

# Voltammetric studies of electrochemical processes at the interface Pt|YSZ between 300 and 600°C

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## Abstract

Electrochemical processes occurring at the interface platinum|yttria-stabilized zirconia were investigated by cyclic voltammetry and potentiostatic current–potential curves, taken under steady-state conditions, in different mixtures of oxygen and nitrogen at temperatures between 300 and 600°C. Point or paste electrodes were used. The exchange current of the rate-determining step of the oxygen reduction becomes very small below 500°C. Therefore, the equilibrium of the oxygen electrode is no longer established. A layer of chemisorbed oxygen atoms is formed anodically on the contact surface of the point electrode, not by the dissociation of O<sub>2</sub> at the three-phase boundary. The shape of the cyclic voltammograms is discussed. © 1997 Elsevier Science S.A.

*Keywords:* Interface; Ionic conductivity; Stabilized zirconia; Cyclic voltammetry

## 1. Introduction

The properties of the interface metal|stabilized zirconia or metal oxide|zirconia and the electrochemical processes at these interfaces determine the satisfactory operation of solid oxide fuel cells and oxygen sensors. Voltammetric techniques were applied successfully under stationary or cyclic conditions in previous papers [1–7] on this subject. While Refs. [1,4] dealt with investigations at relatively large temperatures ( $T \geq 700^\circ\text{C}$ ), the temperature range was extended down to about 300°C in Refs. [2,3,5–7]. This allowed investigation of the formation and reduction of the oxygen layer as well as the reduction and production of O<sub>2</sub> [6]. Here the word ‘oxygen layer’ designates chemisorbed oxygen or an oxide.

The present study of electrochemical processes at the interface platinum|yttria-stabilized zirconia (Pt|YSZ) was not started to repeat some of the experiments described in Refs. [2,3,5–7]. The original purpose was different: the comparison of results, obtained under the same conditions for the interfaces Pt|YSZ and Pt|BICUVOX.10. Here BICUVOX.10 stands [8,9] for the oxygen ion conductor Bi<sub>2</sub>V<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>5.35</sub>. However, it turned out that some of the important questions for such a comparison were not cov-

ered adequately in Refs. [2,3,5–7], making it difficult to use the interface Pt|YSZ as a model interface. In particular, the question of the establishment of the equilibrium of the reaction



at temperatures below 600°C was not considered in the previous work, although it was already concluded in Ref. [10] that the potentiometric response of certain oxygen sensors with the interface Pt|YSZ is non-Nernstian below 600°C. The latter conclusion was confirmed by our previous investigation [11] of the open-circuit behavior of the interface Pt|YSZ at 400°C, using different Pt electrodes. Therefore, a detailed study of electrochemical processes at the interface Pt|YSZ in various gas atmospheres ((100 – X)% N<sub>2</sub> + X% O<sub>2</sub>) was carried out in a temperature range of between 300 and 600°C in our laboratory. The conclusions in this paper are restricted to the above temperature range. It cannot be said without additional studies whether the same conclusions hold at higher temperatures (600 to 1200°C). A large number of investigations of electrochemical processes are devoted to this higher range of temperatures.

Following the suggestion in Ref. [12], Pt electrodes with point contacts were mainly used here to overcome difficulties in the reproducibility of the electrode properties. Such difficulties were encountered in our early work when

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producing the electrodes by sputtering or by paste. The point electrode has the additional advantage that the contribution of the ohmic potential drop  $IR_{cl}$  between the working electrode (WE) and the reference electrode (RE) can be kept small in comparison to the contribution of the polarization resistance  $R_p$ . The situation is similar to that of studies [13] of electrode kinetics with the microelectrode in unbuffered aqueous media where a large  $IR_{cl}$  is present. The influence which the arrangement of the WE, RE and counter electrode (CE) exert on the shape of cyclic voltammograms because of a different current distribution was directly demonstrated in Ref. [14]. The results in Ref. [14] suggest that the distortion (zero line for current is inclined vs. the abscissa) of the cyclic voltammograms in the respective figures of Ref. [3] is caused by the inhomogeneous current distribution.

However, the use of point electrodes has a number of disadvantages, caused by the smallness of the contact area. It is hard to estimate the geometric area of the contact. The positioning of the point electrode at the same spot on the surface of the solid electrolyte is difficult in our arrangement. Occasionally a small hole is 'burned' through the solid electrolyte at the tip during measurements at higher temperatures and larger oxygen partial pressures, probably when the tip touches a defect of the polycrystalline oxygen ion conductor.

The following designations proved useful in the discussion of porous electrodes consisting of small particles of electrocatalyst: total area of active electrocatalyst, contact area between electrocatalyst and solid electrolyte and region of the three-phase boundary. A large number of papers is devoted to the question of where a given electrochemical reaction takes place and to what extent these three regions are involved. The total area can be determined by the BET method or other techniques. The ratio between total area and geometric area of the electrode represents the roughness factor. The contact area and the region of the three-phase boundary are more difficult to characterize. The contact area and the three-phase boundary, measured as the sum of the circumferences of the contact areas of the electrocatalyst particles, were determined by microscopy in Ref. [5] for the interface YSZ single crystal/Pt paste electrode.

## 2. Experimental

The measurements were made in a fully automated set-up described in Ref. [11]. This set-up allows one to take steady-state current–potential curves in the potentiostatic or galvanostatic modes and to carry out cyclic voltammetry, coulometry at a constant potential or the measurement of the potential–time dependence at a constant current. The Solartron 1286A electrochemical interface served as a programmable potentiostat controlled by a PC/486-compatible computer which produces the desired

potential–time profiles and also establishes the temperature by the use of two thermocouples and a special algorithm. The maximum time resolution is determined by the fastest data acquisition rate of the Solartron 1286A (15 readings  $s^{-1}$ ). The data are transferred in digital form to the computer, the memory of which was increased. Measurements and data processing can be done simultaneously by the same computer.

The cell is kept by a special sample holder (see fig. 2 of Ref. [11]) in a closed-end tube of quartz glass which is flushed by the given gas inside a tubular furnace heated by a direct current from a power supply. Three or four electrodes can be attached to the cell.

Different temperature ramps are feasible for which the start, stop and the magnitude of the temperature step can be programmed. Steps of 50°C were used in the present study. The chosen type of electrochemical measurement is made at a constant temperature. Before a measurement is started, the potential difference  $E_o$  between the RE and WE at open circuit is measured. A waiting period is applied until a stable value of this voltage is achieved. The level of stability (millivolts per minute) can be set by the program.

Samples of YSZ were cut from bars (Friatec AG, 8%Y<sub>2</sub>O<sub>3</sub>) of rectangular cross-section with a thickness of 0.1 to 0.12 cm. The two large surfaces were polished to 10 μm and cleaned in an ultrasonic bath. The arrangement of the electrodes is shown schematically in Fig. 1. The CE, produced by unfluxed Pt paste, covered the lower side of the YSZ disk and was contacted by a Pt foil. The RE consisted of a Pt foil pressed by a spring outside the holder onto the solid electrolyte. If the WE had a point contact, it was cut from a Pt foil of 0.1 cm thickness. An electrode with roughly the shape of a four-sided pyramid was obtained by grinding, polishing and cleaning in an ultrasonic bath. The contact area was estimated by optical microscopy and amounted to about  $6 \times 10^{-4} \text{ cm}^2$  if the determination was carried out at the completion of the measurements. The point of the electrode is pressed by a spring against the solid electrolyte. For steady-state measurements the currents of the point electrode became very small and widely scattered. Therefore a Pt electrode, produced by paste in the shape of a small disk, was used. It had a geometric surface of 0.05 cm<sup>2</sup>.

Measurements were usually, but not always, started after keeping the WE at 700°C for 1 h. It will be demon-

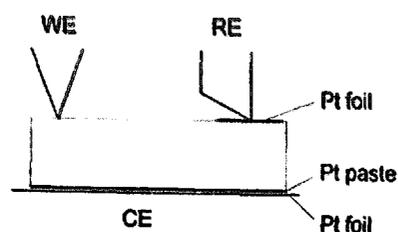


Fig. 1. Schematic diagram of the arrangement of the electrodes.

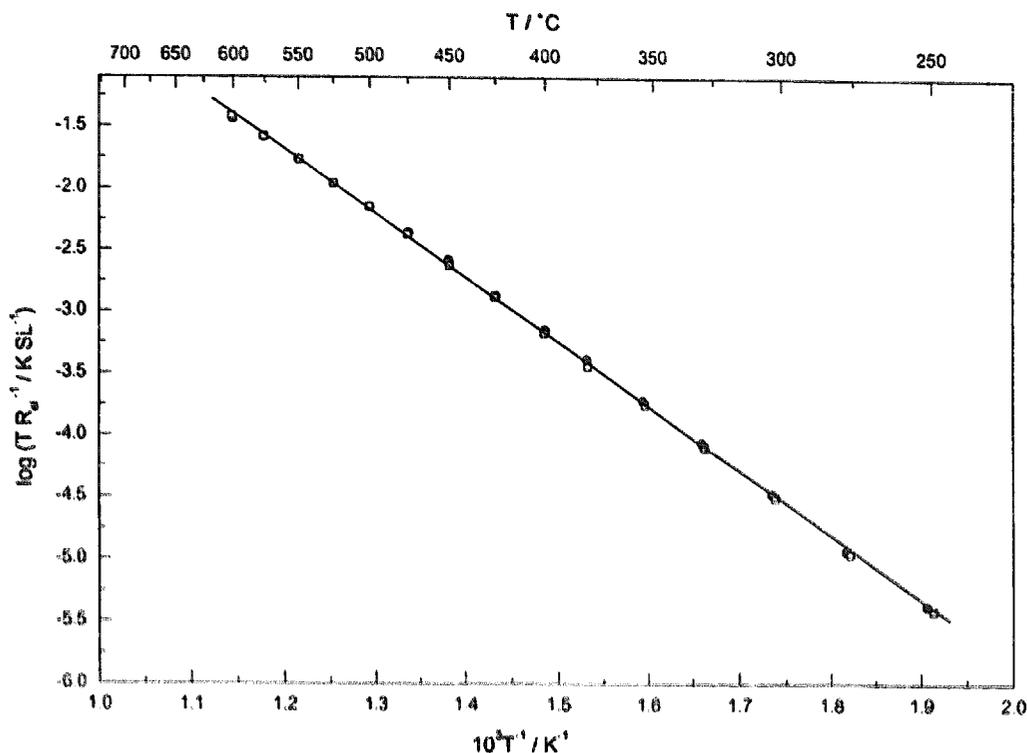


Fig. 2. Semilogarithmic plot of  $T/R_{cl}$  vs.  $1000/T$ .

strated that such a pretreatment procedure is not only necessary for sputtered or paste electrodes, but also for the solid electrodes used in this investigation. As with the experiments in Refs. [5,6] the three electrodes were exposed to the same gas atmosphere.

The determination of the resistance  $R_{cl}$  was carried out for some of the cells with point electrodes in a separate set-up by a four-probe a.c. technique in the way outlined in Ref. [11]. It was found that the cell had to be kept in the same holder for the  $R_{cl}$  determination and the cyclic voltammetry. It could not be removed from the holder between these experiments without changing the value of  $R_{cl}$ . The results of a measurement of  $R_{cl}$  for increasing and decreasing temperatures are given in Fig. 2 in a semilogarithmic plot of  $T/R_{cl}$  vs.  $1000/T$ . A straight line (Arrhenius type) is obtained. The slope of this line leads to an activation energy of 1.03 eV, agreeing well with the activation energy of conductivity determined independently for our solid electrolyte. This result confirms the correctness of the  $IR_{cl}$  determination since  $R_{cl}$  is inversely proportional to the conductivity of the solid electrolyte. The correction of some of the cyclic voltammograms for the  $IR_{cl}$  drop was done numerically by computer to evaluate the influence of the  $IR_{cl}$  drop on the shape of the  $I$ - $E$  curves, taken at  $50 \text{ mV s}^{-1}$ . It was found that corrections above  $500^\circ\text{C}$  affect the  $I$ - $E$  curves only in the region of

oxygen evolution (compare Fig. 5 for the general features of the cyclic voltammograms). Below  $500^\circ\text{C}$  the corrections become larger with decreasing temperature, mainly having an influence in the vicinity of the cathodic peak and at potentials of oxygen evolution. At  $300^\circ\text{C}$  the cathodic peak is shifted by about 0.1 V in our cell because of the  $IR_{cl}$  drop.

### 3. Results

The open-circuit voltage  $E_o$  was practically the same at the start and at the end of the measurements of  $I$ - $E$  curves by cyclic voltammetry.  $E_o$  is shown as a function of the temperature at different oxygen partial pressures in Fig. 3 for increasing and decreasing temperatures. In this case a pretreatment at  $700^\circ\text{C}$  was not done and the measurements were carried out from low to high temperatures and back. The  $E_o$  values for the second heating cycle agreed practically with those of the preceding cooling cycle and are not shown for this reason in Fig. 3.

The following experiments were made to obtain information about the oxygen layer after the pretreatment at  $700^\circ\text{C}$ . The temperature was allowed to cool to the desired value with the WE at open circuit. Then a cathodic sweep was started at  $50 \text{ mV s}^{-1}$  from  $E_o$  to  $-0.7 \text{ V}$ , followed at first by a positive one back to  $E_o$  and then by another

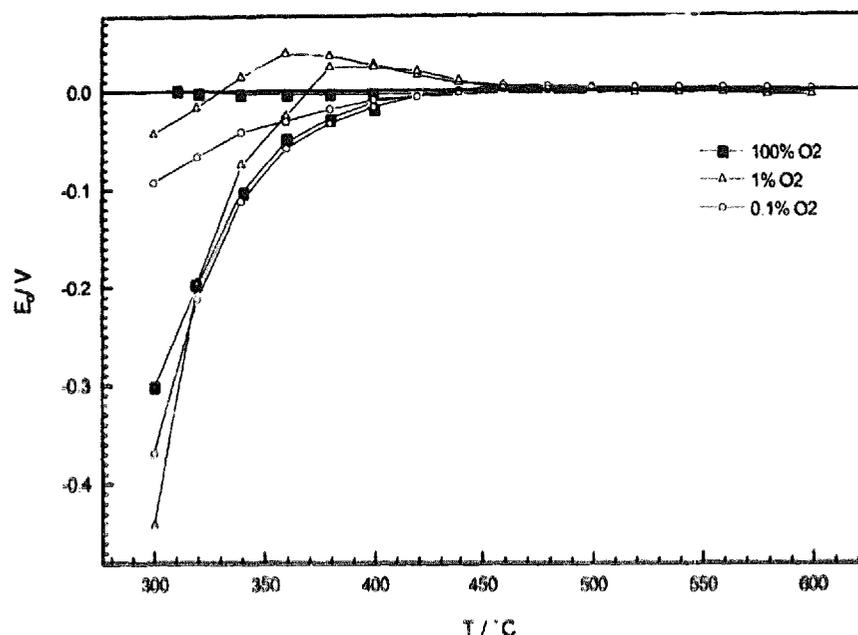


Fig. 3. Open-circuit voltage  $E_o$  at the start of the  $I$ - $E$  curves at different partial pressures of  $O_2$ .

cyclic sweep. The results are presented in Fig. 4 for two temperatures.

If the cyclic voltammogram is taken at 400°C without a preceding pretreatment at 700°C, the inner curve of Fig. 5 is obtained. In contrast, the outer curve is measured after the pretreatment.

Measurements in pure  $N_2$  are shown for different temperatures in Fig. 6. It should be pointed out that the RE is not well defined for these measurements.

The dependence of shape of the cyclic voltammograms upon oxygen partial pressure was relatively small, in agreement with the results in Ref. [5]. A similar behavior, like that in Ref. [5], was found with respect to the dependence of the  $I$ - $E$  curves upon sweep rates between 10 and 200  $mV s^{-1}$ . Therefore, the respective curves are not shown here. However, the dependence of the shape of the curves upon the anodic potential of reversal is illustrated in Fig. 7 for 0.1%  $O_2$  in the temperature range around 500°C.

Steady-state  $I$ - $E$  curves were taken in the potentiostatic mode on a paste electrode at first from  $E_o$  to 0.1 V and back at a given partial pressure of  $O_2$ . Subsequently, the measurement from  $E_o$  to -0.1 V and back to  $E_o$  followed. The lowest temperature for which this was feasible with acceptable scattering of the current was 400°C. Here the steady-state was defined arbitrarily as that point at which the change of the current with time at a constant potential was smaller than 1%  $min^{-1}$ . The  $I$ - $E$  curves in the vicinity of  $E_o$  are presented as an example for 1%  $O_2$  at different temperatures in Fig. 8. The  $I$ - $E$  curves at other partial pressures look similar and are not shown for this

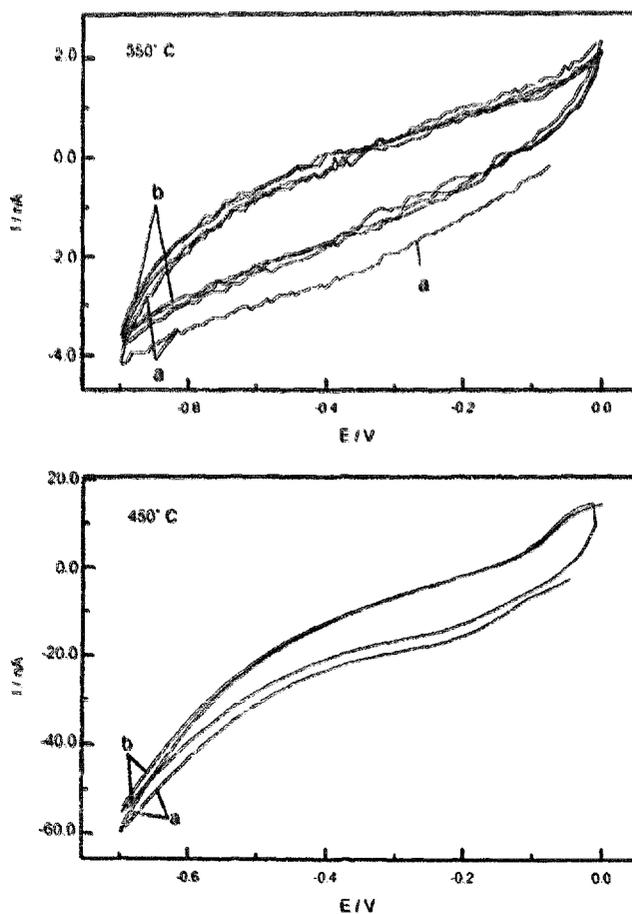


Fig. 4. Negative sweep from  $E_o$  to -0.7 V at  $50 mV s^{-1}$ , followed by a positive one to  $E_o$  (curve (a)) and another cyclic sweep between  $E_o$  and -0.7 V (curve (b)) for 350 and 450°C at 100%  $O_2$ .

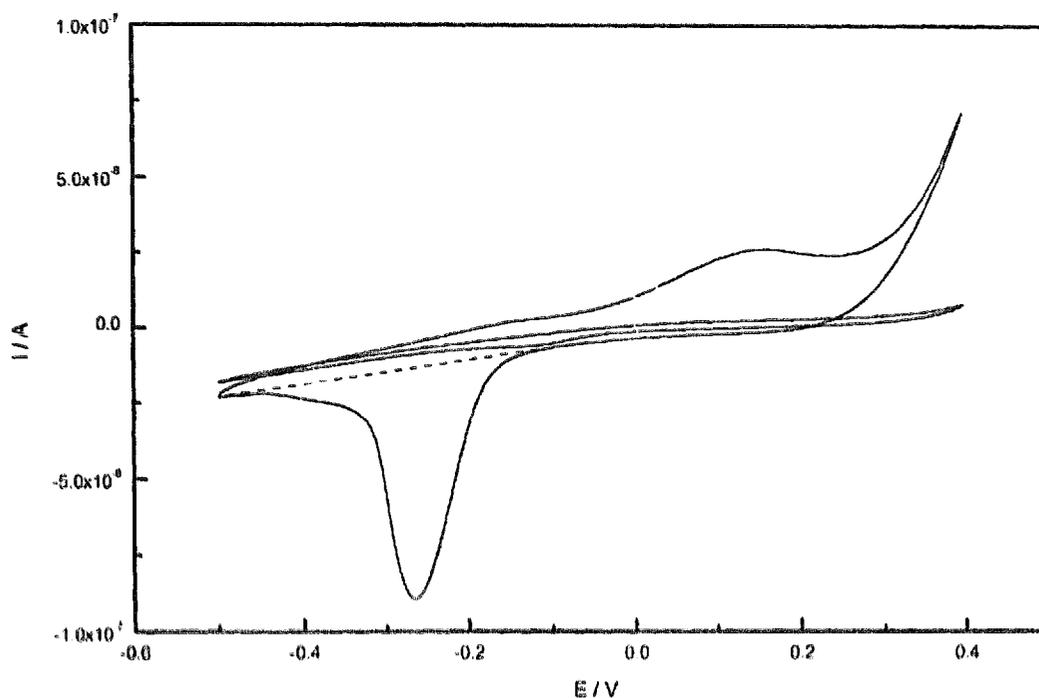


Fig. 5.  $I$ - $E$  curves obtained at 400°C and 50 mV s<sup>-1</sup> in 1% O<sub>2</sub> without (inner curve) and with (outer curve) pretreatment.

reason. The slope  $\Delta E/\Delta I$  was determined from  $I$ - $E$  curves in the vicinity of  $E_0$ . It is

$$R_p = (\Delta E/\Delta I)_{E_0} \quad (2)$$

The exchange current may be computed according to

$$I_0 = RT/FR_p \quad (3)$$

under the assumption that the rate-determining step of the reaction in Eq. (1) is a one-electron transfer reaction.  $R_p$  is

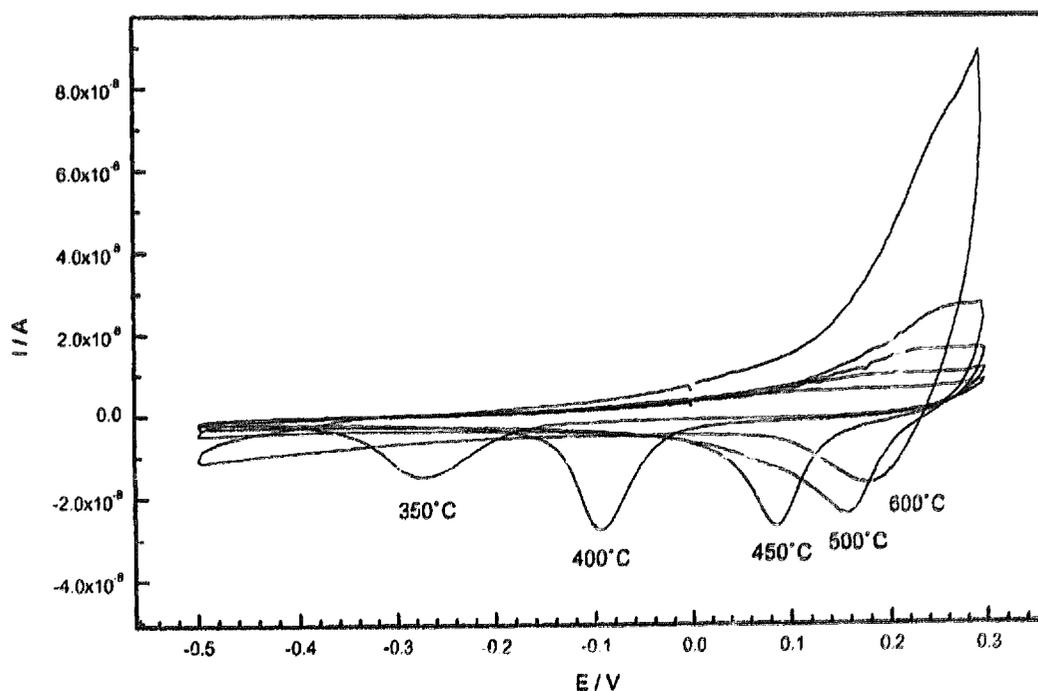


Fig. 6.  $I$ - $E$  curves taken in pure N<sub>2</sub> at 50 mV s<sup>-1</sup> at different temperatures.

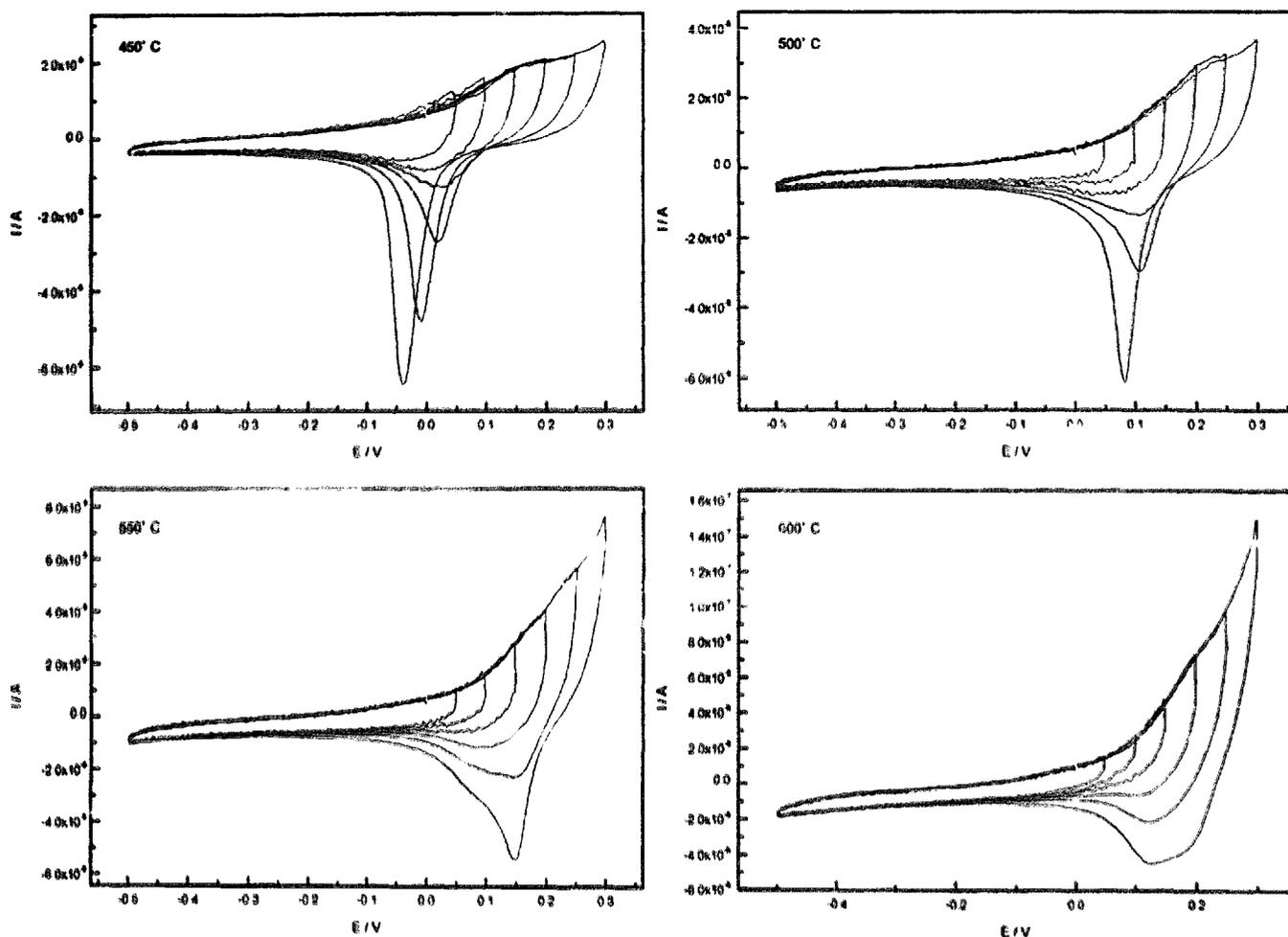


Fig. 7.  $I$ - $E$  curves obtained in 0.1%  $O_2$  at  $50 \text{ mV s}^{-1}$  for different anodic potentials of reversal in the temperature range around  $500^\circ\text{C}$ .

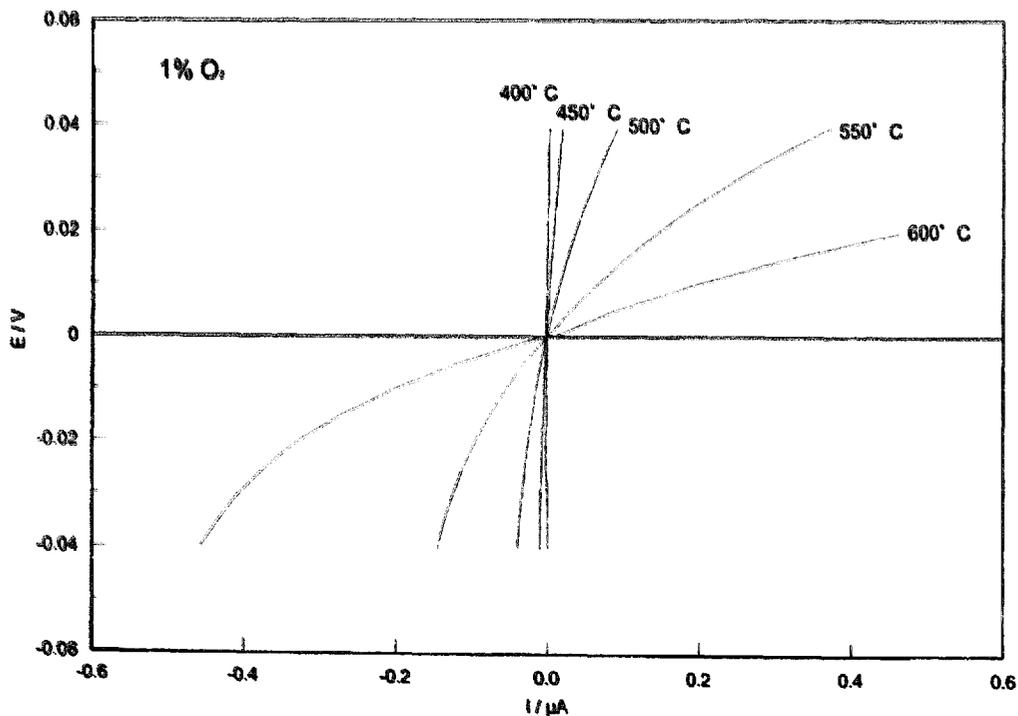


Fig. 8. Steady-state  $I$ - $E$  curves in the vicinity of  $E_0$ , measured potentiostatically at different temperatures for 1%  $O_2$  on the paste electrode.

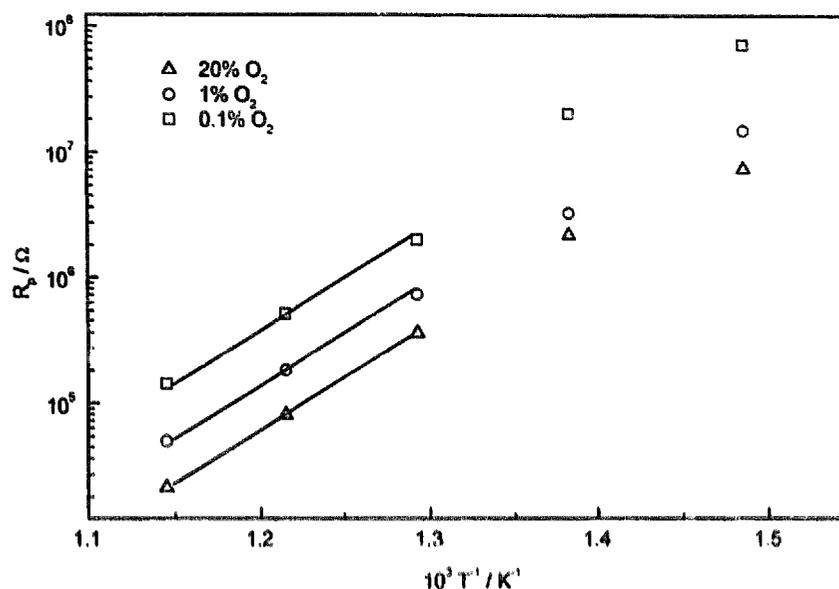


Fig. 9. Slope of the  $I$ - $E$  curves in the vicinity of  $E_o$  for three different oxygen partial pressures as a function of  $1000/T$  in a semilogarithmic plot:  $\Delta$ , 20% O<sub>2</sub>;  $\circ$ , 1% O<sub>2</sub>;  $\square$ , 0.1% O<sub>2</sub>.

plotted vs.  $1000/T$  in a semilogarithmic plot for different partial pressures of O<sub>2</sub> in Fig. 9.

#### 4. Discussion

##### 4.1. Pretreatment of point electrodes

The necessity of a high-temperature pretreatment for paste electrodes has already been pointed out [1–6]. Removal of organic residues and recrystallization of the Pt film are given as the reason. The results in Figs. 3 and 5 demonstrate that such a pretreatment is also required for solid electrodes. If the pretreatment is missing, the value of  $E_o$  is large at low temperatures (Fig. 3). The cyclic voltammogram at 400°C is barely recognizable.

It is suggested that the removal of impurities from the Pt surface and an increase of the contact area between the point electrode and the solid electrolyte during the pretreatment are responsible for the observed effects. The cold-worked point is pressed against a relatively hard substrate. At 700°C the stresses in the Pt electrode are annealed. This leads to enlargement of the contact area by about a factor of two, as found by comparison of the contact area before and after the experiment in the microscope. A sharp point cannot be maintained for this reason, as proved by a special experiment. It was shown in Ref. [5] that the area under the cathodic peak of the voltammogram taken at temperatures up to 400°C with an anodic reversal potential, before a strong contribution of the O<sub>2</sub> evolution sets in, is proportional to the contact area. Although there is an uncertainty in this result because of the difficulty in the determination of the peak area (see the subsequent discussion), the conclusion is considered valid. The geometry of

the point electrode favors the participation of the contact area over that of the region of the three-phase boundary. The voltammograms obtained on our point electrodes are very similar to those obtained on paste electrodes in Ref. [5] if the measurement is done under the same conditions.

##### 4.2. Oxygen layer at $E_o$ after pretreatment at 700°C

The curves in Fig. 4 were taken under conditions of the maximum influence of the oxygen partial pressure (100% O<sub>2</sub>). While the formation of an oxide is not expected to occur at an open circuit at 700°C according to the thermodynamic estimate in Ref. [5], an oxide might be produced during the subsequent cooling to a lower temperature, taking about 1 h at an open circuit in our set-up.

The first negative sweep at 350°C in Fig. 4 does not display a cathodic peak due to the reduction of an oxygen layer. In contrast, a small cathodic peak is recognizable at 450°C. This result is in agreement with similar measurements in air [3]. The cyclic voltammogram, taken subsequently at 350°C, does not show either the formation of the oxygen layer or its reduction. However, small peaks are visible during the positive and negative sweeps at 450°C.

The results in Fig. 4 demonstrate that the formation of the oxygen layer from O<sub>2</sub> at an open circuit is very small at temperatures below about 500°C on our point electrodes. Other evidence for this statement is given by a comparison of the voltammograms with the same upper potential of reversal in Fig. 6 and Fig. 7. The shape of the voltammograms in the region of the anodic formation and cathodic reduction of the oxygen layer is similar, keeping in mind that the  $E$ -scale is not the same since the RE for the curves in Fig. 6 is not well defined. The above results are in disagreement with the conclusions about the formation of

the oxygen layer by the dissociation of  $O_2$  at the three-phase boundary in Refs. [2,6]. Similar statements about the formation of the oxygen layer have already been given in Refs. [3,5].

#### 4.3. Establishment of the equilibrium potential of the reaction in Eq. (1)

The results in Fig. 9 confirm the conclusions in Refs. [10,11] that the equilibrium of the reaction in Eq. (1) is no longer established below about 500°C. It should be pointed out here that earlier work [15] on the oxygen surface exchange and diffusion in fast ionic conductors demonstrated that the reaction in Eq. (1) is dominated by the heterogeneous kinetics of oxygen exchange at the electrolyte surface. The rate constant is below  $10^{-11}$   $\text{cm s}^{-1}$  for Pt|YSZ at 700°C. So it is to be expected that equilibrium with oxygen will not be established below about 500°C.

The points for the higher three temperatures lie on straight lines with the same slope. The straight line is shifted to lower  $R_p$  values with an increase of the oxygen partial pressure. Such a temperature dependence of  $R_p$  is to be expected if the same step of the reaction in Eq. (1) is rate-determining and involves a dependence upon the oxygen partial pressure in some fashion. Systematic deviations occur at 450 and 400°C. The deviations will still be larger at 350 and 300°C. These deviations suggest the presence of additional reactions. The values of  $R_p$  become large at temperatures below 500°C. Using Eq. (3),  $I_0$  has values between  $6 \times 10^{-8}$  and  $6 \times 10^{-7}$  A at 500°C. Such values are not sufficient for the establishment of the equilibrium of the reaction in Eq. (1) below 500°C.

The large values of  $R_p$  also explain why the reaction in Eq. (1) does not contribute to a noticeable extent during the cathodic sweep of cyclic voltammograms at temperatures below 500°C in the range of the sweep rates employed here. The reduction of the oxygen layer is seen predominantly.

The above conclusion is not in disagreement with the results of the cooling cycle in Fig. 3. Heating to 700°C produces the same surface state for the WE and RE. The potential difference between the electrode and solid electrolyte is practically the same for the WE and RE, even when it is determined by a mixed electrode process below 500°C.

Previous determinations of kinetic parameters, for instance of the exchange current density [6], or values of the equilibrium potential of oxides, determined from thermodynamic data [5], have to be considered with caution below 500°C.

#### 4.4. Shape of cyclic voltammograms

The shape of cyclic voltammograms, taken with an upper potential of reversal of 0.3 V at temperatures up to

450°C, can be interpreted by the anodic formation and cathodic reduction of either a thin layer of oxides [5] according to



or of a layer of chemisorbed oxygen [2,6,7] according to



A distinction in favor of oxides was made in Ref. [5] on the basis of the charge/(geometric contact area) determined from the area under the cathodic peak and subsequently converted to charge/(real contact area). The latter quantity was found to be sufficient to form five to seven layers of PtO.

It was not stated [5] if the determination of charge/area was carried out in the same way as in Refs. [2,6], using the dashed line of the outer curve in Fig. 5 as zero line. There is an uncertainty in the procedure of Refs. [2,6] because of the residual cathodic current during the negative sweep. This uncertainty was already recognized in Ref. [3] and becomes larger with increasing temperature above 450°C.

The area under the cathodic peak was obtained for the point electrode by integration with a zero line drawn as in Fig. 5. The results, given in millicoulombs/(square centimeter of geometric area), were: 0.14 at 300°C, 0.145 at 400°C and 0.15 at 500°C. These values correspond [16] to less than a monolayer of chemisorbed oxygen atoms (Pt-O) on solid Pt electrodes in aqueous systems. It is conceivable that our charge densities are somewhat too small, just as the values determined in other papers by the same procedure, because the residual current may also originate from the reduction of the oxygen layer. However, they are considerably smaller than the respective values in Ref. [5] for a paste electrode. Our data, which do not involve a determination of the real surface of the contact area, are in favor of the electrochemical process according to Eq. (5).

It is useful for a detailed discussion of the shape of cyclic voltammograms to consider two temperature ranges: below and above 450°C. The shape of cyclic voltammograms below 450°C has a certain similarity to those taken [16] at polycrystalline Pt electrodes in 2.3 M  $H_2SO_4$  at temperatures between -7 and 70°C and in 1 M  $HClO_4$  at room temperature: there is a broad wave, due to the formation of the oxygen layer, before  $O_2$  evolution sets in during the positive sweep. A relatively narrow reduction wave of the oxygen layer is seen during the negative sweep. A closer comparison of the cyclic voltammograms in the different systems reveals a large difference for the width of the anodic wave. In the said acids the anodic wave starts about 0.4 V below the potential of the oxygen electrode. The beginning of this wave occurs [16] even earlier in alkaline solutions. In contrast, the anodic wave starts at about the potential of the oxygen electrode at the interface Pt|YSZ. Its width amounts to about 0.3 V to the beginning of  $O_2$  evolution at temperatures below 450°C.

A possible mechanism for the formation of the oxygen layer at the interface Pt|YSZ was given in Ref. [6]:



It is suggested here that the intermediate  $\text{Pt-O}^-$  is not seen in the cyclic voltammograms below 450°C. The interpretation for the different shapes of the anodic and cathodic waves of the cyclic voltammograms, advanced for the first time in Ref. [16] for aqueous systems, can also be applied to the above reaction mechanism involving a two-electron transfer. Our conclusion is not in agreement with  $\text{Pt-O}^-$  as the more strongly bonded intermediate [6] determining the shape of the voltammograms with one cathodic peak. Spectroscopic evidence [17] is cited in Ref. [6] in support of  $\text{Pt-O}^-$ . However, this evidence is not strong. A direct peak, corresponding to  $\text{Pt-O}^-$ , was not observed. Instead the presence of such a peak was inferred on the basis of a difference spectrum, constructed from two spectra for YSZ. These two spectra were taken through the porous Pt electrode at open circuit and at an anodic potential. The additional assumptions, made in the construction of the difference spectrum, are not discussed in Ref. [17].

The shape of the cyclic voltammograms begins to change with increasing temperature above 450°C (Fig. 7). The anodic currents become larger. This is attributed to the contribution of the partial current of  $\text{O}_2$  evolution. The hindrance of this reaction decreases with temperature. Simultaneously the cathodic wave becomes broader. A comparison with the curves in a nitrogen atmosphere (Fig. 6) shows the same effect for the anodic wave, and to a lesser extent for the cathodic wave.  $\text{O}_2$  evolution occurs also during the negative sweep at positive potentials. The current, measured in this potential region, is the difference between the anodic current of  $\text{O}_2$  evolution and that of  $\text{Pt-O}$  reduction. The broadening of the cathodic wave may result from this effect. A conclusion on the existence [7] of two cathodic peaks in a broad wave can only be considered certain if the voltammograms, corrected for the partial current of  $\text{O}_2$  evolution, display two peaks.

Although the main part of this investigation deals with the temperature range between 300 and 600°C, a few cyclic voltammograms were run on paste electrodes at temperatures of 700 and 800°C. These curves had a shape like that of the respective curves in Ref. [3] and are not shown for this reason. The reader is referred to Ref. [3].

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