determine the pztc on Pt(111) electrodes [5] and, from it, the pzfc can be estimated, after some non-thermodynamics assumptions [6]. Also, the laser induced temperature jump technique measures the potential of maximum entropy (pme) of interphase formation. At the pme the disorder of water molecules is maximal and its value is close to the pzfc [7]. The coincidence between the values of pme, coming from laser induced temperature jump, and those of pzfc estimated from CO charge displacement is quite remarkable [8]. Further studies have shown that the pzfc of Pt(111) is independent of pH, as the pme is in solutions with pH < 7 [9,10].

Kolotyrkina et al. (reference 69 in [3]), using radiotracers techniques showed the existence of the pzfc, for oxidized platinum electrodes, a result anticipated by Balashova et al. using electrokinetic measures (reference 66 in [3]). In this respect, laser T-jump experiments show an inversion of the response when the surface becomes oxidized, agreeing with the existence of a second change in the orientation of interfacial water [11]. All these data were used by Huang et al. to convincingly model this behavior [12]. In a completely different approach, the use of local probes like nitrous oxide (N_2O) reduction has also been proposed as an effective way to investigate interfacial properties [13,14]. Assuming that N_2O reduction requires the adsorption of a weakly adsorbable molecule, its peak potential would appear when the surface is either free of adsorbed hydrogen or OH, the main adsorbates on platinum electrodes in the absence of anion specific adsorption. Moreover, the peak potential for the reduction of this neutral molecular probe was used further to estimate the local pztc's (from terraces and steps) on high index platinum single crystals electrodes. A good agreement between the local values found using this molecular probe and the overall value from charge displacement was established [15].

Another proposed probe reaction was the reduction of peroxodisulfate (PDS) anion, which is highly sensitive to the surface structure and composition in low index platinum single crystal electrodes [16]. On Pt(111) the reaction at pH 1 takes place in the double layer region and it is inhibited near to 0.36 V vs RHE, whereas at pH 3 the reaction is inhibited around 0.40 V vs RHE. Originally, this inhibition was attributed to hydrogen adsorption or the strong polarization of water molecules for each pH, respectively. On Pt(110) and Pt(100) at pH 1, PDS

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reduction occurs at 0.18 V and 0.45 V vs RHE, both potential values being close to the respective pztc's [16]. Classical studies of peroxodisulfate reduction on mercury electrodes evidenced the sensitivity of the rate of outer sphere electrochemical reactions to the ionic and potential distribution in the diffuse double layer, according to Gouy-Chapman-Stern theory. This is known today as the Frumkin effect.

In this paper we reexamine PDS reduction on Pt(111) to gain further information on the properties of this anionic probe. The reaction on platinum clearly does not follow an outer sphere mechanism and therefore, direct application of Frumkin theory to this case is not possible. Still, we show in the following that the reaction shows a clear sensitivity to the charge on the metal, most likely due to the electrostatic interaction with the negative charge of the anion being reduced. Supporting electrolyte solutions with different pH in the absence of specifically adsorbed anions were used. Results will be compared with other available data, to better understand these electrochemical interphases.

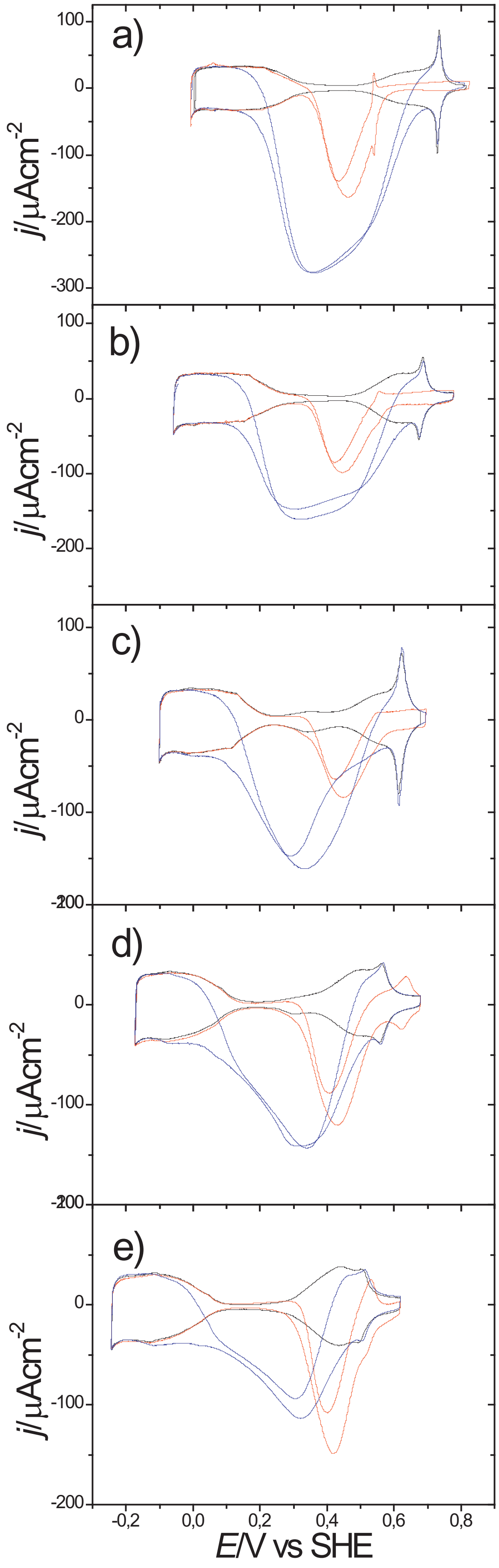
2. Experimental

Electrochemical cell, electrode pretreatments, and electrochemical workstation have been described elsewhere [9]. All working solutions were prepared with ultra-pure water (ELGA, 18.2 MΩ cm), concentrated perchloric acid (Merk, for analysis), sodium fluoride (Merk, suprapur), $K_2S_2O_8$ (Fluka, 99.0%). Hydrogen (N50), Argon (N50) and N_2O (N25) were also used, all from Air Liquide. The pH of the different solutions was calculated from potential measurements of the RHE as previously reported [10].

3. Results and discussion

Fig. 1a shows PDS and N_2O reduction cyclic voltammograms on a well ordered Pt(111) electrode at pH 1. Results agree with those previously published [15,16]. The hydrogen adsorption region can be considered unaltered in the presence of both surface probes. On the other hand, the OH adsorption region is altered in the presence of the anionic probe, likely adsorbed in these conditions, but unaltered in the case of N_2O. Close inspection reveals that the potential of maximum current for N_2O reduction coincides with the potential zone in which the PDS reduction drops to zero (0.3 V SHE; 0.4 V RHE). This behavior most likely reflects the different charge values of each probe, neutral for N_2O and negative for PDS, and how they interact with the surface electrode charge. In this way, the drop in PDS reduction current can be identified with the point when the charge on the electrode changes from positive to negative. That behavior suggests that PDS reduction is a suitable process to study interfacial surface charge.

To check the latter hypothesis, PDS reduction was carried out in a wide pH range. Fig. 1b–e show PDS and N_2O reduction in other different pH solutions, in the SHE scale, in which clear trends are observed: at pH 1 the PDS reduction starts and finishes in the double layer region; for pH 3, the reduction begins in the OH adsorption region while the inhibition appears in the middle of the double layer region; finally, at pH 5 the reaction occurs completely in the OH adsorption region. It is clear from this figure that onset and inhibition potentials are not governed by the presence of adsorbed species (OH or anion and hydrogen, respectively). It is remarkable that the potential window where PDS reaction takes place is the same for all pHs in the SHE scale. Furthermore, the potential where PDS reduction drops to zero coincides with the potential of maximum current for N_2O reduction in the whole pH range studied. At this point, the sign of the charge on the electrode seems to be the main parameter governing PDS reduction instead of other factors (hydrogen/OH adsorption in N_2O reduction). To evidence this point, subtraction of the blank current density from the current density for PDS reduction was performed. The current difference falls to zero at the same potential, 0.28 ± 0.01 V vs SHE, in the whole pH range studied (Fig. 2A–B) and is practically independent of the sweep



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