

The Inhibition of the Electrochemical Oxidation of Glucose at Platinum at pH = 7.4 by Chloride Ions

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In their attempt to develop an implantable fuel cell as power source for an artificial heart or a cardiac pacemaker, several workers¹⁻³ have studied the electrochemical oxidation of glucose on platinum in neutral media. Their experiments were carried out either in physiological solutions^{2,3} or in phosphate or carbonate buffers,¹ where high ionic strengths were obtained by addition of KCl. Glucose showed very little activity in all cases. It will be shown in this communication that chloride ions have a strong inhibitory effect on the electrochemical oxidation of glucose, so the low activity found in the experiments reported was probably caused by the chloride ions in the buffers used.

Experimental. The experiments were carried out at pH=7.4 in a 0.2 M phosphate buffer. The ionic strength was set to 1.0 M by addition of Na₂SO₄. All chemicals were analytical grade from Riedel de Haën, and the water was redistilled from an alkaline KMnO₄ solution. The buffer solution is equivalent to the one used by Rao and Drake¹ in their investigation of the electrooxidation of glucose, except that the KCl is replaced by Na₂SO₄. The temperature was maintained at 25°C by means of a thermostat, and the solution was degassed by bubbling with oxygenfree nitrogen. The electrodes used were either a platinum disk electrode or a platinum wire in the form of a flat spiral of diameter 0.6 cm. The disk electrode was made of a 0.5 cm long platinum cylindrical stud with a diameter of 0.5 cm soldered to a stainless steel rod. The electrode was then covered with a PTFE tube of 1.2 cm external diameter, which was heated to 160°C before it was press fitted over the cold electrode. The end of the electrode was ground with water proof silicon carbide paper and polished with diamond paste. The platinum spiral electrode was made of a piece of 0.7 mm diameter wire. The wire except the spiral was covered with a piece of shrinkable PTFE tube. The counter

electrode was a platinum spiral placed in a pyrex gas dispenser (Sovirel 4.853-2). The sintered glass disk in the dispenser was placed opposite the exposed area of the electrodes. When the disk electrode was used, the reference electrode was a dynamic Pt-black hydrogen electrode loaded with 100 μA/cm² (geometrical area) and placed in a Lugin capillary, while a standard mercurous sulfate electrode (Radiometer type K 601) was placed at the edge of the platinum spiral electrode. The ohmic drop was determined by measuring the impedance at 1 kHz and 3 kHz. It was ca. 4 ohm with the disk electrode and ca. 15 ohm with the spiral electrode. The potentiostat was made at the Fysisk-Kemisk Institut by use of an operational amplifier (Motorola MC 1433) with an input bias current of 0.2 μA. The signal generator was an Exact Waveform Generator type 505B. The current was measured as the potential drop across a resistance in the counter electrode circuit, and the current potential curve was recorded at an X-Y recorder (Omnigraphic 2000 from Houston Instruments). The electrodes were pretreated with a periodic triangular sweep between 0.05 and 1.5 V vs. a standard hydrogen electrode in the same solution (NHE) with a sweep rate of 0.3 V/sec until reproducibility was obtained. The electrode area was determined coulombmetrically from the hydrogen coverage using a sweep rate of 0.3 V/sec. The current potential curve was recorded at 0.3 V/sec and 0.03 V/sec between 0.05 V and 1.5 V vs. NHE in a 0.25 M glucose solution with chloride concentrations between 0 and 5 × 10⁻² M. Both electrode types gave similar results, and the curves were reproducible after a few sweeps.

Results. Current potential curves for buffer solutions, which were 0.25 M in glucose and from 5 × 10⁻⁴ M to 5 × 10⁻² M in chloride, are shown in Figs. 1 to 3. The curves were corrected for double layer charging as well as formation and removal of the Pt-H layer by subtracting the values obtained during the sweep made in the pure buffer solution. This procedure introduces a small error, because the correction is dependent on glucose and chloride concentrations. The effect of glucose is not known, but sweeps made on glucose in 1 M H₂SO₄ (where glucose is not oxidized between 0 V and 0.5 V vs. NHE) showed that the effect is small in that medium. The effect of the chloride ions has been checked by making sweeps in a buffer solution which was 0.5 M in KCl. The chloride ions lowered the hydrogen peaks

between 0.25 V and 0.4 V *vs.* NHE, but the error should not be greater than approx. 20 % with the highest chloride concentration. It is seen from the curves in the Figs. 1 to 3 that glucose (or intermediary products) is oxidized by two mechanisms, the associated current peaks of which are separated in the anodic scan ($dV/dt > 0$) in Fig. 1 but overlap in the cathodic scans

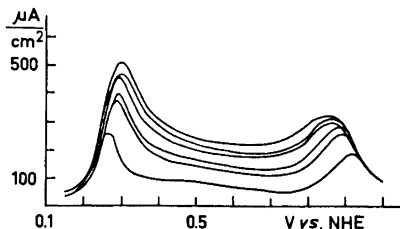


Fig. 1. The oxidation of glucose on platinum in phosphate buffer at pH=7.4 and different chloride concentrations: 0 (largest current), 5×10^{-4} , 10^{-3} , 5×10^{-3} , 10^{-2} , and 5×10^{-2} M (smallest current). Anodic scan. Sweep rate: 0.3 V/sec.

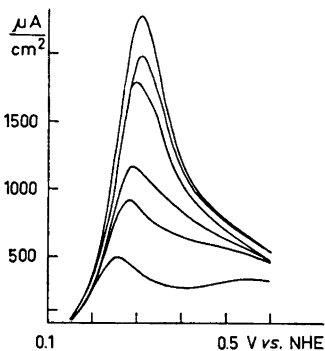


Fig. 2. As Fig. 1. Cathodic scan. Sweep rate: 0.3 V/sec.

($dV/dt < 0$) in Figs. 2 and 3. It can also be seen that the peaks associated with the two mechanisms have differing sweep rate dependencies. There is a third current peak (not shown in Fig. 1) in the anodic scan between 1.1 V and 1.5 V *vs.* NHE, but this is almost unaffected by the chloride ions. The nature of the current peaks will be discussed in a later communication. The effect of the chloride ions is seen to dis-

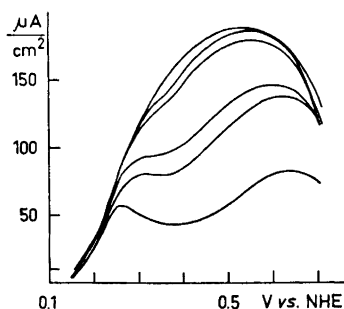


Fig. 3. As Fig. 1. Cathodic scan. Sweep rate: 0.03 V/sec.

appear at 0.95 to 1.0 V *vs.* NHE in the anodic scan, where they probably are removed during the formation of the Pt-O layer. The Pt-O layer is reduced in the cathodic scan from 0.9 V to 0.4 *vs.* NHE.

The dependence of the current on the chloride concentration can be used to find the chloride adsorption isotherms, if it is assumed that the current at a given potential is proportional to the electrode area not covered with chloride ions:

$$i = i_0(1 - \theta)$$

where θ is the surface coverage of chloride ions, and i_0 is the current obtained for the chloride concentration $c_{\text{Cl}^-} = 0$.

Rearrangement gives:

$$\theta = 1 - i/i_0$$

The adsorption isotherm $\theta = f(c_{\text{Cl}^-})$ can be found by plotting $1 - i/i_0$ against different functions of c_{Cl^-} at constant potential.

A plot of $1/\theta$ against $1/c_{\text{Cl}^-}$ corresponding to Langmuir adsorption did not give a straight line, whereas a plot of θ against $\log c_{\text{Cl}^-}$ did give reasonable straight lines, indicating that chloride adsorbs through a logarithmic isotherm: $Kc_{\text{Cl}^-} = e^{(b\theta)}$ or

$$\theta = \frac{2.303}{b} \log K + \frac{2.303}{b} \log c_{\text{Cl}^-}$$

where K is the absorption constant and b an interaction parameter. The slope of such lines gives b and the extrapolation to $\theta = 0$ gives $K = 1/c_{\text{Cl}^-}(\theta = 0)$. Plots of θ (calculated from the curves in Figs. 1, 2, and 3) *vs.* $\log c_{\text{Cl}^-}$ at 0.275, 0.375, and 0.500 V *vs.* NHE are shown in Fig. 4 (a-c), and the corresponding b values and K values are shown in Table 1. The results show,

Table 1. Adsorption constant K and interaction parameter b corresponding to a logarithmic isotherm for the adsorption of chloride on platinum in phosphate buffer at pH=7.4. Subscripts c and a refer to cathodic and anodic scans.

$\pi - \pi_{\text{NHE}}$ V	dV/dt V/sec	b_c	b_a	K_c l/mol	K_a l/mol
0.275	0.3	6.2	11	2.2×10^5	2.0×10^5
	0.03	9.6		1.4×10^5	
0.375	0.3	6.1	7.9	2.9×10^5	3.3×10^5
	0.03	6.6		2.3×10^5	
0.500	0.3	13	9.2	3.3×10^5	4.3×10^5
	0.03	6.8		1.5×10^5	

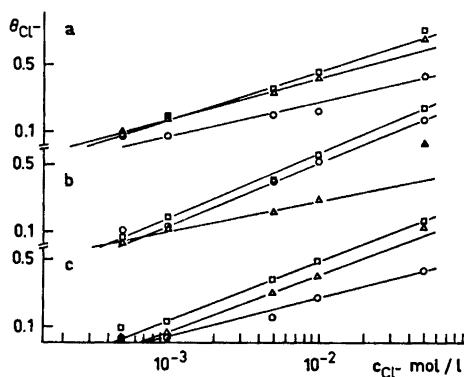


Fig. 4. a. The surface coverage of chloride as function of $\log c_{\text{Cl}^-}$ at different potentials. \circ ~ 0.275 V, \square ~ 0.375 V and \triangle ~ 0.500 V vs. NHE. Anodic scan. Sweep rate: 0.3 V/sec. b. As Fig. 4a. Cathodic scan. Sweep rate: 0.3 V/sec. c. As Fig. 4a. Cathodic scan. Sweep rate: 0.03 V/sec.

that the chloride ion adsorption is higher at 0.375 V than at 0.275 V vs. NHE in all cases. These findings are in agreement with the results obtained by Horanyi, Solt and Nagy⁴ for the chloride adsorption on

platinum in 1 N HClO₄ measured with a tracer technique.

Although their results indicate adsorption through a logarithmic isotherm, an increase in adsorption with potential and b values close to the values found in this work, the K values were of the order of 10^5 to 10^6 l/mol. Also, they reported the hysteresis between the anodic and cathodic scans, which can be seen from Figs. 4a and b. The rise in chloride adsorption at 0.500 V vs. NHE when the sweep rate is changed from 0.3 V/sec to 0.03 V/sec (Figs. 4b and c), can be caused by the time dependence of the reduction of the Pt-O layer, which has been investigated by Vetter and Schultze.⁵

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