ADSORPTION OF SULFUR ON THE PLATINUM ELECTRODE SURFACE IN ONE OR MORE LAYERS

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Received June 16, 1999
Accepted January 6, 2000

The influence of the H_2S concentration on the charge required for oxidation of the adsorbed sulfur and on the nonstationary currents passing through the electrode was studied while hydrogen sulfide was introduced into the solution. At higher concentrations, more sulfur atoms are adsorbed on one platinum surface atom. Upon decreasing the concentration one atom of sulfur per one surface atom results and the number of sulfur atoms blocking two surface atoms starts growing gradually.

Key words: Nonstationary currents; Sulfane; Sulfur; Electrooxidation; Platinum; Electrochemistry.

In the past years much attention was paid to the adsorption of sulfur on the surface of a platinum electrode[1–7]. The results of measurements of some authors differ at some points. When measuring the adsorption in the H_2S solution, Loučka[3] found out that sulfur formed a monolayer on the surface of the platinum electrode. For the adsorption in the double-layer region, it was discovered that the anodic nonstationary currents corresponding to the splitting of both the atoms of hydrogen were passing through the electrode. Two atoms of hydrogen and one atom of adsorbed sulfur pertained to one surface atom of the platinum electrode. On the other hand, the charge used for oxidation of the adsorption layer formed in this way corresponded to six electrons per one surface atom of the platinum electrode (6 e.p.s). If we assume that the adsorbed sulfur is oxidized to sulfate (or hydrogensulfate) anions, the results give evidence that a monolayer of the adsorbed sulfur is formed on the surface of the platinum electrode. Jayaram *et al.*[4], however, found that for lower degrees of the electrode coverage by adsorbed sulfur ($\Theta_s < 0.9$) the charge used for oxidation of the adsorbed sulfur corresponds to the value of 3.8 e.p.s. For higher degrees of surface coverage ($\Theta_s > 0.9$) the charge for the oxidation grows dramatically. Jayaram *et al.*[4] assumed that for a lower degree of surface coverage, 30% of adsorbed sulfur atoms bind to one surface atom and remaining 70% bind to two surface atoms of the platinum electrode. If the surface coverage is high enough ($\Theta_s > 0.9$), more layers of adsorbed sulfur are formed. Horanyi and Rizmayer[5] measured the adsorption of sulfur in H_2S solution on the platinum electrode using sulfur isotope ^{35}S. Their results also proved that the amount of adsorbed sulfur is higher than the monolayer. They also found that sulfur can desorb from the surface of the electrode. The main difference between the above mentioned published data is in the concentrations used for the experiments. Jayaram *et al.*[4] and Horanyi and Rizmayer[5] used a higher concentration (0.01 mol l^{-1}), while Loučka[3] used a lower concentration (10^{-3}–10^{-4} mol l^{-1}). A similar influence of concentration was observed in the adsorption of thiosulfate on the platinum electrode[8], when a monolayer of the adsorbed product was formed at lower concentrations, while more layers were formed at higher concentrations.

To verify the assumption of the influence of H_2S concentration on the adsorption of sulfur on platinum surface, the charge consumed in the oxidation of the adsorbed product was monitored along with the nonstationary currents passing through the electrode after introducing H_2S into the solution.

EXPERIMENTAL

When measuring the Q_{ox} charge, the adsorption was performed in the solution of H_2S in double distilled water while the electric circuit was disconnected. Prior to each measurements, the electrode was activated by applying cathodic and anodic cycles between E = 1.5 and 0 V at a rate of 0.5 V s^{-1} for 20 min. The electrode activity was estimated according to the charge needed for the oxidation of adsorbed hydrogen before and after the measurement. During the measurement, the activity never deviated from the average value more than by 5%. When changing the potential in the positive direction, the potential was stopped at a preselected value E_A, the electrode was removed from the vessel, rinsed thoroughly with oxygen-free double distilled water, and immersed in the solution examined, which had also been deoxygenated by nitrogen. In this solution the electrode was left for the adsorption time t_A. Subsequently, the electrode was rinsed thoroughly with approximately 20 ml of oxygen-free double distilled water and engaged in the electric circuit at the potential E_A, at which it was kept for the desorption time t_D. During the desorption the solution was stirred continuously except for the last 15 s. The time of adsorption was 20 min, the time of desorption 1 min and the potential E_A was 0.6 V *vs* hydrogen electrode in 0.5 M H_2SO_4. Subsequently, the electrode potential was changed to 0 V at a rate 0.2 V s^{-1} (cycle 0) and further cycled periodically between 0 and 1.5 V (cycles 1, 2, 3, ...) at the same rate. For each n-th cycle the following charges were determined:

– The charge consumed in oxidation of the adsorbed sulfur and in formation of the (surface) oxide at the electrode between potentials 0.4 and 1.5 V (Q_1^n);

– The charge consumed in reduction of the oxide between potentials 1.5 and 0.4 V (Q_2^n);

– The charge consumed in the adsorption of hydrogen (plus the charge for an irreversible cathodic process[3]) between potentials 0.4 and 0.0 V (Q_3^n);

– The charge consumed for the desorption of hydrogen between potentials 0.0 and 0.4 V (Q_4^n).

The total charge Q_{ox} necessary for complete oxidation of the adsorbed sulfur[3] was obtained from charge balance for all cycles (7–15 cycles are sufficient for complete removal by oxidation of the adsorbed sulfur) as

$$Q_{ox} = \sum_{n=1}^{k} \left[\left(Q_1^n - Q_2^n \right) - \left(Q_3^n - Q_4^{n+1} \right) \right] .$$

The oxidation was carried out in 0.5 M H_2SO_4. Details of the measurement procedures, instruments and the electrodes used are described in ref.[8], chemicals used for the experiment are listed in ref.[1]. The procedure for measuring the nonstationary currents is explained in a previous paper[3]. The nonstationary currents were integrated and the charge Q_n, corresponding to the atoms of hydrogen split during adsorption of H_2S according to the following equation

$$\mathrm{Pt} + x\ \mathrm{H_2S} = \mathrm{Pt{-}[S_{ads}]}_x + 2x\ \mathrm{H^+} + 2x\ \mathrm{e}$$

was obtained. The nonstationary currents were measured in 0.5 M H_2SO_4 in the double layer region (0.5 V *vs* hydrogen electrode in the same solution). The degree of coverage of the electrode with adsorbed sulfur was evaluated from lowered amount of adsorbed hydrogen[3].

RESULTS AND DISCUSSION

The dependence of the charge Q_n on the concentration of H_2S is shown in Fig. 1. At all concentrations we achieved the total coverage of all surface atoms of the platinum electrode by adsorbed sulfur. The nonstationary currents at concentrations lower than $3 \cdot 10^{-4}$ mol l^{-1} are too small to be measured with satisfactory accuracy. For the H_2S concentration $3 \cdot 10^{-4}$ mol l^{-1}, the charge Q_n = 0.7418 mC. With regard to the size of the charge corresponding to the amount of hydrogen adsorbed on the clean electrode surface Q_H^0 = 0.3995 mC. The value indicates 1.86 electrons per one surface atom. Thus, at these concentrations, approximately one atom of sulfur is adsorbed per one surface atom. At higher concentrations, Q_n increases, the amount of electrons corresponding to one surface atom becomes larger than 2 and more atoms of sulfur belong to one surface atom. For the concentration of 10^{-2} M H_2S, the value of Q_n is closer to 1.30 mC, which corresponds to 3.25 electrons per one surface atom and approximately to 1.5 monolayers of adsorbed sulfur, identically with the measurements carried out by Horanyi and Rizmayer[5].

The dependence of the charge Q_{ox} consumed in the oxidation of adsorbed sulfur on the H_2S concentration (Fig. 2) shows that Q_{ox} grows linearly with the growing concentration. For the H_2S concentration $3 \cdot 10^{-4}$ mol l^{-1} and higher, the surface coverage by the adsorbed sulfur, $\Theta_s = 1$. For lower concentrations the coverage is not complete and Q_{ox} is calculated for full coverage. For the concentration $3 \cdot 10^{-4}$ mol l^{-1} $Q_{ox} = 2.81$ mC, which corresponds to 7 e.p.s. If we assume that the adsorbed sulfur is oxidized to sulfate (or hydrogensulfate) ions, the amount of adsorbed sulfur is close to a monolayer. For higher concentrations, the Q_{ox} charge grows and for this reason the amount of sulfur atoms per one surface atom also grows. For the concentration 10^{-2} mol l^{-1} the charge $Q_{ox} = 3.664$ mC (or 9.17 e.p.s.), which, in agreement with the measurements carried out by Horanyi and Rizmayer[5], corresponds to approximately 1.5 monolayers of adsorbed sulfur. For lower concentrations, Q_{ox} decreases below the value corresponding 6 e.p.s. For the concentration of 10^{-5} M H_2S the measured charge Q_{ox} was 3.98 e.p.s. The lower the concentration, the higher the number of sulfur atoms blocking two surface atoms, which results in a decrease in the number of sulfur atoms which block one surface atom. Having an average of less than one atom of sulfur per one surface atom, the Q_n value expressed in e.p.s. should be lower than two. The occupying of two surface atoms with one atom of adsorbed sulfur occurs at concentrations lower than

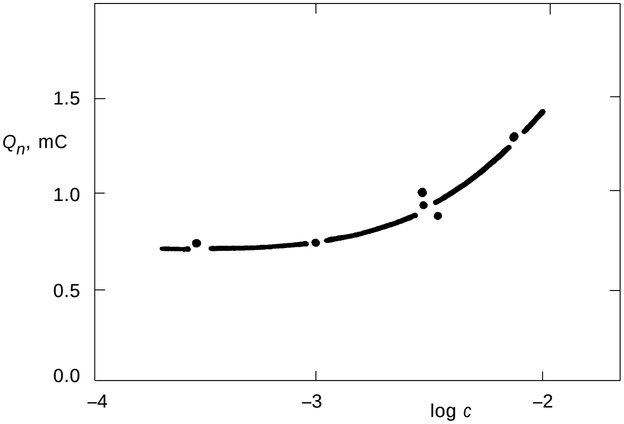

FIG. 1
The dependence of the charge Q_n on the logarithm of resulting H_2S concentration (c in mol l^{-1}) in 0.5 M H_2SO_4. The charge Q_n was obtained by integration of nonstationary currents passing through the platinum electrode on introducing the solution H_2S into the solution. The potential of the platinum electrode was 0.5 V *vs* hydrogen electrode in 0.5 M H_2SO_4

$3 \cdot 10^{-4}$ mol l^{-1}. Measurements of nonstationary currents at these concentrations, however, are not sufficiently accurate.

The fact that some atoms of adsorbed sulfur block one surface atom and other ones block two surface atoms is discussed by Jayaram *et al.*[4], although these authors used different experimental methods.

The decrease in the Q_{ox} to value corresponding to less than 6 e.p.s. at lower concentrations can also be explained by the ability of the adsorbed sulfur to be oxidized to a compound with an oxidation number lower than 6. The compound could be for example dithionate (oxidation number 5). Korzeniewsky *et al.*[9] refer to the occurrence of dithionate in oxidation of the adsorbed sulfur dioxide. The lowest observed Q_{ox} corresponds to 3.8 e.p.s. (Fig. 2) indicating a compound with the oxidation number lower than 4, which seems unlikely.

For these reasons the above results most probably give the evidence that at higher H_2S concentration more layers of adsorbed sulfur are formed, or that one surface atom is occupied by more atoms of sulfur. With the decreasing concentration a monolayer of adsorbed sulfur (one atom of sulfur per one surface atom) is formed at first, the surface coverage of the electrode decreases gradually and the number of adsorbed sulfur atoms which block two surface atoms increases.

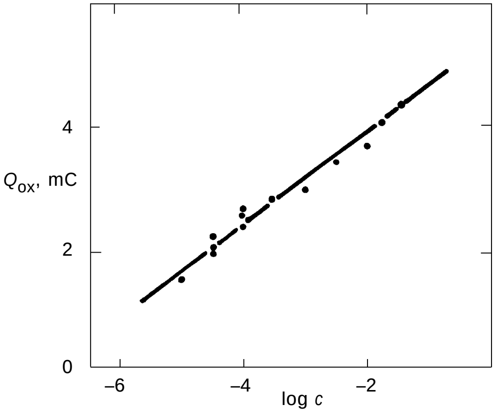

FIG. 2

The dependence of the charge Q_{ox} consumed in the oxidation of adsorbed sulfur on the logarithm of H_2S concentration (*c* in mol l^{-1}). The adsorption was carried out in the H_2S solution in double distilled water while the electric circuit was disconnected. The adsorption and desorption times were t_A = 20 min and t_D = 1 min, respectively. The adsorption potential E_A = 0.6 V *vs* hydrogen electrode in 0.5 M H_2SO_4

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