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Oxidation of ethanol and its derivatives on well defined Pt single crystal electrodes vicinal to Pt(111): a comparative study.

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The oxidation of ethanol (EtOH) at Pt(111) electrodes is dominated by the 4e path leading to acetic acid. The inclusion of surface defects such as those present of deliberately stepped surfaces leads to an increase of the reactivity towards the most desirable 12e path leading to carbon dioxide as final product. Interestingly, this path is also favored when the methyl group is more oxidized as in the case of ethylene glycol (EG). In this latter case, earlier studies [1] showed that the EG molecule spontaneously decomposes to CO on Pt(111) electrodes, thus showing a more effective breaking of the C-C bond. As a result, the current density in the positive-going voltammetric sweep is considerably enhanced (figure 1). Some trends in reactivity can be envisaged when other derivative molecules are compared at well ordered electrodes. This strategy was used in the past [2,3], but the improvement in the electrode pretreatment and the overall information available on the subject suggests that the relevant information is still missing.

The inclusion of steps (a model for surface defects) also contributes to the modification of surface reactivity towards these molecules. For example, EG oxidizes at stepped surfaces vicinal to Pt(111) such as those having step terrace notations Pt(S)[(n-1)(111)x(110)], with Miller indices Pt(n,n, n-2), or Pt(S)[n(111)x(100)] with Miller indices Pt(n+1,n-1,n-1). It is remarkable that the step symmetry induces reactivity changes on electrodes having relatively long terraces. In this respect, figure 2 shows that (110) steps are more effective to increase the overall reactivity than (100) steps.

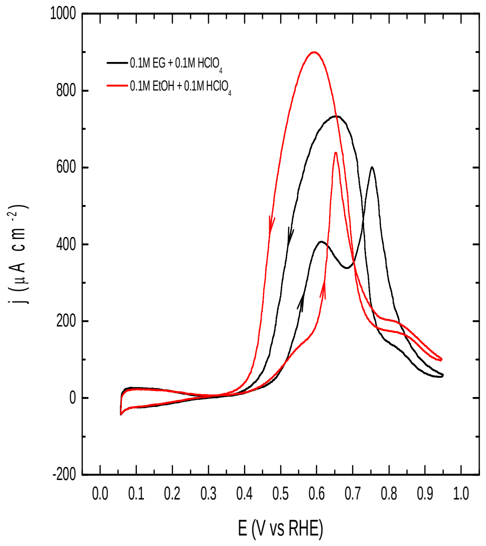

Figure 1. Oxidation of 0.1 M EtOH and 0.1 M EG at Pt(111); 0.1 M perchloric acid; 50 mV/s.

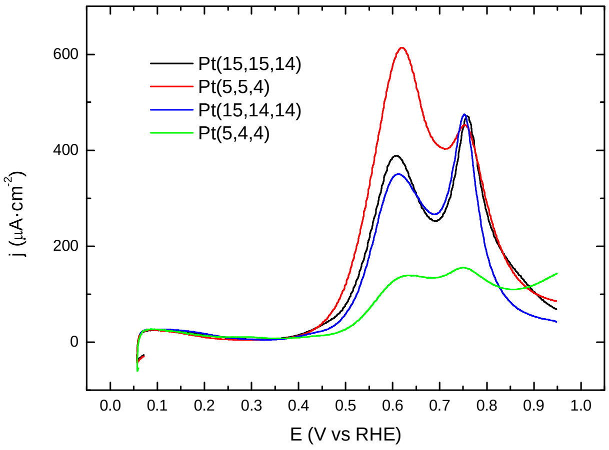

Figure 2. Comparison of EG oxidation at different stepped surfaces vicinal to Pt(111) (positive-going sweeps); 0.1 M perchloric acid; 50 mV/s.

References

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