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SHORT COMMUNICATION

Incidentally occurring cathodic effects in the voltammetric behaviour of glass-sealed electrodes

W. VISSCHER

Laboratory for Electrochemistry, Eindhoven University of Technology, Postbox 513, Eindhoven (The Netherlands)

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We wish to draw attention to spurious effects with glass-sealed electrodes in order to avoid misinterpretations and, moreover, to present means to avoid these effects.

It is a very common technique to prepare Pt-electrodes by sealing Pt-wire into glass tubing. When these types of electrodes are immersed into a solution, spurious potentials can sometimes be measured^{1,2}. During our study of the anodization of Pt^{3,4}, we observed that at high c.d. or potentials the sealing of Pt in glass could sometimes affect the voltammograms recorded for an oxidized electrode. Under these conditions the *anodic* voltammogram could show a cathodic current in the double layer region. It is very likely that this cathodic current is also present in the cathodic voltammogram, but here it cannot be proven as such, since the current over the whole potential range of the cathodic voltammogram is cathodic. This can easily introduce possible errors in the determination of hydrogen or oxygen coverage.

Experimental

All experiments were carried out in a 3-compartment cell, with a Pt-counter electrode and a platinum–hydrogen reference electrode in the same solution (RHE). The working electrode consisted of a smooth Pt-foil (2 cm²) spotwelded to Pt-wire and sealed in pyrex glass tubing. Before use the electrode system was heated in a flame and rinsed with twice distilled water. The potential was controlled with a Wenking potentiostat which was programmed with a Hewlett-Packard function generator (3300 A). The voltammogram was recorded on a Philips XY recorder. The electrolyte was prepared from p.a. H₂SO₄ (Merck), and twice distilled water; the solution was degassed with purified N₂.

Results

Figure 1 gives the voltammogram of an oxidized electrode. This electrode was oxidized for 15 min at 2.3 V, thereafter the potential was set at 1.5 V for 5 min and oxygen was removed by passing N₂ through the solution. Then a potential sweep of 29 mV s⁻¹ is applied from 1.5 V to 0.05 V and back.

Fig. 1. Voltammogram of Pt-electrode after 15 min oxidation at 2.3 V *vs.* RHE. First the cathodic sweep is recorded, immediately followed by the anodic sweep. Sweep rate 29 mV s^{-1} ; electrolyte $3 \text{ M H}_2\text{SO}_4$.

Fig. 2. Voltammogram of Pt-electrode during continuous cycling between 0.05 V and 1.5 V *vs.* RHE; electrolyte $3 \text{ M H}_2\text{SO}_4$.

The voltammogram shows that during the reverse sweep a cathodic current is recorded in the double layer region. For comparison Fig. 2 is given, which shows the characteristic voltammogram of an activated Pt electrode, obtained after cycling a few times between 0.05 and 1.5 V. Both voltammograms are taken at the same electrode in $3 \text{ M H}_2\text{SO}_4$.

A similar behaviour as in Fig. 1 is observed for an electrode of the same type,

Fig. 3. Voltammogram of Pt-electrode recorded after oxidation for 1 h at 100 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$. The first reduction sweep (curve 1a) shows both the oxide I and oxide II reduction peak. The reduction sweeps of curves 2 and 3 subsequently after the first cathodic and anodic sweep, shows only the oxide I reduction peak shifted to more anodic potential. Because of the length of the oxide II peak, curve 1a was recorded on a smaller scale.

oxidized with 100 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$. This oxidation was carried out in a separate cell; after the oxidation the electrode was transferred to the measuring cell, the electrolyte ($1 \text{ M H}_2\text{SO}_4$) was degassed and the voltammogram recorded from 1.5 V to 0.05 V .

This oxidation method yields 2 oxygen reduction peaks, oxide I and II; it is seen in Fig. 3 that here again a cathodic current is observed in the double layer region during the reverse sweep. When the cycling is repeated, this cathodic current gradually decreases (*cf.* curves 2 and 3).

This phenomenon of a cathodic current during the anodic sweep is not caused by an impurity or dissolved O_2 . After repeated careful purifications of the electrolyte the cathodic current could still be observed. This behaviour is shown by some electrodes only.

Two selected electrodes were oxidized with 100 mA cm^{-2} ; the voltammogram of electrode (A) showed the cathodic effect in the double layer region, whereas for electrode B no cathodic current was observed, though both electrodes were measured in the same electrolyte. The Pt foil of electrode A was now cut off and spotwelded to the Pt foil of electrode B. This system was again oxidized with 100 mA cm^{-2} . The voltammogram recorded as above did not show a cathodic current in the anodic sweep. Electrodes consisting of Pt wire with a spotwelded foil without a glass

Fig. 4. Diagram of the electrode construction which avoids electrolyte contact with the Pt-glass seal.

support did not show, after oxidation with 100 mA cm^{-2} , the cathodic current phenomenon. This demonstrated convincingly that the cathodic current phenomenon is connected with the glass sealing of Pt.

We then tried to seal the Pt very carefully in the glass. Several seals were made, varying from a long tapered seal to a seal with as small a glass-Pt contact as possible; both soft and pyrex glass were used. It appeared that the cathodic current phenomenon became more pronounced with increased sealing of Pt-glass. The Pt-glass contact surface should therefore be as small as possible, on the other hand the sealing should be solution-tight. This finally led to a construction (Fig. 4) in which the Pt-wire is sealed in a glass capillary at a point which will be above the solution; N_2 can be passed through the system such that no solution enters the capillary. With this type of electrode construction the cathodic current phenomenon is completely absent and the typical small constant anodic current is obtained in the double layer region during the anodic sweep.

Discussion

A considerable cathodic current in the double layer region was also observed by Balej and Spalek⁵ for Pt-electrodes oxidized at high anodic potentials. They attribute this behaviour to diffusion of oxygen from the bulk of platinum to the surface. Our results however have shown that the phenomenon is due to the Pt-glass-sealing. (Balej and Spalek carried out their experiments with Pt wire electrodes which were sealed at both ends in glass; hence the very pronounced cathodic current effect.) The cathodic current is most likely caused by O_2 because the entire voltammogram at potentials more negative than 0.7 V is affected.

On the basis of these observations we now suppose that, in the case of appearance of the cathodic effect, oxygen evolution has taken place in minute cracks in the glass sealing developed by strain effects during the anodization procedure. An applied cathodic sweep must then show the cathodic effect, which gradually

diminishes during subsequent sweeps. It is likely that this phenomenon will occur with other metal-glass electrodes, *e.g.* Au, Pd, as well.

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