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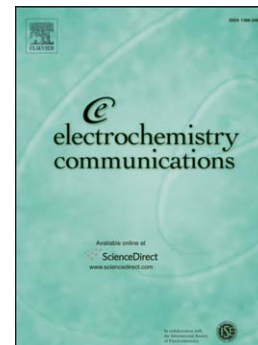
Exploring the interfacial neutral pH region of Pt(111) electrodes

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## Exploring the interfacial neutral pH region of Pt(111) electrodes.

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**ABSTRACT:** The interfacial properties of Pt(111) single crystal electrodes have been investigated in the pH range  $3 < \text{pH} < 5$  in order to obtain information about the acidity of electrosorbed water. Proper experimental conditions are defined to avoid local pH changes while maintaining the absence of specifically adsorbed anions and preserving the cleanliness of the solution. For this purpose, buffer solutions resulting from mixtures of NaF and HClO<sub>4</sub> are used. Total charge curves are obtained at different pHs from the integration of the voltammetric currents in combination with CO charge displacement experiments. Analysis of the composition of the interphase as a function of the pH provides information for the understanding of the notion of interfacial pH.

**KEYWORDS:** Interfacial pH; double layer; single crystal electrode; Pt(111); potential of zero charge; neutral pH buffer.

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## Introduction

Investigation of interfacial properties is a key issue in fundamental electrochemistry. Among the different properties that characterize the structure of the interphase, the potential of zero charge (pzc) is a parameter of paramount importance [1-5]. Regarding the interfacial charge, when adsorption processes participate in the formation of the interphase, distinction should be made between the concepts of total charge (including the charge involved in adsorption processes) and free charge (true electronic charge). Correspondingly, different values for the potential of zero total charge (pztc) and zero free charge (pzfc) should be defined [2, 6]. This is the situation for Pt and other electrocatalytic metals. In these cases, the usually available magnitude is the total charge, from which the free charge can be calculated by using some reasonable assumptions [7-10]. In general, the pztc and the pzfc of Pt(111) have been evaluated in acidic solution [8, 9].

In the case of hydrogen and hydroxyl adsorbing metals, the study of the pH dependence of the total and free charge contains valuable information about the structure of the interface and the state of adsorbed hydrogen and OH species [6]. Recently, experiments have been carried out in a wide pH range, involving an acidic region  $\text{pH} < 4$  and an alkaline region  $\text{pH} > 8$  [7, 10]. Under these conditions, the pseudocapacitive processes remain in equilibrium, and it is reasonable to assume that local pH changes at the interface are negligible. Calculation of the potential of zero free charge (pzfc) involves the extrapolation of the free charge from the so-called double layer region into the hydrogen or OH adsorption regions. The potential where the extrapolated charge is zero has been previously called potential of zero extrapolated charge (pzec) [10]. In acidic solutions, the pzec can be taken as a good approximation to the pzfc while more uncertainty exists in alkaline solutions. Still, when the extrapolation is performed with the data in alkaline solution, while the pztc values change with pH, the pzec remains constant [10].

One of the problems in the analysis of the charge/potential data is that there is a wide pH region in which clean interfaces cannot be maintained under thermodynamic equilibrium [11]. To avoid changes in the local pH at the interphase, the use of buffered solutions is required, but usual buffers normally introduce the specific adsorption of anions. In this paper, we show how the use of  $\text{HClO}_4$  / NaF mixtures allows the study of solutions with pH ranging between 3 and 5 without the interference of anion adsorption. Previous studies with NaF/HF buffered solutions required the use of relatively high concentration of HF acid, hampering the achievement of the high degree of cleanliness required for interfacial studies [12, 13].

## Experimental

Cell components and electrode pretreatments have been described elsewhere [14]. To avoid the use of hydrofluoric acid, which could carry impurities, the buffer solutions were prepared by adding perchloric acid (Merck, suprapur) to 0.1 M solution of sodium fluoride (Merck, suprapur) in appropriate amounts. In both chemicals, specific anion adsorption can be considered negligible. CO displacement experiments were run as described in previous studies [14-16]. Reported charge data correspond to average values of experiments repeated at least five times. Although potentials were measured against RHE, the potential of the RHE was

measured at the end of each experiment versus a Ag/AgCl/KCl (sat) reference electrode. From this measure the pH of the solution was calculated and all potential values converted to the SHE scale.

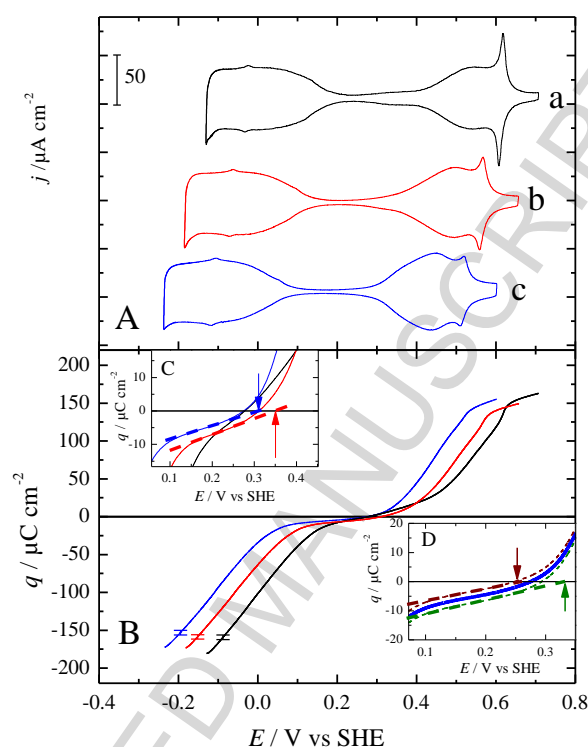


Figure 1: A) Cyclic voltammograms for Pt(111) in NaF + HClO<sub>4</sub> mixtures of different pH: a) 3; b) 4; c) 5. B) Charge curves obtained from the integration of the voltammograms of figure A using the charge displaced by CO at 0.1 V as integration constant. C) Enlargement of the double layer region. D) Charge curve for pH=4 showing the propagation of the uncertainty to the determination of the pztc and pzc.

## Results and discussion.

Figure 1A shows voltammograms of a Pt(111) electrode in contact with buffered solutions of different pH values between 3 and 5. The voltammogram recorded at pH=3 is essentially identical to that reported for perchloric acid / perchlorate mixtures [8] of the same pH and shows the broad increase in current in the double layer region, around 0.35 V, which was attributed to solvent reorientation [17]. Unlike the results in unbuffered solutions [11], the voltammograms in figure 1A recorded for pH>3 show symmetric H and OH adsorption regions, demonstrating the absence of significant local pH changes. Both regions shift nearly 59 mV / pH unit, as expected. The charge under the hydrogen region remains essentially unaffected by the pH change, with a value around 150  $\mu\text{Ccm}^{-2}$ . This value is slightly lower than that reported for hydrogen adsorption at pH=1 (160  $\mu\text{Ccm}^{-2}$ ). On the other hand, the OH adsorption region shows a redistribution of charges, an increase in the broad feature (OH<sub>b</sub>), accompanied by a diminution of the sharp peak (OH<sub>s</sub>). The overall charge for OH adsorption slightly increases with the increase of pH, from 120  $\mu\text{Ccm}^{-2}$  (pH=3) to 140  $\mu\text{Ccm}^{-2}$  (pH=5). The broad peak in the double layer region (at 0.35 V), attributed to solvent reorientation, does not shift with the pH and therefore is progressively overlapped with the OH<sub>ads</sub> region. While the onset of this

process is still visible in the double layer region at pH=4, it is almost absent in the voltammogram at pH=5.

CO displacement experiments were performed at 0.1 V. From the integration of the voltammogram, total charge/potential curves are obtained, after correction to account for the remaining charge on the interphase after CO adsorption [18, 19]. The resulting charge/potential plots are given in figure 1B. In this figure, points correspond to experimental charge values and error bars represent experimental uncertainty between different charge displacement experiments. It can be seen that the pztc's lie in the so-called double layer region, in which the contribution of pseudocapacitive processes is minimal. Thus, pztc and pzfc are nearly equal in all cases. It should be stressed that small uncertainties in the charge curve (1-2  $\mu\text{C cm}^{-2}$ ) may shift the determination of the pztc by tenths of mV and for this reason a reasonable statistics has to be made. The inset of figure 1 shows how the uncertainty in the charge propagates to the determination of the pztc. To minimize the uncertainty, a minimum of 5 displacement experiments have been performed for each pH value. The main source of uncertainty in the determination of charge comes from the CO displacement experiment. This uncertainty can be pH dependent.

Close inspection of the double layer region (see enlargement in the inset of figure 1B) reveals that pztc and pzec are strictly identical only for pH=3. For pH=4 and 5, a short extrapolation need to be done from the inflection point such as the pztc and the pzec are not identical. Interestingly, the extrapolation has to be done to higher potentials, indicating that at the pztc negative free charge is compensated with positive charge due to OH adsorption. Measurements previously reported for pH<3 [7, 9] indicated that in acidic pHs at the pztc positive free charge compensates negative charge due to H adsorption.

To improve the accuracy in the determination of the charges, it can be recalled that, in the presence of a strongly adsorbing anion, all the properties of the interphase can be considered pH independent in the high potential region. In this way, the relative position of the total charge/potential curves measured at different pH can be determined with high accuracy from their coincidence in the high potential region [8]. Also, at low enough potentials, the anion is completely desorbed and the interphase should become independent of the presence of the anion. In this way, the charge values can be also determined in the OH adsorption region, by comparing charge curves recorded with and without the anion.

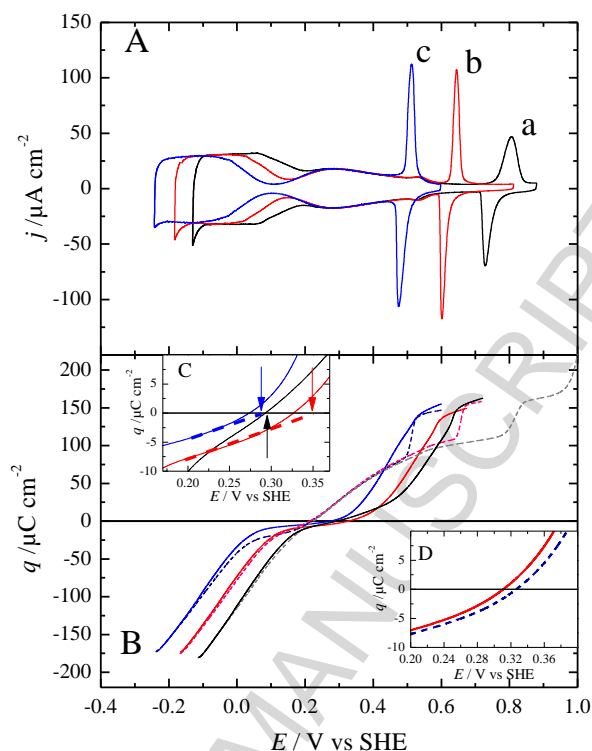


Figure 2: A) Cyclic voltammograms for Pt(111) in NaF + HClO<sub>4</sub> mixtures containing 1mM NaCl, of different pH: a) 3; b) 4; c) 5. B) Charge curves obtained from the integration of the voltammograms recorded in the absence (solid lines) and in the presence of chloride (dashed lines) (see text for details). C) Enlargement of the double layer region showing the determination of the pztc and pzec. D) Enlargement of the double layer region comparing the charge curve at pH=4 obtained with the CO displacement (solid line) and with the chloride involving methodology (dashed line)

Figure 2 illustrates the procedure, when chloride adsorption is used to suppress OH adsorption. The coincidence of the voltammograms in the region between 0.2 and 0.5 V (Figure 2A) supports the idea that the charge is pH independent under these conditions. A new peak is observed at high potentials, presumably due to the replacement of chlorine by OH. A potential value of 0.3 V is selected for the determination of the integration constant. For this, the charge curves obtained in the presence of chloride are shifted vertically until they coincide at 0.3 V (dashed lines in figure 2B). Then, for each pH, curves with and without chloride are shifted until they coincide at the onset of hydrogen evolution. In this way, the relative position of the curves at the three studied pH values is determined with high accuracy. To know the absolute position (i.e., the integration constant) of the curves, the charge displaced at a single pH value can be used. The charge displaced at the most acidic solution, pH=3, was used to define the position of the curves in figure 2B. It is worth stressing that this methodology avoids the uncertainty associated with the variation of the remaining charge on the CO covered surface after the charge displacement experiment. Figure 2B shows the resulting charge curves with and without chloride. Figure 2D shows an enlargement of the double layer region, while Figure 2C compares the charges obtained for pH=4 in the region around the pztc.

Figure 3 summarizes the values for the  $pztc$  and  $pzec$  obtained at the three investigated solutions with the two methodologies. At  $pH = 3$ ,  $pztc$  and  $pzec$  ( $pzfc$ ) values coincide. Moreover, at  $pH=3$  both methodologies provide same values for the two properties since curves at this  $pH$  share the same value of the integration constant. While a small difference is observed between both methodologies at  $pH=4$ , almost identical values are again obtained at  $pH=5$ , demonstrating the accuracy of both measurements.

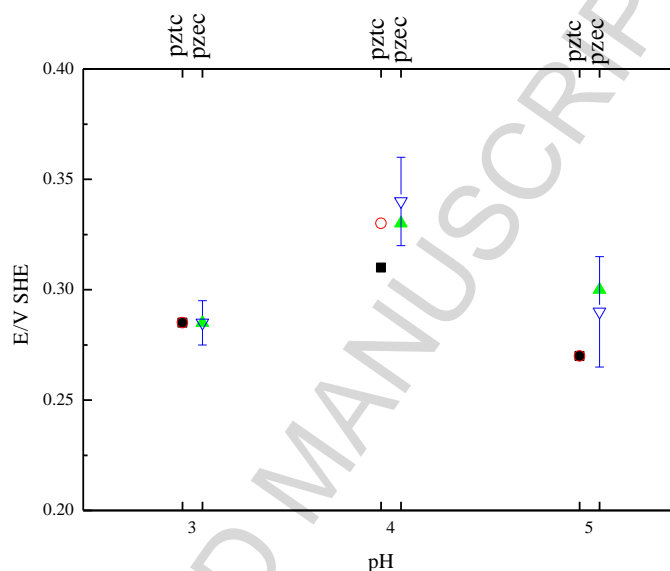


Figure 3: Values of the  $pztc$  (on the left) and  $pzec$  (on the right) as a function of the  $pH$ , as determined from the charge curves using CO displacement (solid symbols) or chloride (open symbols).

## Conclusions

Variation of the  $pztc$  and  $pzfc$  for Pt(111) within the  $pH$  region  $3 < pH < 5$  has been carefully investigated using the methodology of CO charge displacement and an indirect method that involves specific adsorption of chloride. In this  $pH$  region,  $pztc$  and  $pzfc$  lie in the double layer region and therefore, very close to each other. Close inspection of the charge curves around the  $pztc$  reveals the following interesting observation. For  $pH < 3$ , the  $pzfc < pztc$ , therefore, at the  $pzfc$  excess hydrogen is adsorbed on the surface. On the other hand, for  $pH > 4$  the  $pzfc > pztc$  and at the  $pzfc$ , excess OH is adsorbed on the surface. This is the same situation as in strong alkaline solutions. Comparing the composition of the interphase for different  $pH$  solutions, taking as reference the situation where the free charge is zero, i.e., the  $pzfc$ , we come to the conclusion that the  $pH$  that corresponds to equal amounts of H and OH is around  $pH=3$ . At this  $pH$ , the Pt(111) surface is free of adsorbates and is in equilibrium with water.

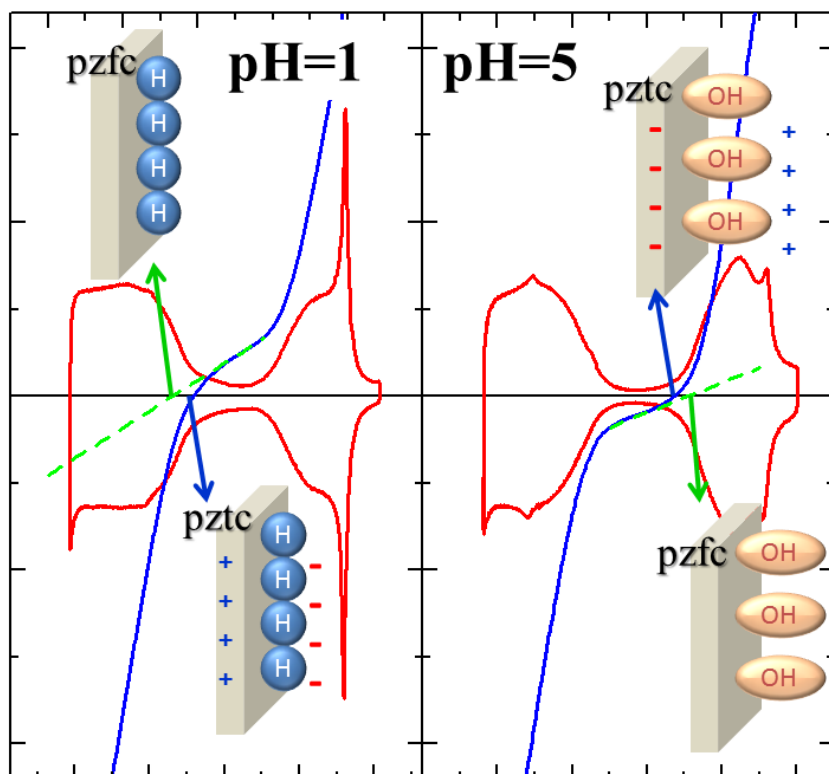
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Graphical abstract

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### Highlights

The interfacial properties of Pt(111) are investigated in neutral pH solutions.

New buffer solutions are selected to avoid specific anion adsorption.

Potential of zero total charge are determined from charge displacement experiments.

Potential of zero free charge are estimated from extrapolation of the charge curves.

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