Selective Electrocatalysis of Ammonia Oxidation on Pt(100) Sites in Alkaline Medium

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The electrochemical oxidation of NH_3 has long received attention and different mechanisms for its oxidation on platinized Pt have been proposed [1,2,3].

Figure 1 shows the oxidation of NH_3 in a 0.1 M NaOH solution on a polyoriented single crystal platinum bead for which extensive surface oxidation has been avoided (blank solution dotted line). It is remarkable that the main voltammetric peak has a well-marked shoulder at 0.57 V, suggesting that the NH_3 oxidation could be a structure-sensitive process.

In order to test this possibility, experiments were carried out by using well-defined single crystal electrodes. In a first attempt, platinum electrodes oriented following the three basal plane directions were chosen. Figure 2 shows clearly that ammonia oxidation is a structure-sensitive process the activity of the three electrodes being significantly different. Whereas Pt(100) shows a well-defined single oxidation peak at 0.57 V, i.e. at the same potential that of the shoulder for the polyoriented single crystal bead, almost negligible oxidation processes were observed for the other two electrodes.

It seems straightforward that the shoulder in figure 1 corresponds to the oxidation of the ammonia on the Pt(100) facets present on the surface of the polyoriented electrode.

In order to investigate if the ammonia oxidation is especially sensitive to the bidimensional arrangement of (100) surface domains, despite the small size of the molecule, stepped surfaces containing (100) terraces and (111) monoatomic steps were used. This orientation of the step was selected because the corresponding basal plane was more active than that of the (110) plane.

Voltammograms for a 0.1 M NaOH solution are shown in figure 3 for the different stepped electrodes.

The oxidation of ammonia in three of these stepped surfaces is shown in figure 4, which also includes the oxidation on Pt(100) basal plane for sake of comparison. It can be seen that ammonia oxidation is very sensitive to the width of (100) domains. The main peak current density diminishes and the peak potential shifts to more positive potential values as the terrace length diminishes. This means that the main peak of ammonia on polyoriented platinum may be explained by taking into account the contribution from small (100) domains on the surface. As a conclusion, the oxidation of ammonia on platinum is a structure sensitive process that takes place almost exclusively on Pt(100) sites. The electrocatalytic process is amazingly dependent on the size of the (100) terraces.

References

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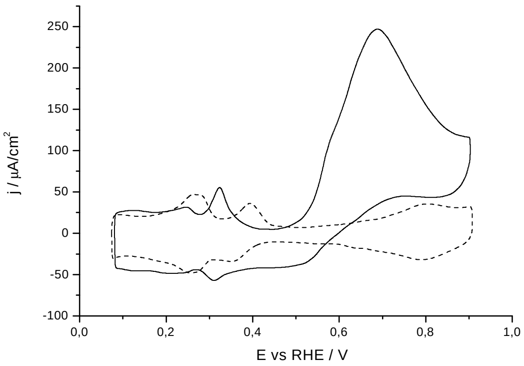

Fig. 1: Voltammetric profiles of a polycrystalline Pt electrode in 0.1 M NaOH in absence (doted line) and presence (full line) of 10^{-3} M NH_3. Scan rate 50 mV· s^{-1}

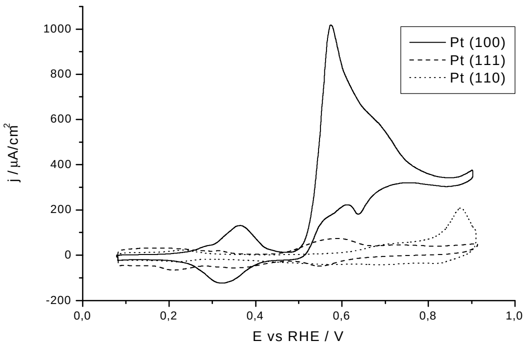

Fig. 2. Voltammetric profiles of Pt(100), Pt (111) and Pt(110) electrodes in 0.1 M NaOH + 10^{-3} M NH_3. Scan rate 50 mV· s^{-1}

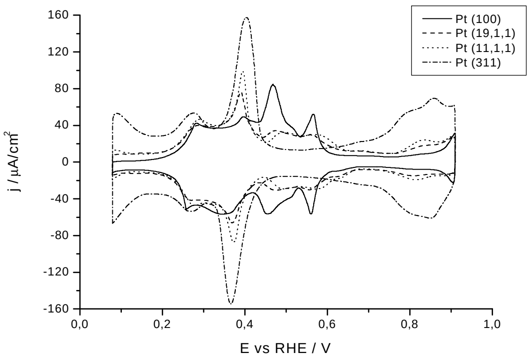

Fig. 3. Voltammetric profiles of Pt(100), Pt(19,1,1), Pt(11,1,1) and Pt(311) in 0.1 M NaOH. Scan rate 50 mV· s^{-1}

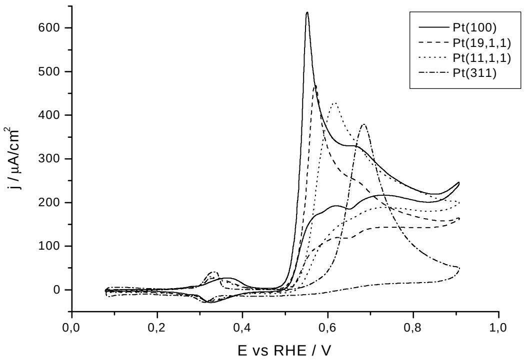

Fig. 4. Voltammetric profiles of Pt(100), Pt(19,1,1), Pt(11,1,1) and Pt(311) in 0.1 M NaOH and 10^{-3} M NH_3. Scan rate 10 mV· s^{-1}