



# Voltammetric studies of electrochemical processes at the interface Pt/BICUVOX.10 between 300 and 600°C

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**Abstract**—Electrochemical processes occurring at the interface Pt/BICUVOX.10 were investigated by cyclic voltammetry and potentiostatic current–potential curves, taken under steady-state conditions, in different mixtures of nitrogen and oxygen at temperatures between 300 and 600°C. Similar experiments were carried out for comparison at the Pt/YSZ interface. Point or paste electrodes were used. The equilibrium of the oxygen electrode is not established below 500°C at both interfaces any more. Reasons for this behavior are presented. It is concluded on the basis of a comparison of the shape of voltammograms at different interfaces that BICUVOX.10 is reduced and oxidised electrochemically. Simultaneously a reoxidation of the solid electrolyte by O<sub>2</sub> from the gas phase occurs. At temperatures below 500°C the reoxidation is not fast enough to avoid a hysteresis at cathodic currents of the voltammograms. At higher temperatures and larger partial pressures of O<sub>2</sub> the hysteresis disappears. © 1997 Elsevier Science Ltd

*Key words:* voltammetry, interface, platinum, oxygen ion conductor, oxygen electrode, gas phase.

## INTRODUCTION

The designation BICUVOX.10 was given to the ternary oxide Bi<sub>2</sub>V<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>5.35</sub> in the first publications [1, 2] on the new oxygen ion conductor which has a much better conductivity at temperatures below 700°C than stabilised zirconia. The high conductivity was attributed [1, 2] to the stabilisation of the  $\gamma$ -phase of the parent compound Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> [3] by partial substitution of vanadium by copper. Detailed investigations have been published on the structure [1, 2, 4], the temperature dependence of the ionic conductivity [1, 5, 6], the thermal stability [5, 7] and the electronic conductivity [8] of BICUVOX.10. In contrast, results on the electrochemical stability are scarce in the literature. The results in [8] indicate that a significant reduction of BICUVOX.10 is likely to occur below  $-0.4$  to  $-0.3$  V with respect to the oxygen electrode in air. After applying a cathodic voltage of 2 V for 2 min, the potential decay was measured [8] at open circuit under a controlled oxygen atmosphere. The potential  $E_w$  of a second plateau in the potential–time curves was regarded as

a measure of the cathodic limit of the potential region of electrochemical stability. After heating to high temperature the sample appeared more easily reducible.

Studies of the electrochemical stability of the interface Pt/BICUVOX.10 by voltammetric techniques which are very useful for this purpose are reported in this communication for the temperature range 300 to 600°C in various gas mixtures ((100 – X)%N<sub>2</sub> + X%O<sub>2</sub>). A few cyclic voltammograms were also taken with gold electrodes to obtain some information about the influence of the electrocatalyst on the shape of the curves. Since yttria stabilised zirconia (YSZ) can be considered as a stable oxide at temperatures between 300 and 600°C, the same measurements were also carried out at the interface Pt/YSZ for which several voltammetric studies were reported [9–12]. Results for the interfaces Pt/BICUVOX and Pt/YSZ, involving platinum as the electrocatalyst, are compared.

## EXPERIMENTAL

The measurements were made at constant temperature in a fully automated set-up for which a detailed

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description is given in [13]. The thin cells with solid-electrolyte were kept by a special holder in a quartz glass tube flushed by the desired gas. Samples of YSZ were cut from bars (Friatec AG, 8%  $Y_2O_3$ ) of rectangular cross section with a thickness of 0.1 to 0.12 cm. Disks of BICUVOX.10 with a diameter of 1 cm and a thickness of 0.1 cm were prepared with an average density of 92% as in [14]. The large surfaces of both types of samples were polished to  $10\ \mu\text{m}$  and cleaned in an ultrasonic bath.

Point electrodes and porous electrodes, produced from unfluxed Pt paste, were used. The point electrodes were cut from a Pt foil of 0.1 cm thickness and were given the shape of a four-sided pyramid by polishing. The arrangement of the Pt point electrodes is shown in Fig. 1 for the two oxygen ion conductors. The working electrode (WE), counter electrode (CE) and reference electrode (RE) are exposed to the same gas. There is a slight difference between Pt/YSZ and Pt/BICUVOX.10. The pretreatment at  $700^\circ\text{C}$  in 100%  $O_2$  leads to a flattening of the Pt point pressed by a spring of the holder against the relatively hard zirconia. The contact area of the flat portion of the Pt tip was determined at the end of the experiment by microscopy and amounted to  $6 \cdot 10^{-4}\ \text{cm}^2$ . In contrast, the Pt tip penetrated slightly into the relatively soft BICUVOX.10 and did not change its shape during the pretreatment at  $700^\circ\text{C}$ . Using microscopy, it was estimated that the contact area between Pt and BICUVOX.10 was about  $10^{-3}\ \text{cm}^2$ . The geometric area of the paste electrode was  $0.05\ \text{cm}^2$ . A Pt foil, pressed against the solid electrolyte, was used as

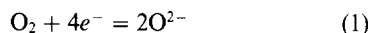
reference electrode in the experiments with YSZ and BICUVOX.10.

Since gold is a relatively soft material it was not possible to produce a real point electrode. The deformation at  $700^\circ\text{C}$  under the spring pressure is large. At the beginning of the experiments the electrode had the shape of a small cylinder which was bent in contact with the solid electrolyte. The contact area was difficult to reproduce and was not determined by microscopy for this reason.

A composite cell consisting of both solid electrolytes was made for the measurement of the open-circuit potential as a function of temperature and  $O_2$  partial pressure. Again both sides of the cell were exposed to the same gas. It was found by separate experiments that a strong bond between YSZ and BICUVOX.10 may be obtained in the following way. After applying Pt paste electrodes on one side of the BICUVOX.10 disk and of the YSZ sample and sintering them at  $700^\circ\text{C}$  for 1 h, the YSZ piece was put on top of the BICUVOX.10 disk. Pressure was exerted by an  $Al_2O_3$  block of 250 g on top of the YSZ. Heating to  $811^\circ\text{C}$  with subsequent cooling at  $3^\circ\text{C}/\text{min}$  followed. The YSZ piece sank slightly into the BICUVOX.10 sample and was firmly attached to it.

## RESULTS

Results obtained in investigations about the establishment of the equilibrium of the reaction



are described at first. The open-circuit potential  $E_o$  of the composite cell Pt/YSZ/BICUVOX.10/Pt is shown as a function of temperature for different oxygen partial pressures in Fig. 2. Both sides of the cell were exposed to the same gas. The Pt/YSZ interface served as the reference electrode. By using a preamplifier with an input impedance of  $10^{14}\ \Omega$  in one run, it was verified that the input impedance (about  $10^{10}\ \Omega$ ) of the Solartron 1286A Electrochemical Interface which served as a programmable potentiostat did not affect the  $E_o$ -measurement.

After defining a change of less than 1 mV/min as satisfactory for the achievement of steady state, the  $I$ - $E$  curves were measured potentiostatically on paste electrodes in the vicinity of  $E_o$  at different temperatures and partial pressures of  $O_2$ . The anodic branch was measured up to 0.1 V and back to 0 at constant partial pressure of  $O_2$ . It followed the measurement of the cathodic branch at the same partial pressure. An example is presented in Fig. 3.

The slope  $\Delta E/\Delta I$  was determined from curves like those in Fig. 3. It is:

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

A semilogarithmic plot of the polarisation resistance  $R_p$  vs  $1000/T$  is given in Fig. 4(a) for Pt/YST

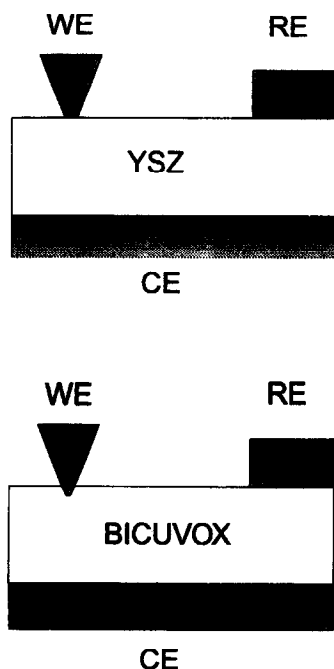


Fig. 1. Schematic diagram of the arrangement of point electrodes for YSZ and BICUVOX.10.

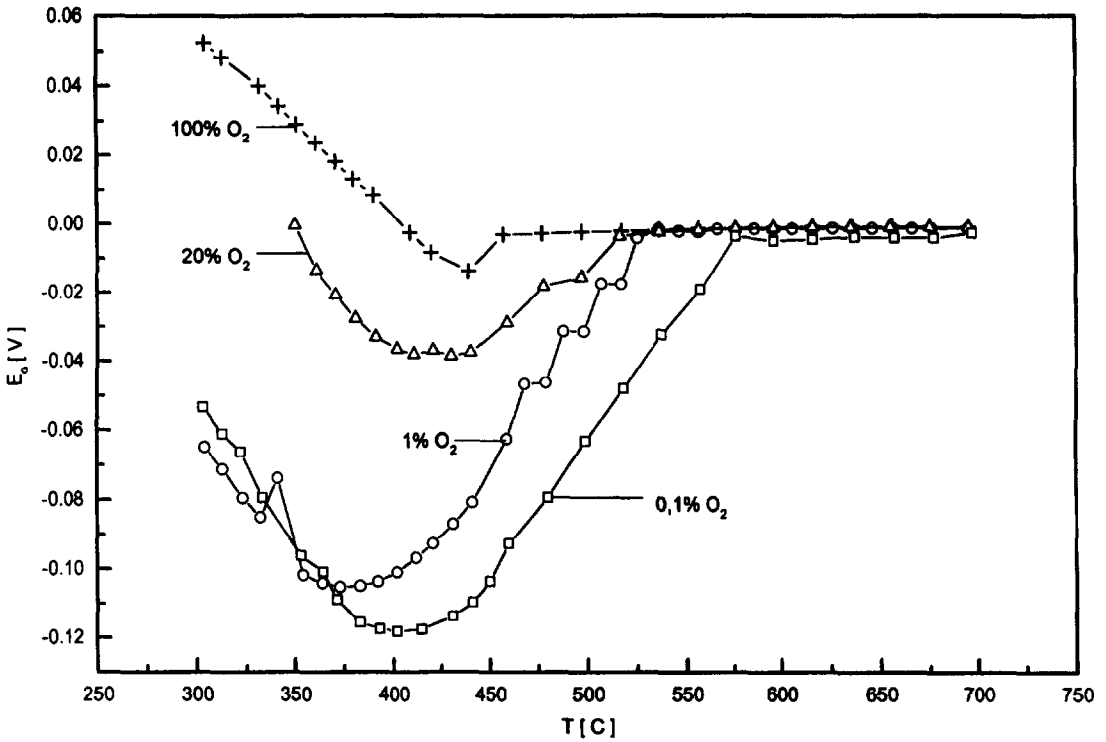


Fig. 2. Open-circuit potential  $E_o$  of the composite cell Pt/BICUVOX.10/YSZ/Pt as a function of temperature for several partial pressures of oxygen.

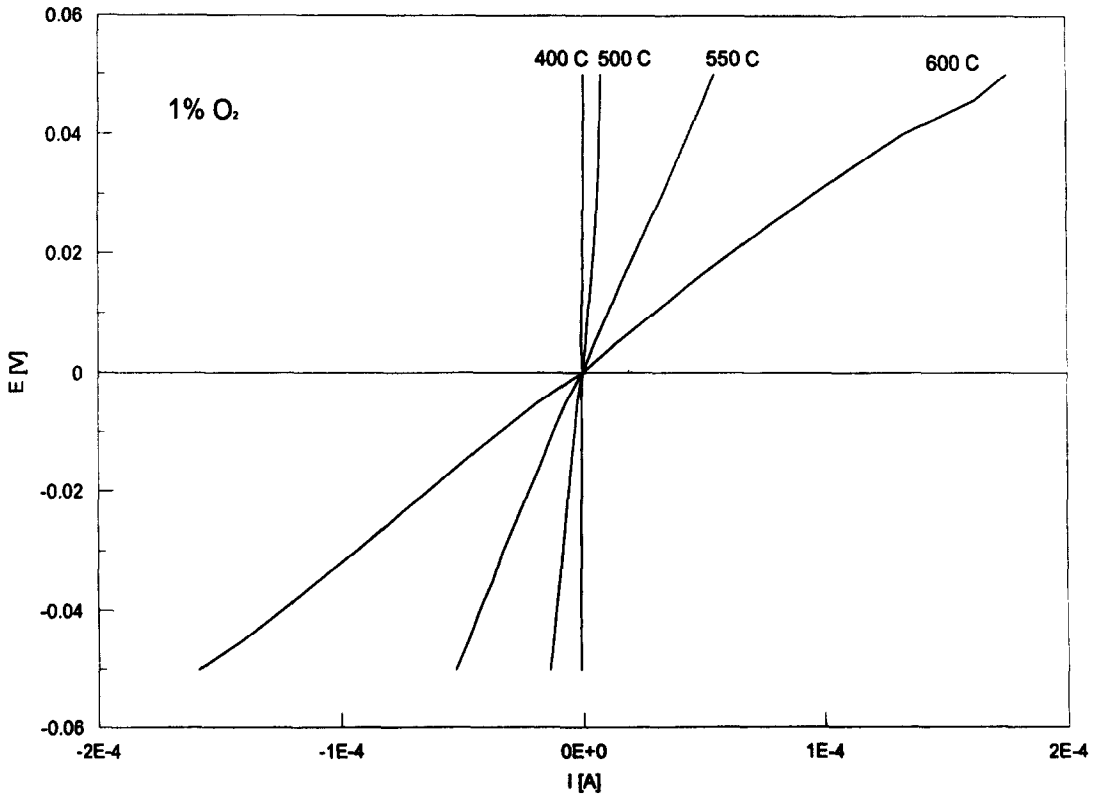


Fig. 3. Steady-state  $I-E$  curves, measured potentiostatically on cells with Pt/BICUVOX.10 at different temperatures in the vicinity of  $E_o$ .

and (b) for Pt/BICUVOX.10 as a function of the partial pressure of  $O_2$ .

Cyclic voltammograms at 50 mV/sec are shown in Fig. 5 for the interfaces Pt/YSZ (a) and Pt/BICUVOX.10 (b) and for Au/YSZ (a) and Au/BICUVOX.10 (b) in Fig. 6. Point electrodes were used.

The anodic potential of reversal of cyclic voltammograms was kept constant while the reversal at the cathodic side was gradually moved to more negative potentials. The results are presented for 400°C as an example in Fig. 7.

Cyclic voltammograms taken with 5 mV/sec at Pt/BICUVOX.10 are presented in Fig. 8 at 300 and 400°C for the two extreme partial oxygen pressures used in this work. The respective plots at 500 and

600°C are contained in Fig. 9. Point electrodes were employed. Voltammograms measured with different sweep rates at Pt/BICUVOX.10 at 500°C are not displayed in Fig. 9.

## DISCUSSION

### Establishment of the equilibrium potential of reaction (1)

Figure 2 demonstrates that the value of  $E_o$  is close to 0 for temperatures between 575 and 700°C, independent of the oxygen partial pressure. The increase of the partial pressure leads to an extension of the temperature range to about 550 for 1%  $O_2$ , to

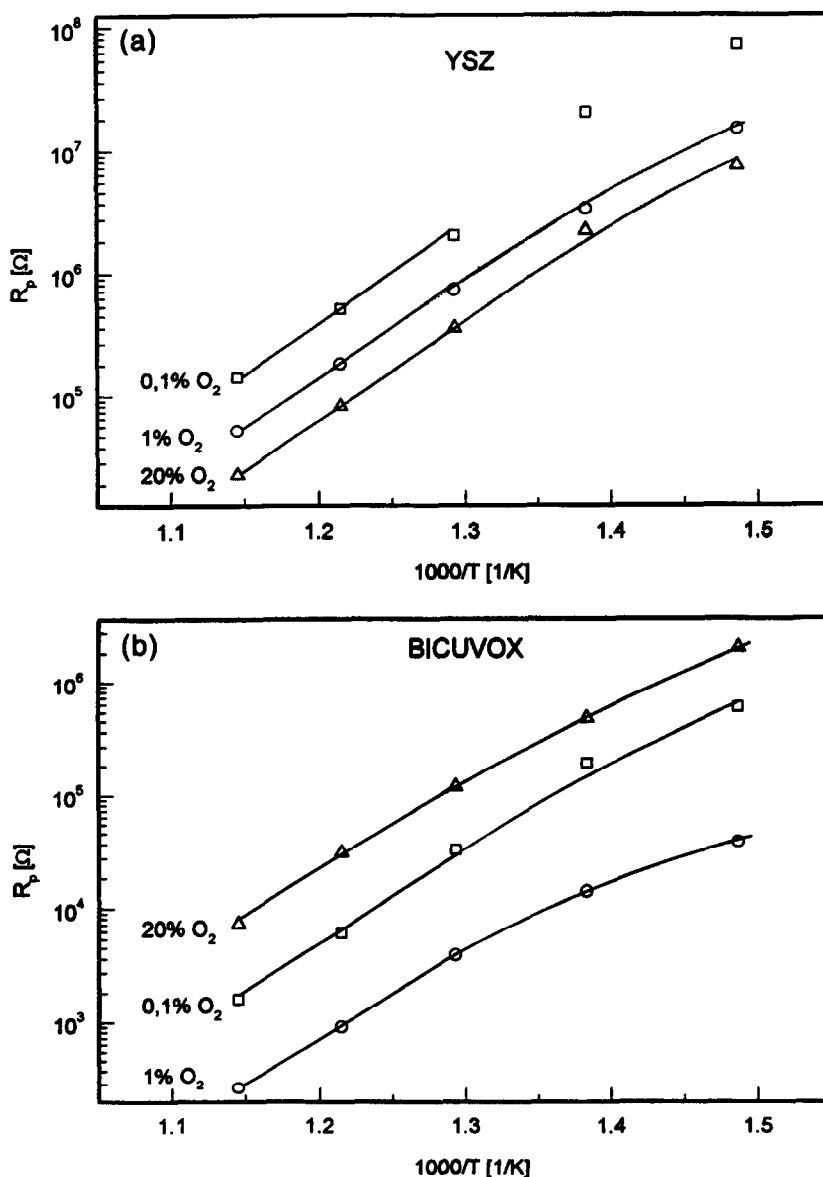


Fig. 4. Semilogarithmic plot of the polarisation resistance for cells with Pt/YSZ (a) and Pt/BICUVOX.10 (b) vs  $1000/T$  for different partial pressures of oxygen.

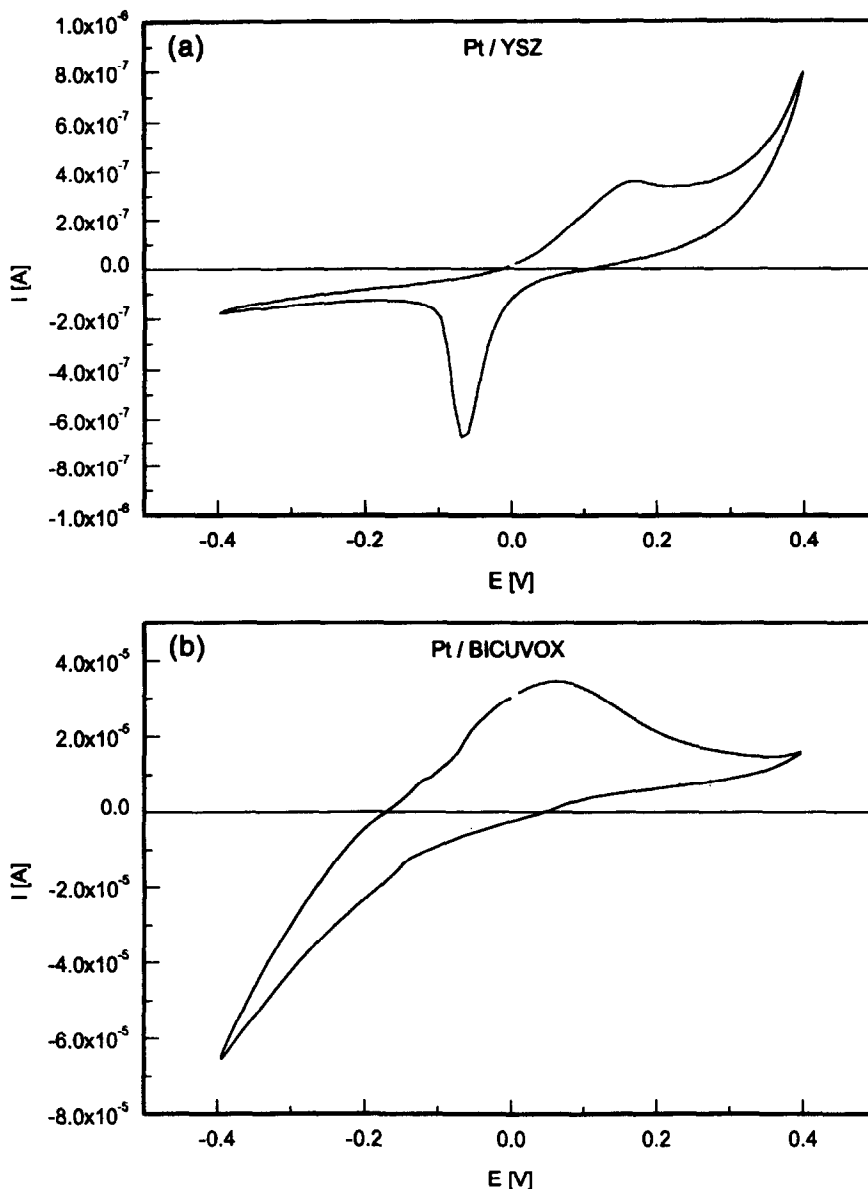


Fig. 5. Voltammograms, obtained at 400°C and 1% O<sub>2</sub> with 50 mV/sec at the interfaces (a) Pt/YSZ and (b) Pt/BICUVOX.10.

about 525°C for 20% O<sub>2</sub> and to about 450°C for 100% O<sub>2</sub>. It is well known that the equilibrium of reaction (1) is established at the interface Pt/YSZ at higher temperatures. Therefore the conclusion about the establishment of this equilibrium may also be drawn for the interface Pt/BICUVOX.10 for the temperature ranges stated for a given partial pressure of O<sub>2</sub>. The deviation of  $E_0$  from 0 at lower temperatures is discussed next.

The semilogarithmic plot of  $R_p$  vs  $1000/T$  for Pt/YSZ in Fig. 4 yields straight lines (Arrhenius) with the same slope at temperatures between 500 and 600°C. The experimental points begin to deviate from the straight lines below 500°C. It is concluded that side reactions which take place at a relatively small

rate begin to affect the establishment of the equilibrium of reaction (1) because the  $R_p$  values are very large. A mixed electrode potential is measured.

The temperature dependence of the  $R_p$  values for the interface Pt/BICUVOX.10 is similar to that for the interface Pt/YSZ. The slopes of the linear portions of the curves in Fig. 4 is practically the same for both interfaces. This suggests that the same step of net reaction (1) is rate-determining as already suggested in [15]. The  $R_p$  values are considerably smaller for the interface Pt/BICUVOX.10 than those for the interface Pt/YSZ. The latter result is in general agreement with earlier work [15] about the oxygen transfer on yttria substituted ZrO<sub>2</sub> and erbia substituted Bi<sub>2</sub>O<sub>3</sub> with Pt electrodes.

The pressure dependence of  $R_p$ , observed in the present study, differs for the two interfaces. The polarisation resistance decreases with the partial pressure of  $O_2$  for Pt/YSZ. For Pt/BICUVOX.10 a pressure dependence does not exist or is too complicated to be established on the basis of the present measurements. In [15] the pressure dependence of the polarisation resistances of the total cell, also containing a contribution from the counter electrode, was determined. In addition the compositions of the solid electrolytes and the production of the Pt electrodes differ from those in the present study. The same type of pressure dependence which is rather complicated [15] need not be expected for

different systems for the above reasons. Older work on the pressure dependence of the polarisation resistance of the cell is reviewed in [15].

The  $R_p$  values for Pt/BICUVOX.10 are not yet sufficiently small for temperatures below  $500^\circ\text{C}$  to explain a disturbance of the equilibrium of reaction (1) by a side reaction occurring at a small rate. There must be another reason. It is suggested that an electrochemical reaction involving the solid electrolyte itself takes place at a reasonable rate. Evidence that such an electrochemical reaction exists is discussed subsequently in connection with the voltammograms. A mixed potential is measured at the interface Pt/BICUVOX.10 below the tempera-

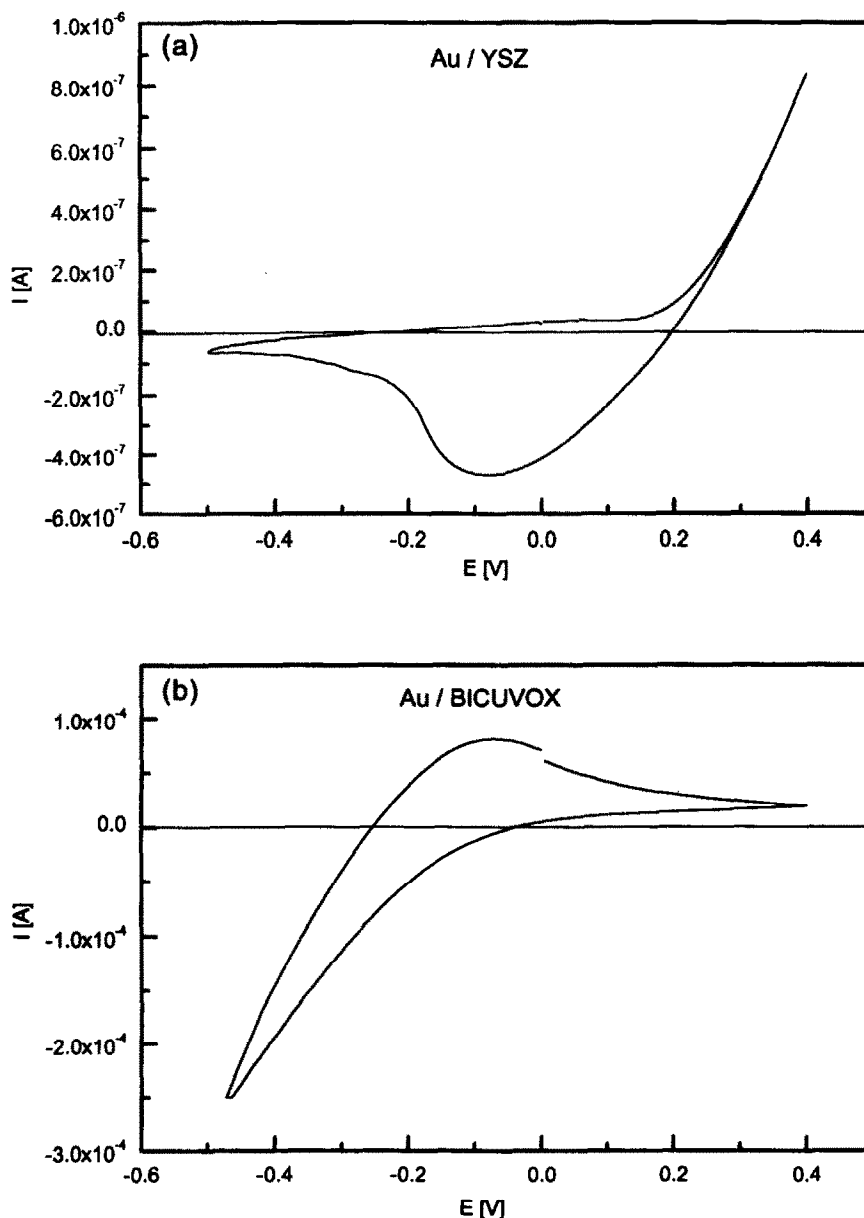


Fig. 6. Voltammograms obtained at  $450^\circ\text{C}$  and 1%  $O_2$  with 50 mV/sec at the interfaces (a) Au/YSZ and (b) Au/BICUVOX.10.

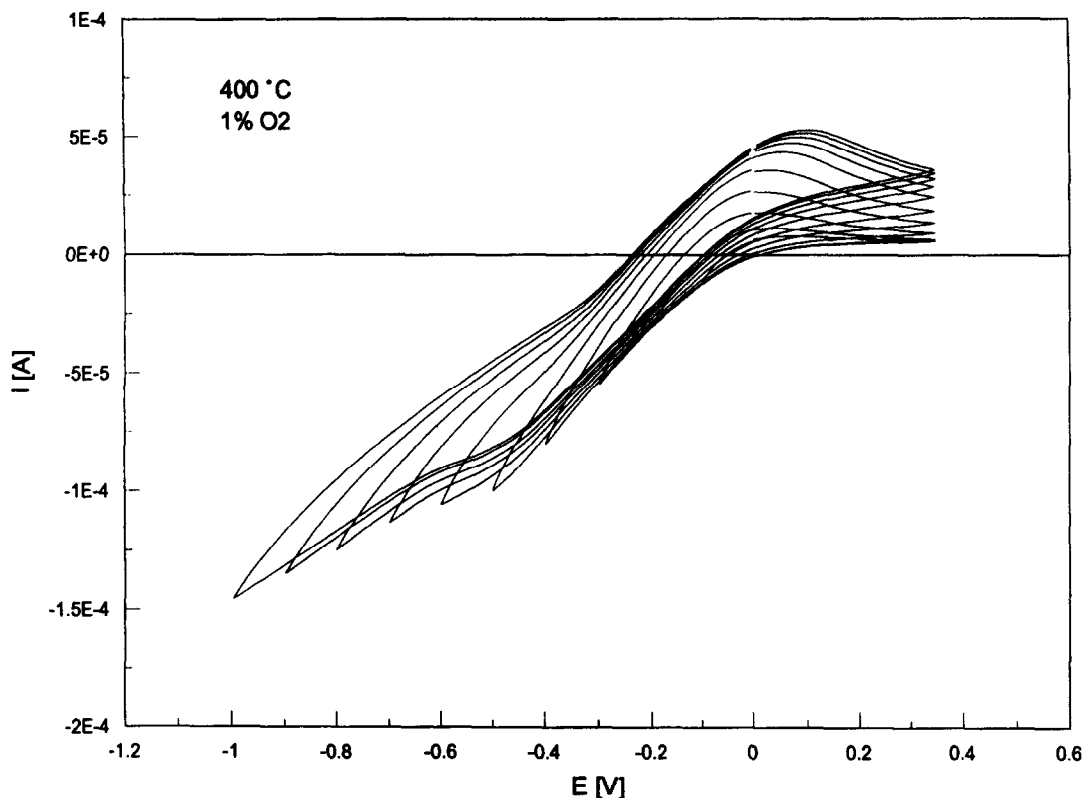


Fig. 7. Voltammograms with constant anodic and variable cathodic potential of reversal taken at the interface Pt/BICUVOX.10 with 10 mV/sec at 400°C.

tures stated above for the different partial pressures of  $O_2$ . The reduction of  $O_2$  is the cathodic process while the oxidation of the solid electrolyte represents the anodic process.

It should be mentioned here that an attempt was made to simulate the experimental current-potential curves, measured under steady-state conditions between 0.1 V and  $-0.1$  V *vs* RE at different partial pressures of  $O_2$ , by theoretical curves. The latter curves were computed under the simplifying assumptions that a one-electron transfer step is rate-determining for the net reaction and that the coverage with  $O_{ad}$  is constant. The agreement between simulated and experimental  $I-E$  curves was not satisfactory. The respective curves are not shown. It is likely that a more complicated mechanism, as suggested for instance in [16], has to be considered in the simulation.

#### Conclusions from the comparison of voltammograms at different interfaces below 500°C

The formation of an oxygen layer, accompanied by oxygen evolution at larger potentials, is reflected (upper curves in Figs 5 and 6) by the shape of the cyclic voltammograms during the anodic sweep for Pt/YSZ [9–12] and Au/YSZ [17]. Here “oxygen layer” designates chemisorbed oxygen atoms or a thin oxide. The reduction of the oxygen layer is

shown by waves of different width during the cathodic sweep. Pt and Au behave differently in aqueous solutions [18]. As to be expected there is also a great difference in the shape of the voltammograms on Pt/YSZ and Au/YSZ.

In contrast, the voltammograms for Pt/BICUVOX.10 and Au/BICUVOX.10 look very similar (lower voltammograms in Figs 5 and 6). There is no indication of the formation or reduction of an oxygen layer on the electrocatalyst for Pt/BICUVOX.10 and Au/BICUVOX.10. The currents are considerably larger in the lower voltammograms than in the higher ones. For Pt this difference cannot be explained by a different size of the contact area between electrocatalyst and solid electrolyte. The geometric contact area for Pt/BICUVOX.10 is only about twice that for Pt/YSZ.

During the cathodic sweep the voltammograms for cells with BICUVOX.10 do not reveal the presence of a wave. The current is anodic at first and passes through zero before becoming cathodic. It is a smooth curve. There is a large hysteresis between this curve and the declining branch in the first part of the anodic sweep. The hysteresis becomes larger when the potential of reversal moves into the cathodic direction (Fig. 7). Simultaneously the height of the wave during the subsequent anodic sweep increases. The anodic wave is of considerable width.

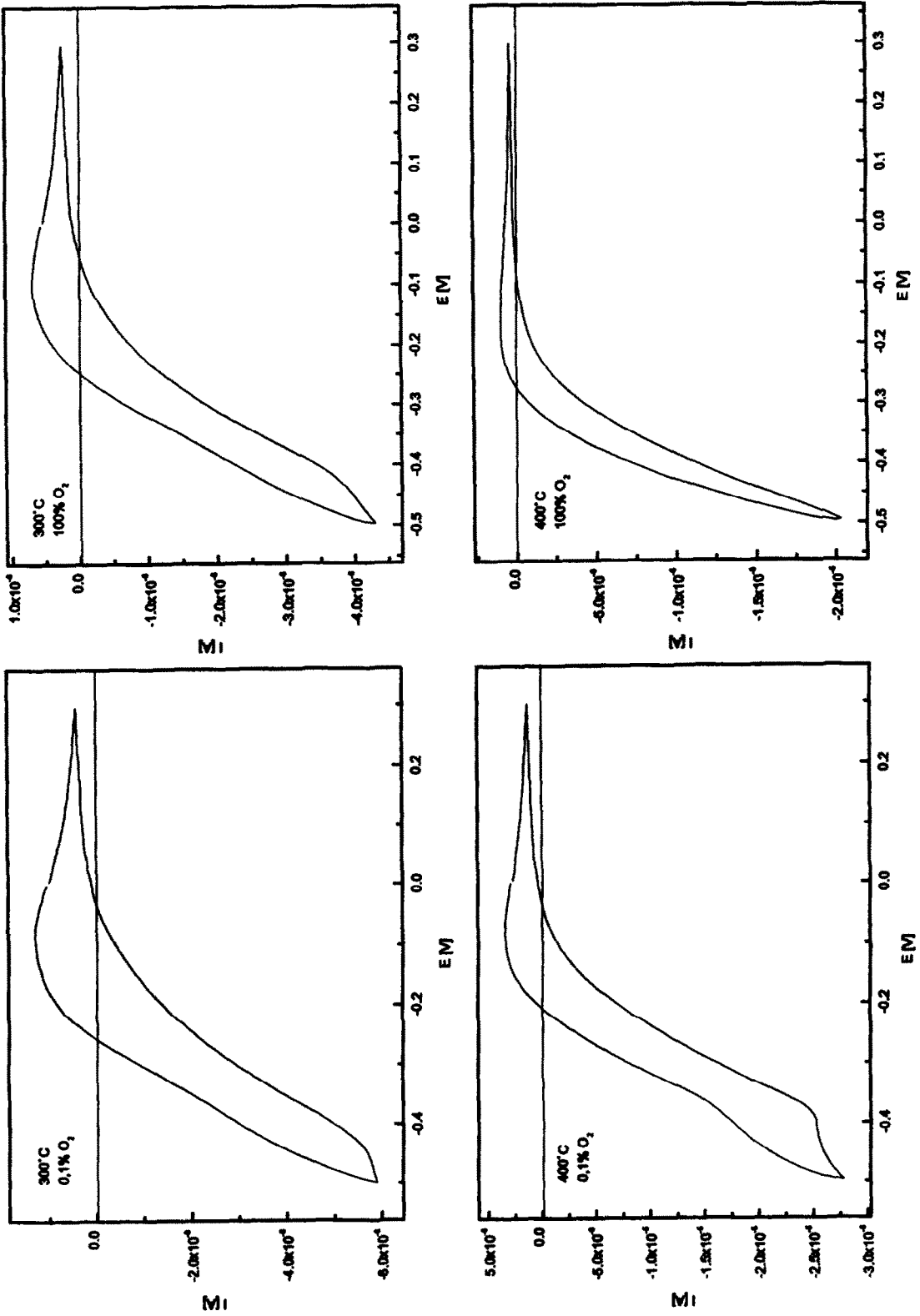


Fig. 8. Voltammograms taken with 5 mV/sec at 300 and 400°C at different oxygen partial pressures at Pt/BICUVOX.10.



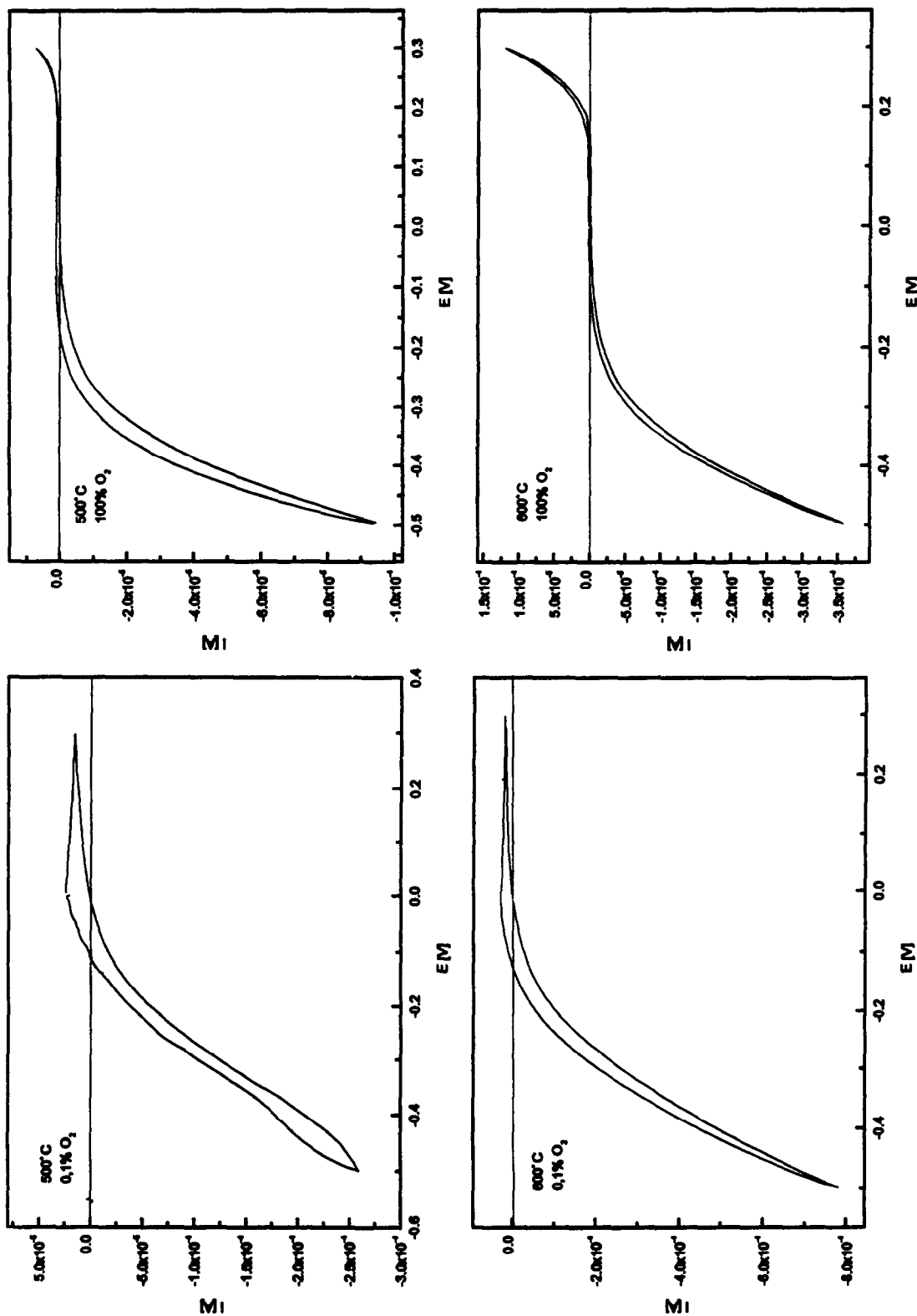


Fig. 9. Voltammograms taken with 5 mV/sec at 500 and 600°C at different oxygen partial pressures at Pt/BICUVOX.10.

It is suggested that a portion  $P$  of the oxygen which is reduced during the cathodic sweep originates from a reduction of the ternary oxide itself. A noticeable reduction of the ternary oxide starts at about  $-0.3$  V in agreement with the results of [8]. The rest  $(1 - P)$  of the oxygen comes from  $O_2$ . The portion  $P$  is replaced by reoxidation of the ternary oxide at potentials of the anodic wave. Finally it should be mentioned that some voltammograms were also taken in  $N_2$  ( $P = 1$ ). Their shape was similar to that of curves at 0.1%  $O_2$ , confirming the above conclusion. The hysteresis of the voltammograms at cathodic currents can be understood. Oxygen is more readily available from the ternary oxide during the latter part of the cathodic sweep than during the first part of the anodic sweep. The extent of the hysteresis depends also upon temperature and sweep rate.

The above conclusions are confirmed by the results in Fig. 8. In addition, another effect may be recognised. An increase of the partial pressure of  $O_2$  reduces the hysteresis at negative potentials. Simultaneously, the anodic wave representing the reoxidation of the ternary oxide becomes smaller. It is suggested that a partial reoxidation of the depleted ternary oxide occurs directly from  $O_2$ .

#### Properties of the interface Pt/BICUVOX.10 at temperatures above 500°C

The voltammograms in Fig. 9 were taken with different equilibrium potentials of reaction (1) because of the large difference in the partial pressure of  $O_2$ . This explains that the beginning of  $O_2$  evolution is visible in the curves at 100%, but not in those for 0.1%  $O_2$ . They reveal a considerable decrease of the hysteresis, discussed above, with increasing temperature and partial pressure of  $O_2$ . The  $I-E$  curve taken at 5 mV/sec at 600°C and 100%  $O_2$  does not differ from a steady-state curve any more. Depletion or addition of oxygen of the ternary oxide are not observed any longer.

The reciprocal polarisation resistance  $1/R_p$ , the mobility of  $O^{2-}$  and probably also the rate of reoxidation of the ternary oxide by  $O_2$  increase with temperature. Therefore it cannot be said which of the individual processes is responsible for the described behavior of BICUVOX.10 at temperatures above 500°C. Polycrystalline BICUVOX.10 may be useful for oxygen pumps if an appropriate cell design can be found to compensate for the poor mechanical strength and if the long-term stability can be proven. In contrast, the new results on the behavior of the interface Pt/BICUVOX.10 at low partial pressures

of  $O_2$  and cathodic potentials raise doubts that BICUVOX.10 can be used with Pt as electrocatalyst for the anode in the solid oxide fuel cell. The results of this paper are indicative that the oxide will be reduced at potentials in the vicinity of the hydrogen electrode. Unfortunately, direct tests of this hypothesis could not be carried out because polycrystalline disks of BICUVOX.10, sealed by glass to an alpha alumina tube, cracked [19] during the subsequent heating of the cell.

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