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On the influence of the annealing temperature and heavy current treatments on the porous structure of platinum electrodes and on the kinetics of the oxygen reaction at high temperatures

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The influence of high temperature annealing and heavy current treatments of porous Pt electrodes is investigated with scanning electron microscopy. The results are discussed on the basis of the kinetic behaviour of these electrodes, known from the literature or deduced from our still unpublished results.

It is demonstrated that both the structure and the catalytic activity are influenced by the treatments.

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1. Introduction

Platinum metal electrodes are generally used as current collectors and electrocatalytically active substrates for oxygen electrodes at high temperatures, when stabilized zirconia is used as the ionically conducting electrolyte. Whilst these electrodes are relatively easily prepared, their behaviour is quite complicated. As an example, it has been independently proved by Bauerle [1] and Karpachev and Ovchinnikov [2] that the catalytic behaviour of Pt films suitably deposited on zirconia, depends markedly on the preparation procedure and anodic pretreatment. Bauerle's results, reported in Fig. 1, show that the electrode resistance, measured by the complex admittance method, decreases as soon as the sputtered Pt electrodes are (supposedly) made artificially porous by heavy current treatment. Karpachev and Ovchinnikov, moreover, showed that the overvoltage for the cathodic polarization of porous Pt electrodes in air or oxygen is consistently lowered, as shown

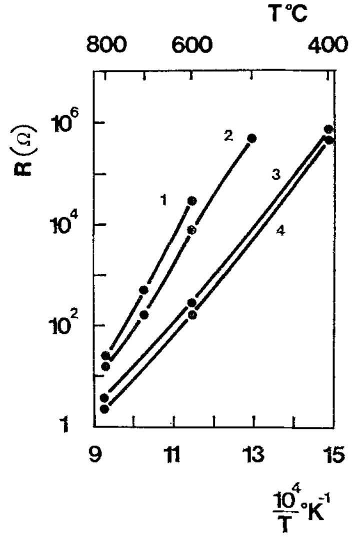


Fig. 1. Temperature dependence of the electrode resistance (after Bauerle [1]) 1. sputtered Pt, 13000 Å thick; 2. sputtered Pt, 2000 Å thick; 3. and 4. Pt paste electrodes after heavy current treatment.

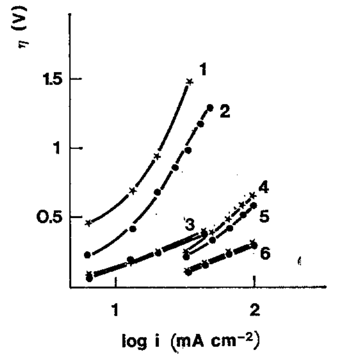


Fig. 2. Cathodic polarization of Pt electrodes (after Karpachev and Ovchinnikov [2]) 1. in air at 800°C before anodic treatment; 2. in pure oxygen at 800°C before anodic polarization; 3. in air and oxygen at 800°C after anodic polarization; 4. and 5. in air and oxygen at 1000°C before anodic treatment; 6. in air and oxygen after anodic treatment.

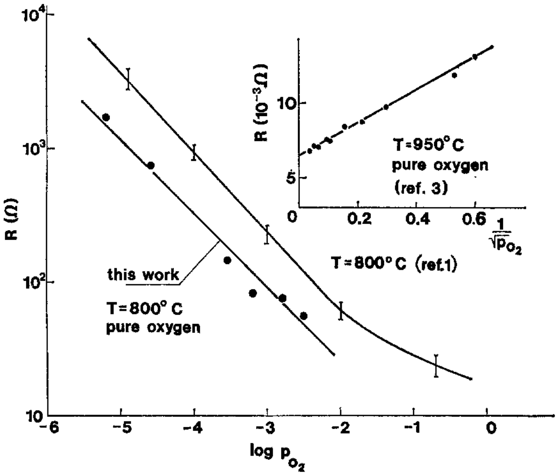


Fig. 3. Experimental dependence of the electrode resistance on the partial pressure of oxygen.

in Fig. 2, by anodic heavy current (300 mA cm^{-2}) treatment.

It is also remarkable that the behaviour of Pt electrodes, consisting either of a small Pt tip, as in those used by Kleitz [3], or of a porous Pt film obtained by decomposing Pt paste [4] or chloroplatinic acid [5], is quite different with respect to the dependence on the oxygen pressure of both the electrode resistence R_e or the cathodic limiting current i_{lim}.

One observes, for example, in Fig. 3, which reports relevant literature data, that the electrode resistance

$$R_e = \left(\frac{\partial V}{\partial i}\right)_{i\to 0} \tag{1}$$

is well-described by an adsorption-like isotherm of the type

$$\frac{1}{R_e} = A\left(\frac{p}{B+p}\right)^{w} \quad 0{\cdot}8 < w < 0{\cdot}6 \tag{2}$$

where A and B are constants and p is the partial pressure of oxygen, which approximates to a square root dependence on the pressure in the case of porous electrodes made from Pt paste [4] and of sputtered Pt electrodes [1]. On the other hand, an equation of the type

$$R_e = A + \frac{BT}{\sqrt{p}} \tag{3}$$

better accounts for the behaviour of Pt tip electrodes [3].

A linear dependence on the partial pressure of oxygen is eventually achieved when using porous Pt electrodes made from chloroplatinic acid [5]. As for the cathodic limiting currents at Pt electrodes, one observes a square root dependence on the partial pressure of oxygen both in the case of porous Pt electrodes made from Pt paste [4], as illustrated in Fig. 4, and in the case of Pt tip electrodes. On the other hand, a linear dependence is observed in the case of porous Pt electrodes made from chloroplatinic acid [5], as shown in Fig. 5. The authors of reference 5 claim, moreover, that the polarization effects are independent of the previous history of the electrodes and that in practice the electrode structure is not sensitive to temperature and anodic treatment. It has been already shown [5, 6] that a square root dependence of the cathodic limiting current

$$i_{\text{lim}} = k_1 p^{1/2} \tag{4}$$

or of the reciprocal of the electrode resistance

$$\frac{1}{R_e} = k_2 p^{1/2} \tag{5}$$

is accounted for by assuming that the reaction partner in the rate determining step of the electrode reaction is atomic oxygen, whilst a direct proportionality to the partial pressure of oxygen of both i_{lim} and $1/R$ is well accounted for, by supposing that molecular oxygen is involved in the rate-determining step.

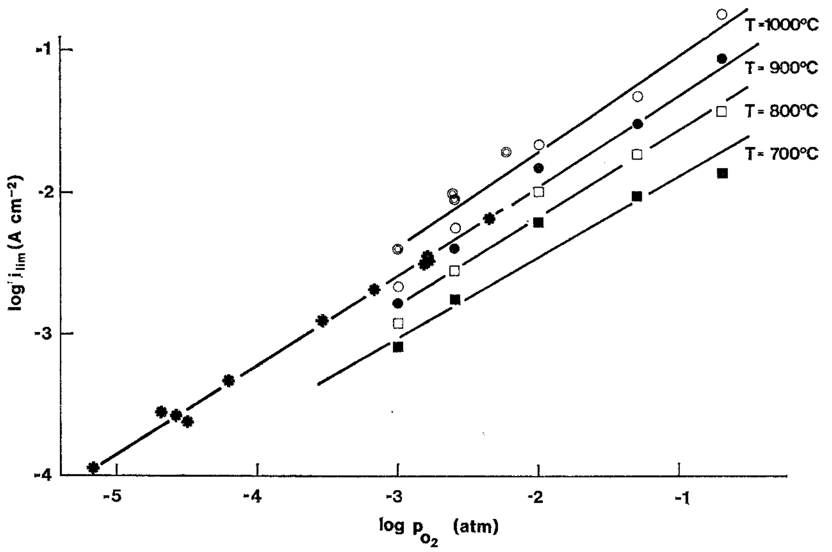


Fig. 4. Experimental dependence of the cathodic limiting current on the partial pressure of oxygen. Stars refer to an experiment carried out with pure oxygen at 800°C, other points refer to experiments carried out in oxygen nitrogen mixtures. Pt electrodes from fired platinum paste.

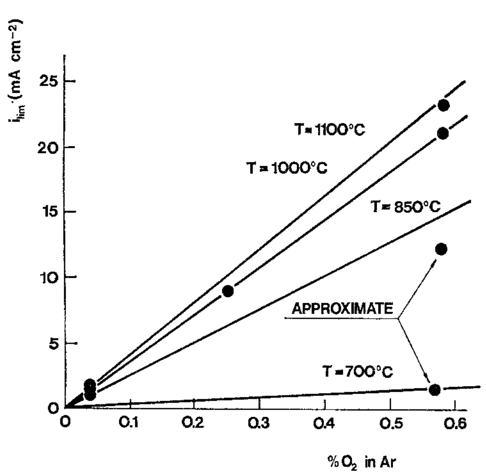


Fig. 5. Dependence of the cathodic limiting current at porous Pt electrodes on the oxygen partial pressure (after Etsell and Flengas [5])

A detailed discussion of the various possible reaction mechanisms accounting for the different experimental results, has been given in references 3, 5, 6 and 7. But we have shown in a previous paper [7] that oxygen chemisorption and oxygen surface diffusion are strongly supported as being the rate-determining steps for the cathodic oxygen reduction at porous Pt electrodes by experimental evidence. One then surmises that the catalytic activity of the metallic support is influenced by the preparation procedure, thermal treatments and heavy current anodic polarization.

Support for this conclusion also results from experiments dealing with the influence of both the preliminary high temperature annealing of the electrode and of the flow rate of oxygen-containing inert gases on the open circuit voltage of a cell like (I) below

$$\text{Pt, } O_2(p_1)|\text{electrolyte}|O_2(p_2)\text{, Pt} \qquad \text{(I)}$$

when the partial pressure of oxygen to be measured (p_2) is reduced below 10^{-7} atm or, often, below 10^{-5} atm, p_1 being the reference pressure.

Fig. 6 shows that, depending on the annealing temperature of the Pt electrode, the e.m.f. of the cell I, measured at 800°C, either exhibits a voltage which corresponds to partial pressure of oxygen orders of magnitude below the experimental one (a few p.p.m. of oxygen in nitrogen) or, when the annealing is performed at 1000°C, a voltage plateau close to the theoretical voltage, up to a flow rate of about 12 l h^{-1} (curves A and B, respectively) [8].

Results comparable with those of curve B of Fig. 6 have been reported by Etsell and Flengas [9], who supposed that this small flow rate

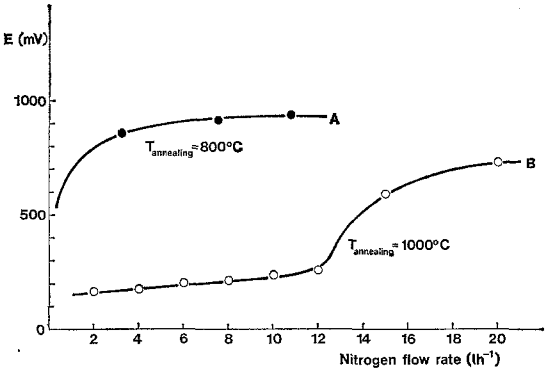


Fig. 6. Experimental dependence of the e.m.f. of an oxygen gas concentration cell (air as reference, 10 p.p.m. oxygen in the measuring compartment) on the flow rate and annealing temperature of the porous Pt electrode.

dependence at the low flow rates could be accounted for by the small but not at all negligible permeability to molecular or atomic oxygen of the zirconia-base electrolyte.

They did not mention, however, any tendency of the oxygen electrode to shift to higher potentials at high flow rates, which is also, however, a common effect experienced in commercial oxygen meters at low partial pressures of oxygen, when the fluid being monitored is a low oxygen content inert gas.

One guesses that traces of carbonaceous substances coming from the firing of the organic suspension medium of colloidal Pt, and dissolved in the Pt grains, could drastically reduce the oxygen partial pressure at the metal/electrolyte interface, to values corresponding to the occurrence of reactions involving CO and CO_2. This would not be the case for electrodes prepared with chloroplatinic acid, as the formic aldehyde added for improving the film texture should be removed at low temperatures, without leaving residual carbon in the film.

In any case, apparently, high temperature annealing in oxidizing atmospheres or anodic treatments of electrodes prepared from Pt paste, are capable either of removing the poisoning effects of carbonaceous substances or of modifying the electrode texture, so that the in-pore diffusion, which is shown to be the rate-determining step when the pore size is within the submicron size [7], should be no longer considered as a source of kinetic hindrances.

In order to start to elucidate the influence of the electrode texture on the kinetics of the oxygen electrode and to find criteria for the preparation of reliable oxygen electrodes, it has been found necessary to investigate, with the scanning electron microscope, the influence of high temperature annealing and anodic polarization on the structure of porous Pt films.

2. Experimental

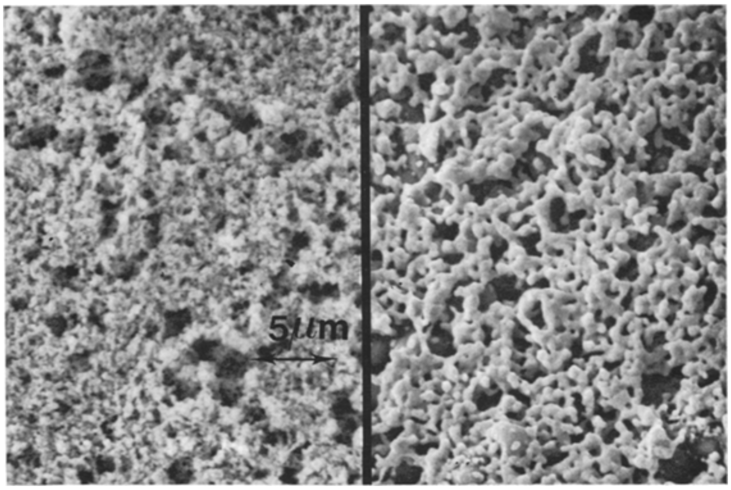
Both electrodes prepared by firing Hanovia 6082 Pt paste and by thermally decomposing chloroplatinic acid and formic aldehyde [9] have been investigated. The paste is thinly smeared on the surface of a ZrO_2-Y_2O_3 8 mole % pellet, decomposed at 600°C and then annealed at five different temperatures up to 1000°C.

The chloroplatinic acid solution is sprayed on a stabilized zirconia support (supplied by Zirconium Corporation of America) as the pellets we prepared are too porous. The support is held at 100–120°C and driven slowly by means of a mandrel for homogeneous deposition. The deposited film is then fired at different temperatures from 600–1000°C.

Whereas a bright Pt layer is obtained even at the lowest temperatures when firing Pt paste, a black Pt layer is obtained when decomposing the chloroplatinic acid solution at 600°C, which then takes on a bright appearance when annealed at higher temperatures. In order to test the influence of the anodic treatment, a second set of five different probes (from Pt paste), consisting of a YSZ pellet platinized on both sides and preliminarily annealed at 600 up to 1000°C for four hours, has been used. These pellets were then polarized in air for four hours at different temperatures and at a current density slightly below that corresponding to the limiting current for the cathodic process (see Fig. 4). This precaution has been used in order to avoid a possible parasitic influence of incipient decomposition of the electrolyte when the limiting current is exceeded.

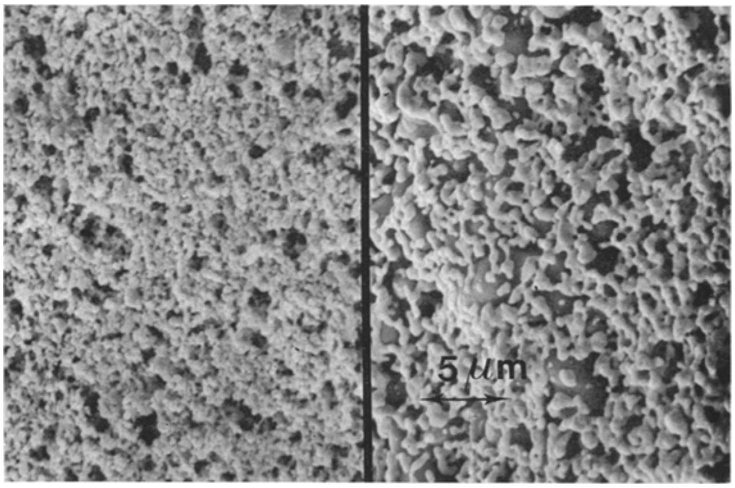
Samples from Pt paste decomposition before and after the anodic polarization, as well as samples from chloroplatinic acid decomposition have been examined for surface texture using a scanning electron microscope. Results are reported in Figs. 7, 8 and 9.

T = 600°C 30 mA, 4 h



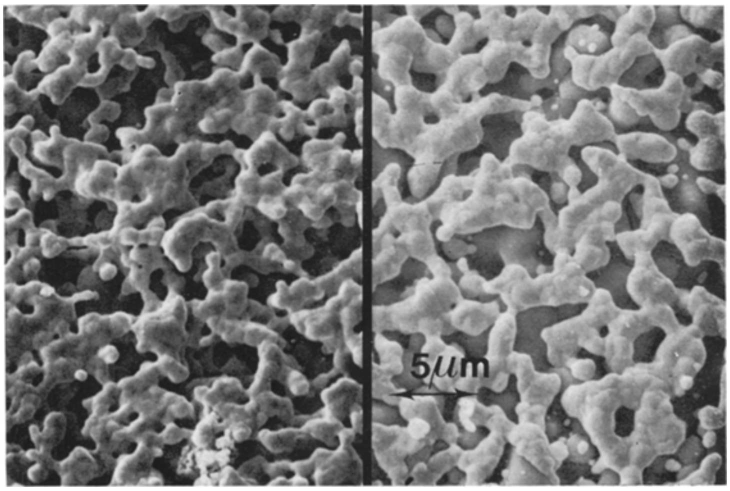
7 (a)

T = 700°C 50 mA, 4 h



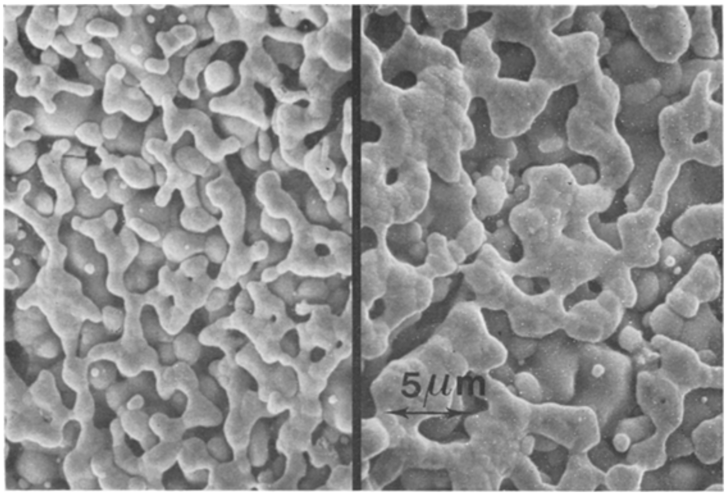
7 (b)

T = 800°C 100 mA, 4 h



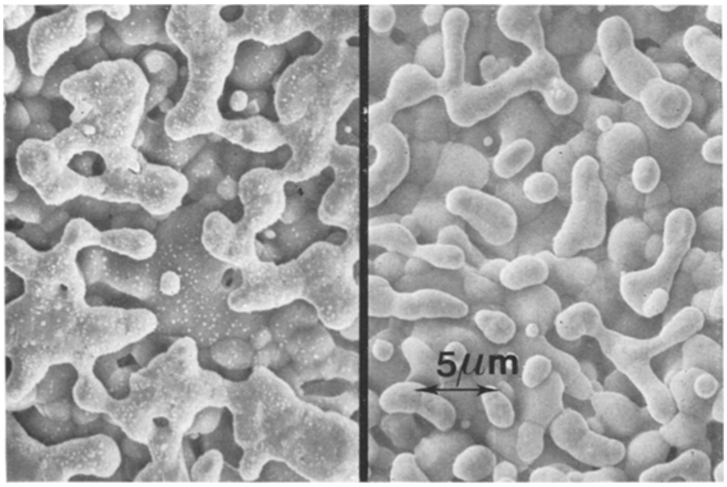
7 (c)

T = 900°C   200 mA, 4 h



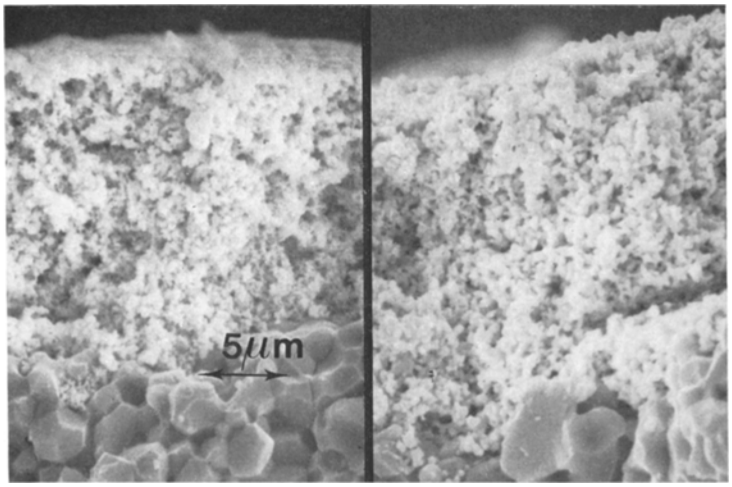
7 (d)

T = 1000°C   300 mA, 4 h



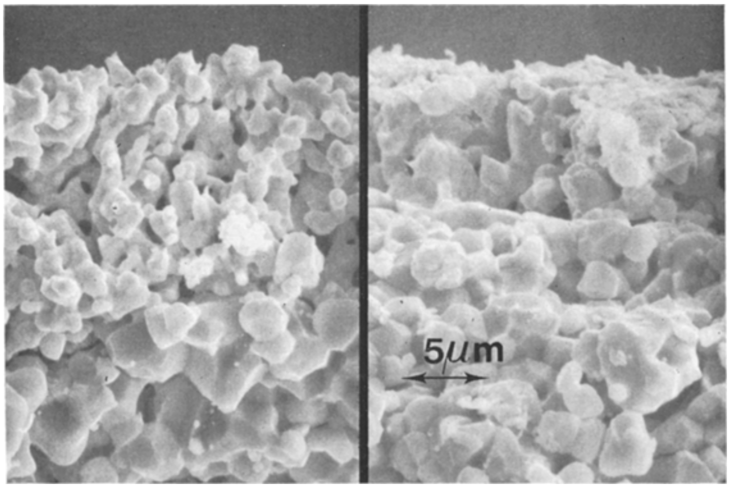
7 (e)

Fig. 7. Views of platinum electrodes prepared by thermal decomposition of Hanovia Pt paste. Influence of annealing temperature and anodic treatment.



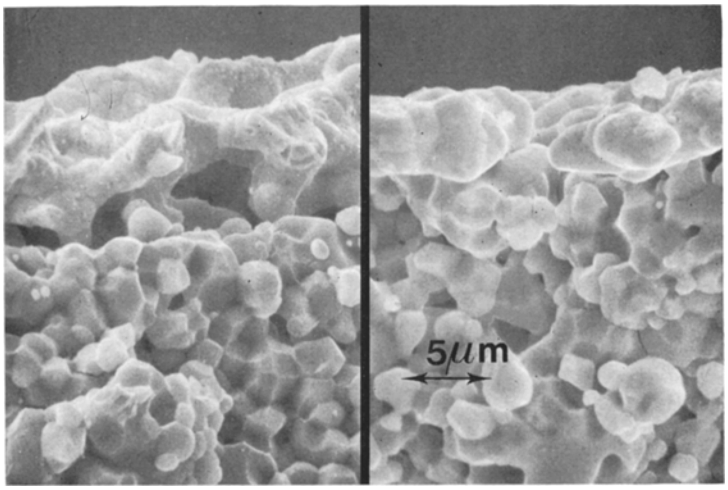
T = 600°C   30 mA, 4 h

8 (a)



T = 800°C   100 mA, 4h

8 (b)

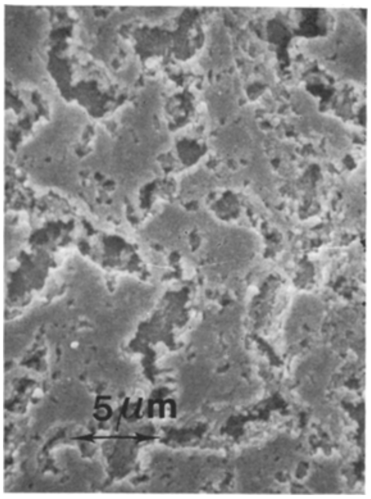


T = 1000°C   300 mA, 4h

8 (c)

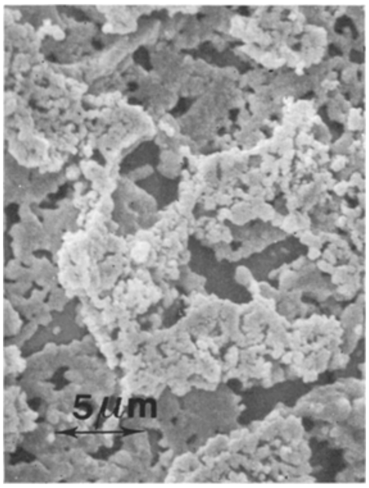
Fig. 8. Sections of platinum electrodes prepared by thermal decomposition Hanovia Pt paste. Influence of annealing and anodic polarization.

T = 600°C



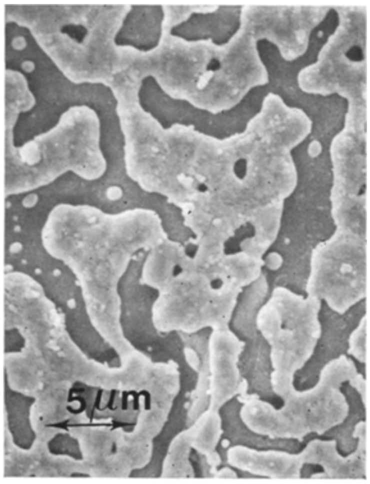
9 (i)

T = 800°C



9 (ii)

T = 1000°C



9 (iii)

Fig. 9. Views of platinum electrodes prepared by thermal decomposition of chloroplatinic acid: influence of the annealing temperatur

3. Results and discussion

The influence of the high temperature annealing and anodic polarization can be seen, for films prepared from Pt paste, in Fig. 7 (views) and 8 (sections). The sections have been prepared by breaking the sample with a sharp tool, as the normal metallographic procedures yielded erroneous results, due to the differing hardnesses of the film and of the substrate. Possibly even better results could be obtained by deep freezing the sample to the liquid nitrogen temperature, in order to enhance the tendency to brittle fracture. The effect of temperature on the film structure is apparent both from the views and the sections. One observes that up to 700°C the fine-grained and thin porous structure of the film remains practically unchanged. The few large pores seen on the surface do not correspond to open channels to the metal/electrolyte boundary, as one can see from the corresponding sections. An average pore size less than 0·5 μm is probably a good estimate for low temperature prepared films. From 800°C to higher temperatures, sintering of film takes place, which leads to large aggregates of Pt grains. At these temperatures, a number of large channels, having an average diameter well in excess of 1 μm, permit the direct access of the oxygen gas to the metal/electrolyte boundary from the outer atmosphere.

The effect of the anodic treatment at the lowest temperatures is quite impressive. It leads to bigger pores, which seem to originate from enhanced sintering rather than from the mechanical action of gas bubbles or from a generically defined oxygen overpressure. The adherence of the Pt film to the electrolyte after the anodic treatment is in fact very good and seems to be improved at higher currents (and temperatures).

The anodic treatment, therefore, seems to play an important role in determining the interfacial tension at the Pt/electrolyte contact. From the pore size experimentally observed for films prepared from Pt paste, one could exclude that the rate determining step is the molecular oxygen in-pore diffusion, at least at the higher temperatures, or even at the lowest temperatures, provided the electrodes are carefully and preliminarily annealed at temperatures around 1000°C. Experimental results for cathodic polarization reported in Fig. 4 show, in fact, that for pure oxygen at reduced pressures, from 10^{-2} to 10^{-5} atm, the limiting current density ranges between 10^{-2} to 10^{-4} A cm^{-2}, whereas the calculated values, on the basis that the in-pore diffusion process is a sort of Knudsen diffusion, are orders of magnitude higher.

In order to calculate the diffusion limiting currents, a steady state condition is assumed and a form of Fick's first law is assumed to hold

$$i_{\text{lim}} = \frac{4FD_{\text{K}}\varepsilon\Delta p}{RT\,v\,L} \qquad (6)$$

where it is assumed that the free mean path of the oxygen molecules is bigger than the pore radius r. D_{K} is the Knudsen diffusion coefficient

$$D_{\text{K}} = \frac{2}{3}\,r\,\sqrt{\left(\frac{8\,RT}{\pi\,M}\right)} \qquad (7)$$

ε and v are the porosity and tortuosity, respectively; the ratio ε/v is taken to equal 0·1 and L is the film thickness. Under stationary conditions, the term Δp in Equation 6 equals the oxygen pressure p in the gaseous environment of the electrode, as the pressure at the metal/electrolyte interface is negligibly small. Calculated limiting currents $i_{\text{D,K}}$ are reported in Figs. 10 and 11, which show that at 800°C and at a pressure of 10^{-2} atm for a film thickness of about 15 μm and a pore size in excess of 1 μm, a limiting current of the order of 10 A cm^{-2} is obtained, which is at least three orders of magnitude higher than the experimental one (10^{-2} A cm^{-2}). The comparison of the surface texture of Pt films prepared by decomposing chloroplatinic acid and Pt paste is particularly interesting. One observes in Fig. 9 the very fine-grained film and the very small pores, which could severely hinder oxygen diffusion from the gas phase to the Pt/electrolyte interface. In this case the interdiffusion of oxygen in an oxygen/nitrogen mixture through the pores of the porous metal is the rate determining step, as proposed for this kind of electrode by Etsell and Flengas. Their experimental figure for the limiting current of $1{\cdot}5 \times 10^{-3}$ A cm^{-2} (see Fig. 5) is well accounted for at a pressure of $5{\cdot}8 \times 10^{-3}$ atm, if the film thickness is of the order of 150 μm at an average pore size of about 0·01 μm at 700°C.

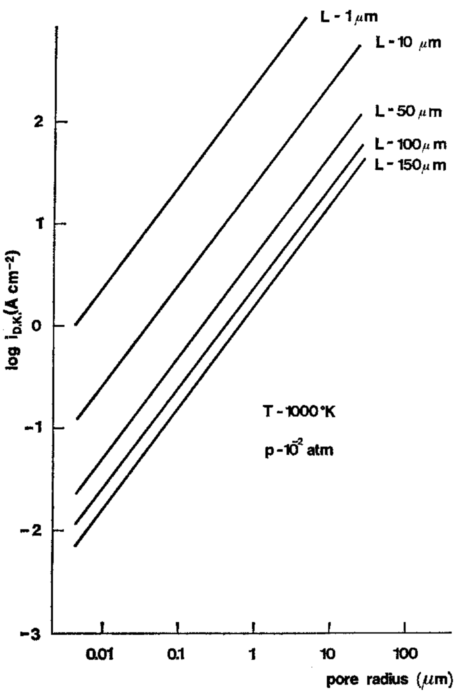


Fig. 10. Calculated cathodic limiting currents as a function of the pore radius and film thickness by assuming the Knudsen diffusion of oxygen molecules into the pores of the film as the rate determining step.

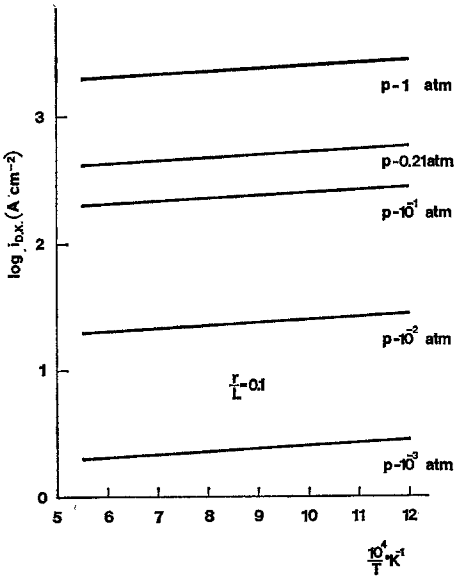


Fig. 11. Calculated limiting currents (Knudsen in-pore diffusion) as a function of the temperature and partial pressure of oxygen.

It appears from Fig. 9 that an average pore size of ≃0·01 μm is representative of the film texture at low temperatures but not at all at temperatures around 1000°C where the values of the pore radius and film thickness are comparable with those of Pt films prepared by firing Pt paste. In this latter case, if the in-pore diffusion were the rate-determining step, one should observe cathodic limiting current density values orders of magnitude higher than those (20 mA cm^{-2}) measured by Etsell and Flengas.

We therefore conclude that other mechanisms, different from the in-pore diffusion one, are rate-determining for both high temperature annealed and anodically polarized electrodes and that the assumption, that by only improving the film texture the reaction rate is enhanced, is untenable.

It has been already suggested, on the basis of the values of the activation energy for the electrode resistance, that the rate determining step for the oxygen reduction reaction at porous Pt electrodes, at temperatures greater than 650–700°C, is the desorption of strongly chemisorbed oxygen, whilst it is oxygen surface diffusion at lower temperatures [7].

As it is known that water vapour is competitively adsorbed with oxygen at a Pt surface [10], we have tried to see whether water vapour could influence the absolute values of the cathodic limiting currents for the oxygen reduction. Experiments have been carried out with porous Pt electrodes made by firing Pt paste at 600°C and annealing at 1000°C. Results, reported in Fig. 12, show that at temperatures around 700°C, where we expect significant changes in the slopes of the i_{lim} versus $1/T$ curves due to the change in the rate-determining step for the electrode reaction, water lowers appreciably the limiting current level. This corresponds also with the slight deviation of the experimental points, obtained with anhydrous gases, from the curve drawn by extrapolation from the lower temperatures [4, 8].

The fact that water acts as a poison only at temperatures where the chemisorption is claimed to be the rate-determining step, is a good argument in favour of it, as, qualitatively, the strongly chemisorbed water should not hinder

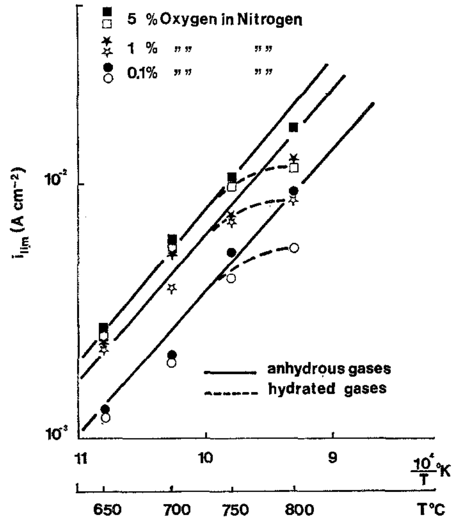


Fig. 12. Experimental temperature dependence of the cathodic limiting currents. Influence of the water vapour content in the oxygen-nitrogen mixture.

appreciably the surface diffusion of oxygen. It should, however, influence the overall reaction rate when desorption of chemisorbed oxygen is rate-determining, because of the lower number of active spots available for oxygen reduction.

The most probable explanation for the enhancement of the reaction rate due to anodic polarization is therefore that heavy current treatment increases the number of active spots on the Pt surface, where oxygen is adsorbed and dissociated.

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