Hydrogen adsorption on Pt(111) electrodes in basic media. Surface order effects.

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The electrochemical properties of platinum single crystal electrodes has been widely investigated in acidic media. As a result of these studies, criteria dealing with surface cleanliness as well as surface order have been well established. In comparison, the number of studies dealing with this subject in basic solution is quite limited. This is probably related to the difficulties inherent to the use of alkaline electrolytes under clean conditions.

Taking advantage of the experience in working with Pt single crystal electrodes in acid media, the problem of alkaline solutions can be revisited. The aim is to rationalize the observations at the same level of experimental rigor than in acidic solution.

Figure 1 shows the voltammetric profile of a clean Pt(111) electrode in 0.1 M NaOH after flame annealing and cooling down in Ar-H_2 atmosphere. In the potential region below 0.4 V (RHE), the adsorption process can be related to hydrogen adsorption and involved 126 μC cm^{-2} from the potential of zero total charge (0.33 V RHE). The double layer region shows the presence of a small reversible hump at 0.49 V. This feature is only observed with clean and well-ordered electrodes. The adsorption of OH (at potentials above 0.63 V) shifts slightly the peak potential of this process in the negative going scan.

The presence of steps in the Pt(111) surface lead to the apparition on new peaks at higher potential values than those observed in acid media relative to the RHE scale. For surfaces with (110) steps (fig. 2, full line) a quasi-reversible peak at ca. 0.26 V appears. On the other hand, surfaces with (100) steps show a new irreversible peak at 0.42 V in the positive going scan and 0.36 V in the negative going scan (fig. 2, dashed line). The sharp couple of peaks observed in acid media are no longer present.

In some occasions, a peak at 0.56 V in the negative going scan has been reported. We have observed this peak only when aged NaOH solutions are used (fig. 3). If the electrode is cycled in this solution, this new peak grows and a new peak at 0.665 V appears in the positive going scan. Moreover, these peaks grow faster if the potential is stopped in the hydrogen adsorption region. Parallel to the peak growth, hydrogen adsorption below 0.4 V diminishes. Although these peaks have been attributed to OH adsorption on platinum sites, the observed electrochemical behavior resembles that of an irreversible adsorption process of a metal on platinum at trace concentrations. The oxidized form of the metal would remain on the surface as an oxide in alkaline media.

In order to check that hypothesis, irreversible adsorption experiments with several metals were carried out and the voltammetric profile of the modified electrode was then compared to that obtained in figure 3 after long accumulation. For Fe modified electrodes, the final voltammetric profile showed the same peaks as observed in figure 3. Additionally, XPS spectra was acquired after figure 3, and compared to the spectra obtained after figure 1. As figure 4 demonstrates, the characteristic band for Fe 2p3 is detected on the electrode surface when the electrode is transferred to the UHV.

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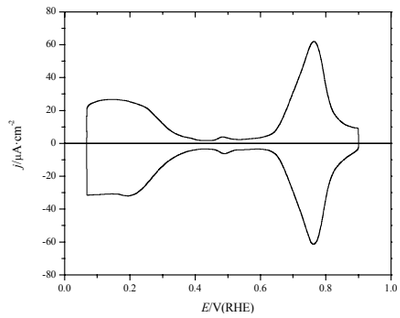

Figure 1. Cyclic voltammogram of a Pt(111) electrode in 0.1 M NaOH. Scan rate: 50 mV s^{-1}.

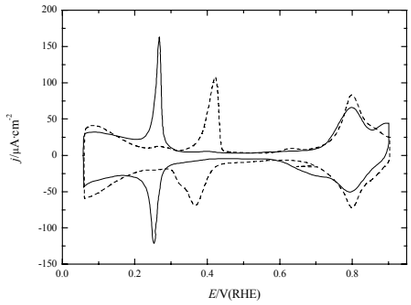

Figure 2. Cyclic voltammogram of a Pt(332) (——) and Pt(533) (- - -) electrodes in 0.1 M NaOH. Scan rate: 50 mV s^{-1}.

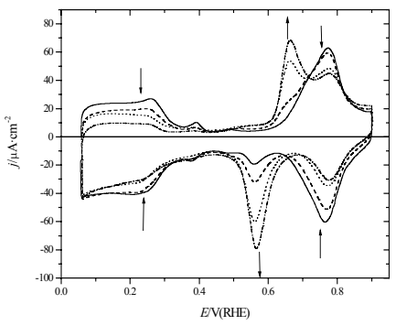

Figure 3. Evolution of the voltammetric profile of the Pt(111) electrode in aged 0.1 M NaOH solution. Scan rate: 50 mV s^{-1}.

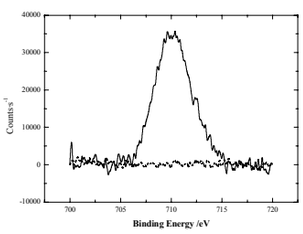

Figure 4. XPS spectra of Fe 2p3 band for the Pt(111) electrode after figure 3 (——) and figure 1 (- - -).