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The influence of electrode porosity and temperature on electrochemical gas evolution at platinum and rhodium

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The influence of electrode porosity and temperature on the rate of electrochemical gas evolving processes (H_2, Cl_2, O_2) was investigated. The experiments were carried out at electrodes with small pores ($\leqslant 3$ nm) and at smooth electrodes. To understand the results the hydrogen evolution process was used for detailed investigations. It was shown that the pores are only effective if the gas evolving process is an irreversible one (as with oxygen). The pores do not operate in the case of hydrogen and chlorine evolution. An explanation of this different behaviour is given. The temperature dependencies of the overvoltages of the chlorine and hydrogen processes are in contrast. An increase of hydrogen overvoltage with rising temperature is not yet fully understood. It can be stated, however, that the effectiveness of the hydrogen transport from the electrode surface into the bulk of solution decreases with increasing temperature.

1. Introduction

The most common procedure of intensifying an electrode process is by increasing the surface roughness of the electrodes and by raising the temperature. The influence of these factors on the rate of the technically important gas evolving processes (H_2, Cl_2, O_2), however, seems to be not yet fully understood. From the literature [1–3] it follows that the overvoltage of the chlorine evolution does not depend on the surface roughness factor of platinized platinum (Pt/Pt) electrodes and RuO_2-anodes. On the other hand a substantial rise of the rate of oxygen evolution was obtained by increasing the roughness factor of RuO_2-anodes [4]. In order to explain this, other investigators [4] assumed that oxygen is evolved on the total surface area including the pores. By contrast with oxygen, chlorine evolution is assumed to take place only at the outer surface. That is, the pores do not operate in this case. This latter effect has remained unexplained until now.

The aim of this paper is to provide an explanation for the influence of the electrode surface porosity on the rate of gas evolution. For this purpose the gas evolving processes, especially hydrogen evolution, were studied at platinum and rhodium electrodes with very different surface roughness factors. Also, the dependence of the rate of gas evolution on temperature was investigated. The outcome of these investigations is considered to hold scientific as well as technical interest.

2. Experimental details

Hydrogen was evolved from a 0.5 M H_2SO_4 solution saturated with hydrogen. For chlorine evolution a solution of 4 M NaCl (pH = 2.7) was used. The electrode materials were smooth and platinized platinum, smooth rhodium and a platinum electrode, covered with an electrochemically plated layer of rhodium (rhodinized electrode). Thee platinized and rhodinized electrodes were produced by the same methods, as proposed in [5]. The porous layers of platinum and rhodium had a thickness of about 5–10 μm. The electrodes were sheets ($5 \times 5\,\mathrm{mm}^2$), which were vertically positioned in the cell. The surface layer of a platinized platinum was investigated earlier by the method of standard porosimetry [6]. The degree of porosity was about 20% and the main diameter of the pores was about 3 nm [6]. By the same method we tried to obtain these parameters for a rhodinized electrode but, at the same pressures used for Pt/Pt, it was not possible to remove the benzene from the porous rhodium layer. From this we concluded that the pores in the rhodium layer must be 1.5–2.0 nm at most. The total surface areas of the used electrodes were determined by means of the hydrogen region of charging curves measured in a 0.5 M H_2SO_4 solution.

The overvoltage of the hydrogen evolution at a constant current density was obtained as the difference between the potential of the reversible hydrogen electrode in the hydrogen saturated solution and the potential measured 20–100 μs after opening the circuit.

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During this time the potential is constant and corresponds to the potential of the process at the given current density without the ohmic potential drop. On this basis the polarization curves were constructed. A P-5827M potentiostat and a S8-13 storage oscilloscope were employed in these measurements.

In order to investigate the dependence of the gas evolution rate on temperature the measurements were carried out between 293 and 353 K. The quantities of hydrogen and chlorine reaching the bulk of the solution in form of bubbles were determined by a volumetric method [7].

All measurements were carried out in unstirred solutions saturated with the corresponding gas. The solutions were made from twice distilled sulphuric acid or from NaCl + HCl (pH = 2.7) of the 'p.a.' quality and twice distilled water.

3. Results and discussion

3.1. *Influence of the electrode porosity*

Fig. 1 shows the *i*-*E* curves of the hydrogen evolution at smooth and platinized Pt-electrodes (curves 1 and 1'). The two curves do not differ very much, although the total surface areas of the both electrodes differ by a factor of about 500. The polarization curves of hydrogen evolution obtained at a smooth rhodium electrode and at a rhodinized electrode (curves 2 and 2') show a small difference. The currents of hydrogen evolution at the porous rhodium layer at the same overvoltage are about four times higher whereas the ratio of the total surface areas of the two electrodes is more than 10^3. On the basis of these results it may be concluded that for the case of hydrogen evolution the pores do not operate at the Pt- and Rh-electrodes used by us. Hydrogen is evolved only at the outer surface of the electrodes. The polarization curves of chlorine evolution at platinized electrodes with different roughness factors lead to the same results [3], as for hydrogen evolution. It must therefore be assumed that the reason for this behaviour is the same in both cases.

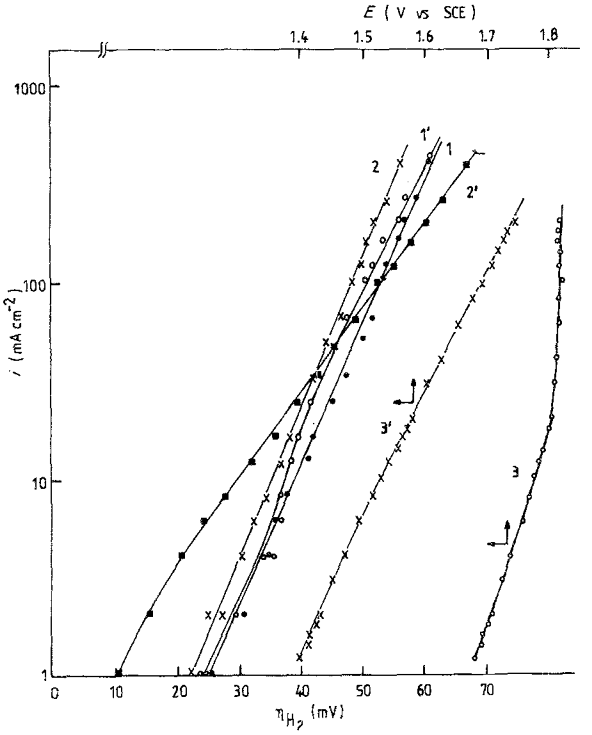

Fig. 1. Polarization curves for H_2-evolution (curves 1, 1', 2, 2') and O_2-evolution (curves 3, 3') in 0.5 M H_2SO_4 at 293 K. 1 and 3: Pt smooth (R_f = 2.0); 1 and 3: Pt/Pt (R_f = 910); 2: Rh smooth (R_f = 5.9); 2': Rh/Pt (R_f = 13 000).

In order to explain these results, potential decay curves were taken. From the region 10 ms < *t* < 50 ms, which shows an almost linear dependence of overvoltage on time, the total polarization capacity C_{pol} was determined from the equation:

$$i_0 = C_{pol} \frac{d\eta}{dt} \qquad (1)$$

where i_0 is the steady state current before circuit interruption, and η is the overvoltage.

The dependence of the total polarization capacity, the adsorption capacity and the hydrogen supersaturation of the solution at the electrode surface. An unambiguous interpretation of C_{pol} at a gas evolving electrode is not possible. The fact, however, that the values of C_{pol} obtained from potential decay curves at a rotating smooth platinum electrode with a high rotation speed [8] are much more lower (Fig. 2, curve 5) than ours (Fig. 2, curve 1) shows, that the influence of the hydrogen supersaturation on the value of C_{pol} must be very important. This conclusion can also be drawn on the basis of the estimated values of C_{pol}, which are much higher than could be expected if the double layer or adsorption capacity were dominating. The value of C_{pol} is mainly determined by the change of the overvoltage due to the H_2 diffusion from the supersaturated layer into the bulk solution.

In Fig. 2 it can be seen that the values of C_{pol} do not differ very much from one to another for the 4 elec-

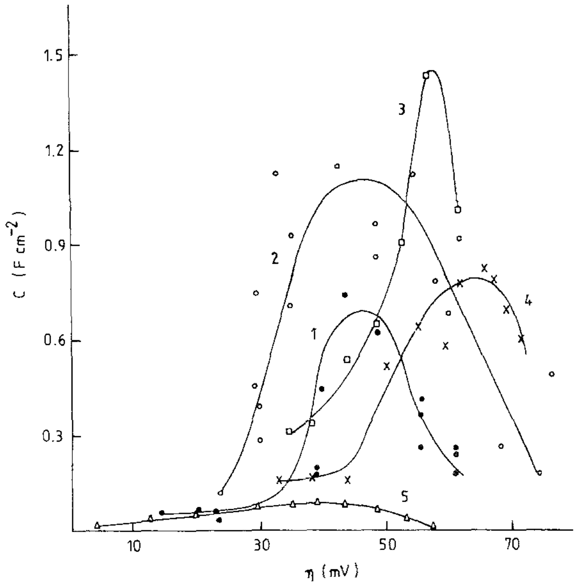

Fig. 2. Dependence of the total polarization capacity C_{pol} on the overvoltage for H_2 evolution in 0.5 M H_2SO_4 at 293 K. 1: Pt smooth (R_f = 2.8); 2: Pt/Pt (R_f = 1 300); 3: Rh smooth (R_f = 5.9); 4: Rh/Pt (R_f = 4 600); and 5: Pt smooth (f = 3 600 min^{-1}) [8].

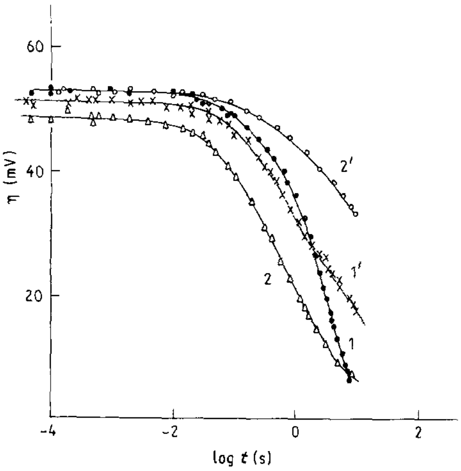

Fig. 3. Potential decay curves after current interruption for H_2-evolution in 0.5 M H_2SO_4 at 293 K, i_0 = 100 mA cm^{-2} (for indication of electrodes see Fig. 1).

trode types (curves 1–4), although the true surface areas for these electrodes differ greatly. These results lead to the conclusion, that the pores of the electrode surface layer have no marked influence on C_{pol}. This may be the case, if the supersaturation in the pores has the same value as immediately at the electrode surface.

Such a behaviour characterizes reversible processes, for which the rate determining step is the transfer of the reaction product (H_2) from the electrode surface into the bulk of the solution. The overvoltage in such a case is determined by the supersaturation of H_2 immediately at the electrode surface.

The reversibility of the H_2-evolution at our electrodes is also indicated by the shape of the potential decay curves (Fig. 3): after a potential drop caused by ohmic components in the circuit the potential remains almost constant for some time ($\leqslant$ 10 ms). Potential decay curves of the same kind were also obtained for the process of chlorine evolution.

Assuming the reversibility of the hydrogen evolving process, the following experimental results may easily be explained:

(1) the small dependence of the hydrogen evolution rate of the electrode material (Pt, Rh).

(2) the fact, that the rate of hydrogen evolution at smooth Pt does not change by a partial poisoning of the electrode surface (~ 80%) by methanol oxidation products.

Taking into account the reported results it is possible to explain the fact that the pores of the platinized and rhodinized electrodes have no influence on the rate of the hydrogen and chlorine evolution. The most probable explanation is that in the pores, very soon after the current is switched on, the supersaturation attains a value corresponding to the overvoltage of the process. In the case of a reversible process the value of supersaturation in the pores must be nearly the same as at the outer electrode surface. Therefore, there can only be a negligible diffusion gradient in the pores, i.e. the rate of the gas evolving process in the pores is almost zero. Bubble transport out of the pores can be excluded because bubbles cannot be formed in the small pores of our electrodes. Theoretical calculations show [9] that for a reversible gas evolving process the critical bubble radius must be ~ 15 nm at an overvoltage of 60 mV, corresponding to a supersaturation of 100. This radius is much bigger than the radius of the pores in our platinized and rhodinized layers.

A second possible explanation of why the pores do not operate entails the assumption that bubbles are formed in the pores and, through their growth, push solution out of the pores. But this interpretation must be rejected. It should be true independently on the rate-determining step of the gas evolving process. Our experiments, however, show that in the process of oxygen evolution the pores are fully working, i.e. the main part of oxygen is formed in the pores (Fig. 1, curves 3 and 3'). The oxygen evolution is an irreversible process with a high overvoltage, which is determined by a slow electrochemical process. The oxygen supersaturation in the pores is high but diminishes the real rate of the oxygen evolving process in the pores insufficiently. As a consequence of a lower rate of

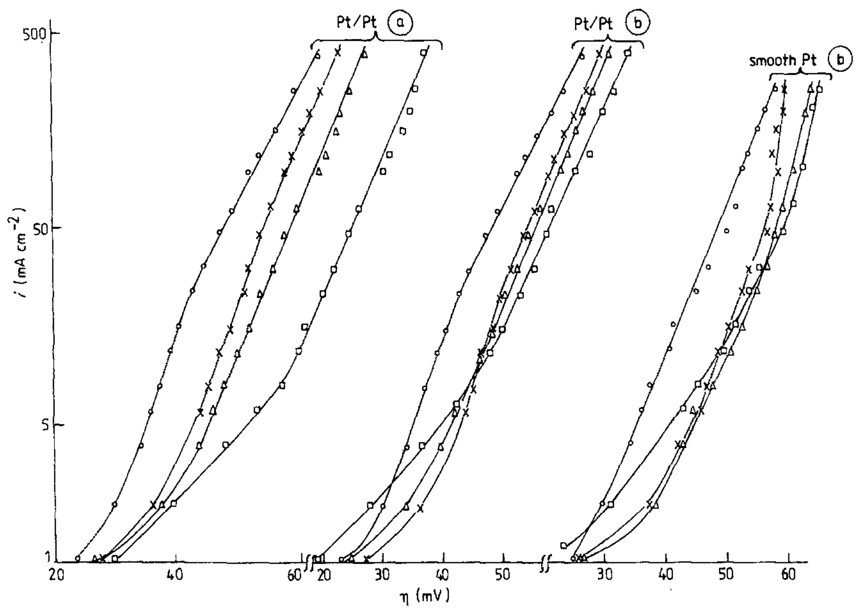

Fig. 4. Polarization curves of H_2-evolution in 0.5 M H_2SO_4 at smooth Pt (R_f = 2.0) and Pt/Pt (R_f = 910) electrodes for various temperatures (○) – 293 K; × – 313 K; △ – 333 K; □ – 353 K). Curves (a) – experimental; curves (b) – after correction for H_2O vapour pressure.

oxygen diffusion out of the pores, compared with the oxygen transport rate from the surface into the solution, the supersaturation at the outer surface must be markedly lower than in the pores. Thus there exists a concentration gradient of dissolved oxygen in the pores towards the outer electrode/solution interface. A high overvoltage and an existing concentration gradient are responsible for the operation of the pores in a gas evolving process. The pores can only be effective if the process of gas evolution is irreversible. The degree of their effectiveness is greater the bigger the overvoltage of the process and the higher the concentration gradient in the pores.

3.2 *Temperature dependence*

Unusual results were obtained on investigating the dependence of the hydrogen evolution rate on temperature. At all four types of electrodes the rate of the hydrogen evolution, at a constant overvoltage, decreaes with an increase of temperature (Fig. 4, curves a). This unexpected effect diminishes after correcting the reversible potential due to the increase of the vapour pressure of the 0.5 M sulphuric acid solution with increasing temperature (Fig. 4, curves b). With the rise of the partial vapour pressure of the electrolyte solution the partial pressure of hydrogen is lowered at a constant total pressure. The overvoltages of the curves b in Fig. 4 are derived from the directly measured curves a. The correction ΔE_0 of the reversible potential E_0 measured in the bulk of solution due to the changes in partial vapour pressures of the electrolyte solution is

$$\Delta E_0 = \frac{2.3RT}{2F} \log\left(\frac{p_0 - h}{p_0}\right) \tag{2}$$

where p_0 is the constant atmospheric pressure, and h represents the vapour pressure of water in a 0.5 M H_2SO_4 solution.

With this correction the overvoltages in curves b refer to the reversible hydrogen partial pressure equal to one atmosphere at all temperatures.

The polarization curves for hydrogen evolution (Fig. 5), measured at different temperatures at a smooth rhodium and a rhodinized electrode, show the same behaviour. However, in the case of a rhodinized electrode the decrease of the rate of hydrogen evolution with increase of temperature (at constant overvoltage) is much less pronounced and can be observed only at current densities higher than 50 mA cm^{-2}.

In order to estimate qualitatively the influence of temperature on the rate of the hydrogen evolving process the equation of stationary diffusion was used, corresponding to the transfer of the produced hydrogen into the bulk solution:

$$i = \frac{2FD_e(c_s - c_0)}{\delta_e} \tag{3}$$

where c_s is the concentration of hydrogen at the electrode surface; c_0 is the concentration of hydrogen in the bulk of solution; D_e is the effective diffusion coefficient; and δ_e is the effective diffusion layer thickness.

Taking into account that the overvoltage of hydrogen evolution at our electrodes is determined by the hydrogen supersaturation at the electrode surface, c_s in Equation 3 can be substituted by

$$c_s = c_0 \exp\left(\frac{2F\eta}{RT}\right) \tag{4}$$

At high overvoltages $\exp(2F\eta/RT) \gg 1$. Hence, it follows:

$$i = \frac{2FD_e c_0}{\delta_e} \exp\left(\frac{2F\eta}{RT}\right) \tag{5a}$$

$$\frac{\delta \ln i}{\delta T} = -\frac{2F}{RT^2} + \frac{1}{c_0}\frac{dc_0}{dT} + \frac{\delta \ln (D_e/\delta_e)}{\delta T} \tag{5b}$$

With the help of Equation 5b it is possible to estimate qualitatively the influence of some temperature dependent parameters of the process on the rate at constant overvoltage.

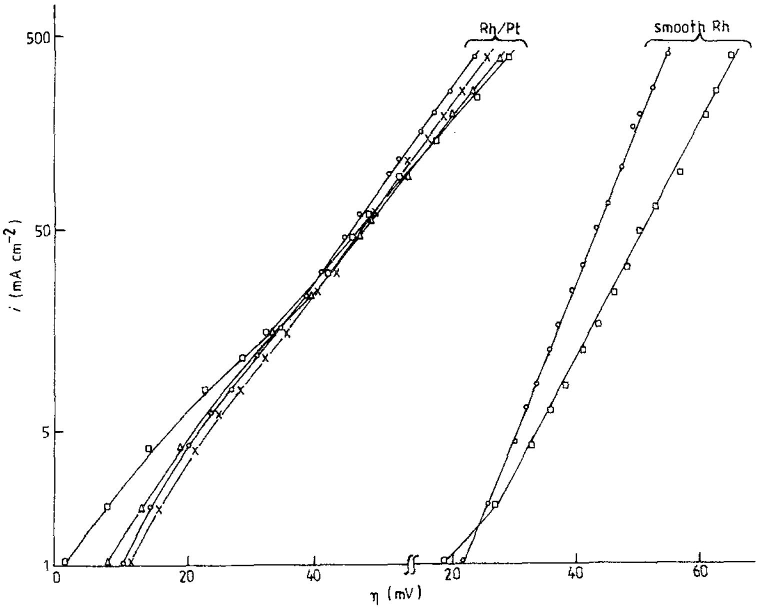

Fig. 5. Polarization curves of H_2-evolution in 0.5 M H_2SO_4 at smooth Rh (R_f = 5.9) and Rh/Pt (R_f = 13 000) for various temperatures (○–293 K; ×–313 K; △–333 K; □–353 K) after correction of H_2O vapour pressure.

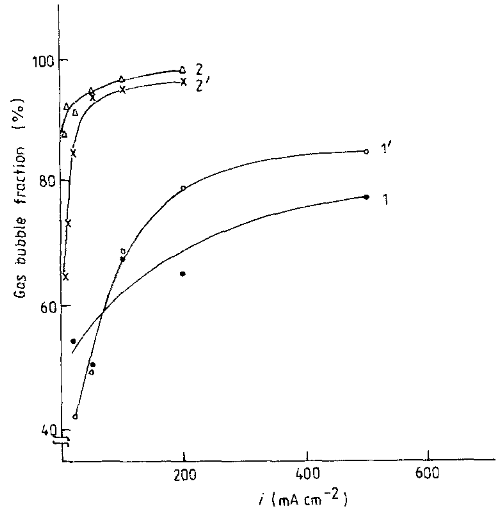

Fig. 6. Fraction of gas bubbles departing the electrode boundary layer for Cl_2 evolution in 4 M NaCl (pH = 2.7) at smooth Pt (curves 1, 1′) and for H_2-evolution at Pt/Pt in 0.5 M H_2SO_4 (curves 2, 2′).

At $\eta = 50\,\mathrm{mV}$, $T = 323\,\mathrm{K}$ and $\Delta T = (333 - 313)\,\mathrm{K} = 20\,\mathrm{K}$ we get $c_0 = 0.0141\,\mathrm{cm^3\,cm^{-3}}\,H_2O$ and $\Delta c_0 = -0.024\,\mathrm{cm^3\,cm^{-3}}\,H_2O$ (between 313 and 333 K)

$$\frac{\Delta \ln i}{\Delta T} = -\frac{4}{323} + \frac{1}{0.0141} \times \frac{-0.0024}{20} + \frac{\Delta \ln (D_e/\delta_e)}{\Delta T} \qquad (6)$$

The first and the second term of Equation 6 lead, in the specified temperature range, to a decrease of the rate of hydrogen evolution by ~1.5 times. In the experiments (excluding rhodinized electrodes) the rate was found to decrease much more strongly. This difference must be due to the third term of Equation 6 which expresses the complexity of all the gas evolving processes. It is very difficult to plausibly estimate δ_e and D_e as both parameters involve the circumstances that at high overvoltages hydrogen is removed from the electrode surface by diffusion and to a larger extent by gas bubbles. At present it is only possible to state that, in the case of hydrogen evolution, the effectiveness of the transport processes of hydrogen from the electrode surface into the solution decreases with increasing temperature. The effectiveness of the transport processes depends on the portion of hydrogen transported by bubbles from the adherent supersaturated layer in front of the electrode surface into the bulk of solution. As seen from Fig. 6 (curves 2 and 2′) the quantity of H_2 reaching the volume of the solution in the form of bubbles decreases with increasing temperature. The effects are not very large, because in the case of H_2 almost all the dissolved H_2, the primary product of the hydrogen evolution, is taken up by the bubbles in the supersaturated layer. But the curves 2 and 2′ show (Fig. 6) that the supersaturation at the electrode surface should increase with temperature.

The temperature dependence of the chlorine evolution process is shown in Fig. 7. The overvoltage decreases with increase in temperature. This means that, in this case, the transport of dissolved gas from the electrode surface increases with temperature. It was experimentally established that the part of chlorine transferred from the electrode surface into the solution by bubbles increases (Fig. 6 curves 1 and 1′) with rising temperature. Taking into consideration that the bubble transport is more effective than the transport of dissolved gas by convective diffusion, the observed results in the case of chlorine evolution may be understood. The acceleration of the transport processes must be large enough to overcompensate the decrease if the chlorine evolution rate, connected with the first and the second term of Equation 6.

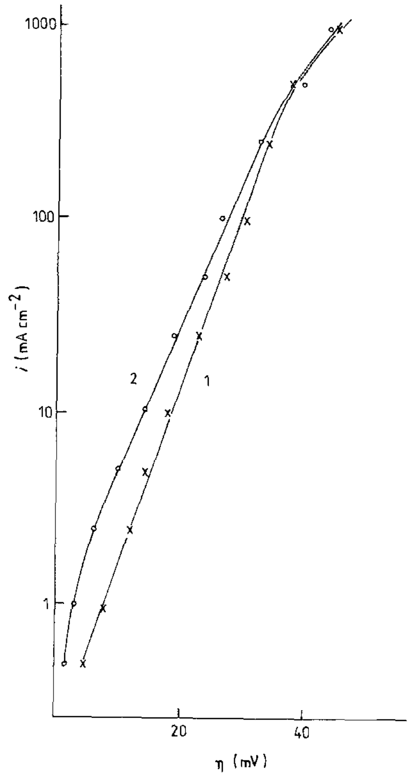

Fig. 7. Polarization curves of chlorine evolution in 4 M NaCl (pH = 2.7) at smooth Pt for 293 K (curve 1) and 333 K (curve 2).

The oxygen evolution process, which is an irreversible one, shows an expected behaviour: the rate of the process increases with increasing temperature, as is usual for a kinetically determined process.

4. Conclusion

The different dependencies of the electrochemical gas evolving processes on the porosity of the electrode surface layer and on the temperature show that in order to intensify these technical processes it is necessary to know the rate determining reactions under the given conditions.

When the gas evolving process is irreversible its rate can be accelerated by increasing the porosity of the electrode surface layer and by increasing the temperature. Otherwise, when the gas evolving process is reversible, the small pores of the surface layer do not operate if the overvoltage is determined by the gas supersaturation. This is true for hydrogen and chlorine evolution. The temperature dependencies of the rate of the chlorine and hydrogen processes are quite different. The rate of the chlorine evolution process increases with rising temperature.

Our results show, therefore, that the effectiveness of a gas evolving process cannot be in every case increased by roughening the surface layer or by a temperature rise. On the contrary, there may also occur a negative effect as was observed for reversible hydrogen evolution.

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