

Self-poisoning reaction from HCOOH on Pt[(n-1)(111)×(110)] and Pt[n(111)H(100)] electrodes modified by irreversibly adsorbed adatoms.

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It is well known that adsorbed CO is formed during formic acid oxidation on platinum electrodes. This adsorbed CO acts as a poison for the oxidation of formic acid through the active intermediate. The formation of CO is a spontaneous process that takes place at open circuit. In order to gain insight into this process, the spontaneous formation of adsorbed CO from HCOOH on different platinum stepped surfaces modified by adatoms has been investigated. CO was formed at open circuit during two minutes from a solution containing formic acid in order to achieve the maximum poison coverage. This coverage was evaluated from the CO stripping charge obtained in 0.5 M H₂SO₄.

As starting surfaces, Pt(775) and Pt(755) electrodes, which have a 6 atom-wide terrace and a (110) and (100) step respectively, were selected. These surfaces were chosen on basis of the results of the same poisoning reaction on Pt(111) [1]. Those results seem to indicate that bismuth was able to inhibit poison formation on the Pt(111) at a distance of 6-8 atoms from the deposited bismuth. The effect of Bi, Te, As and Se modified electrodes for the poison formation from formic acid was investigated in order to understand the role of the adatom and the step symmetry in the poison formation reaction.

Two different limiting behaviors were obtained. In the first one, poison formation decays linearly with the adatom coverage and becomes negligible at high adatom coverage (figure 1). In the second one, a sharp decrease of the poison coverage is observed only when the adatom begins to adsorb on the terrace sites after all the step sites have been covered (figure 2). For these cases, adsorption on step sites has not significant effect on the poison formation reaction.

For Bi or Te adsorbed on the steps surfaces, these two different behaviors were obtained depending on the terrace width. Thus, the surfaces having narrow terraces displayed a behavior similar to that depicted in figure 1, whereas the behavior of surfaces with wide terraces was similar to that showed in figure 2. In the case of the most electronegative adatom, Se, a linear decrease in poisoning is always observed, irrespectively of the terrace width.

The case of As deserves particular attention. In the case of Pt [(n-1)(111)×(110)] electrodes a behavior similar to that described for Bi and Te was observed, i.e., surfaces with long terraces behave like the surface in figure 2. When the Pt[n(111)×(100)] electrodes were used, however, the behavior of the As modified resembles that observed in the case of Se.

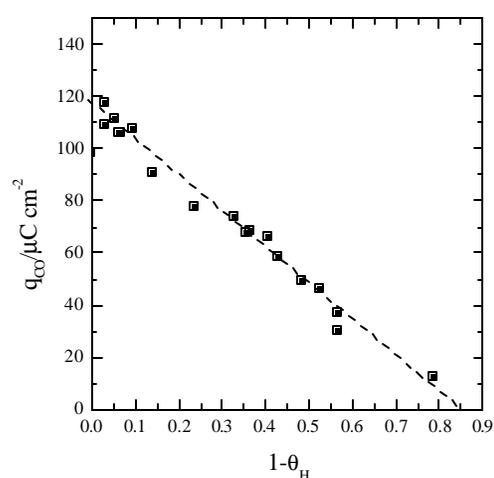
The different behavior may be related to the poison formation on the step sites and the possibility of step decoration in relation to the adatom electronegativity. Thus, it can be proposed that poison formation only takes place on the step sites [2]. Those adatoms that deposit preferentially on the step site will inhibit the poison formation sharply once all the step sites have been covered. The possibility of step decoration has been related to the electronegativity of the adatom with respect to the surface

[3]. The adatoms that have lower electronegativity than platinum, i.e., Bi and Te, are able to decorate the surface, whereas Se, which has higher electronegativity than platinum, does not preferentially decorate the step. For As, step decoration is easily achieved on (110) steps, but not on (100) steps.

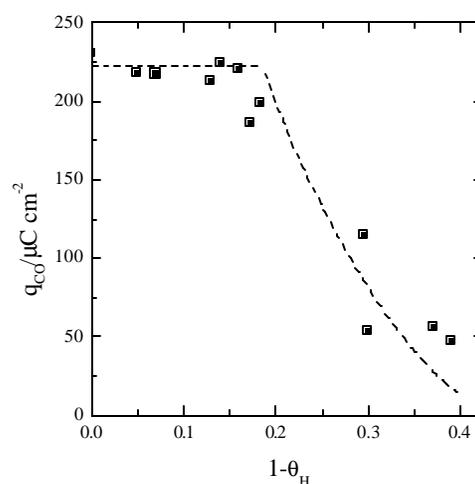
References.

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Figures.



1. CO stripping charge obtained for poison formation from formic acid for the Pt(776) electrode modified with Se.



2. CO stripping charge obtained for poison formation from formic acid for the Pt(554) electrode modified with Te.