ELSEVIER

Journal of Electroanalytical Chemistry 436 (1997) 155–159

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Voltammetric studies of the Au|YSZ interface at temperatures between 300 and 600°C

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Received 13 March 1997

Abstract

Electrochemical processes occurring at the gold|yttria stabilised zirconia interface were studied by cyclic voltammetry and steady-state current potential curves in different mixtures of oxygen and nitrogen at temperatures between 300 and 600°C. Point and paste electrodes were employed. The equilibrium of the oxygen electrode is not established at temperatures below 450°C any more. Contrary to Pt electrodes, the electrochemical formation and reduction of an oxide are reflected by the shape of cyclic voltammograms. However, gold oxide is not formed from O_2 in the gas phase. © 1997 Elsevier Science S.A.

Keywords: Interface; Gold electrode; Stabilised zirconia; Cyclic voltammetry

1. Introduction

The results of voltammetric studies of the interface between different types of Pt electrodes and yttria stabilised zirconia (YSZ) have been reported and discussed in a number of papers [1–7]. Gold is widely used as an electrocatalyst for the oxygen electrode on YSZ. Cyclic voltammetry was applied [8] to the investigation of the Au|YSZ interface only at higher temperatures (700 to 900°C). A mechanism of the electrode polarisation at this interface was discussed for the said temperature range in Ref. [9]. Results, obtained by steady-state current-potential curves and impedance spectroscopy, were reported and analysed in Ref. [10] for temperatures above 700°C.

The open-circuit voltage E^0 of the cell M|YMSZ|Pt was studied [11] at different temperatures between 300 and 700°C with M = Pt, Au or Ag. The gas at the Pt electrode consisted of air while the M electrode was exposed to various gas mixtures containing different amounts of an oxidisable gas. Deviations of E^0 from 0 were already observed if small amounts of an oxidisable gas were present. The selective oxidation of propene and 1-butene [12] and ethane [13] was studied under oxygen pumping conditions at porous gold films in the Au|YSZ|Ag system at 475°C. It was found that the partial oxidation of propene or 1-butene did not occur without electrochemical oxygen pumping in a gas phase containing O_2 besides the organic molecules. It was stated in agreement with comments in Ref. [14] that Au electrodes can be considered 'catalytically inert'.

The investigations of the Au|YSZ interface by voltammetric techniques were extended to lower temperatures (300 to 600°C) now. The results are discussed in this communication. The experiments were made under conditions similar to those in the recent study [7] of the Pt|YSZ interface, allowing a good comparison of the behaviour of Pt and Au electrodes on YSZ.

2. Experimental

The measurements were carried out in a fully automated set-up. Different types of electrochemical measurements (steady-state current-potential curves in the galvanostatic or potentiostatic mode, single or cyclic voltammograms, current-time curves at constant potential, coulometry) are feasible. Details are given in Ref. [15]. The cell consisted of a rectangular slab of YSZ (Friatec, 8% Y_2O_3) with a thickness of about 0.1 cm and three electrodes. It was inside a closed-end tube of Quartz glass, flushed by N_2–O_2 mixtures ($(1-X)\%N_2 + X\%O_2$). The tube was in a tubular furnace. All the electrodes were exposed to the same gas.

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PII S0022-0728(97)00322-7

The YSZ slab was polished to 10 μm before applying the electrodes. The counter electrode (CE) was produced by unfluxed Pt paste on one of the large sides of the slab. The reference electrode (RE) was a piece of Pt foil pressed against the YSZ on one part of the other large side. The working electrode (WE) was a paste electrode for the investigations of the equilibrium of the reaction

$$O_2 + 4e^- = 2O^{2-} \quad (1)$$

and a point electrode [16] for the rest of the studies. The arrangement of the electrodes was like that in Fig. 1 of Ref. [7].

Since gold is a relatively soft metal, it is difficult to produce a point electrode. The deformation of the Au point which occurs during the pretreatment at 700°C for 1 h under the pressure of the spring of the cell holder is relatively large. After trying out several configurations the Au electrode was given the form of a small cylinder which was bent in contact with YSZ. The contact area could not be reproduced well. Therefore no attempt was made to determine the contact area by microscopy.

3. Results

The open-circuit potential E^o of a pasted Au electrode, measured vs. the Pt reference electrode in the same gas mixture, is plotted as a function of temperature for different partial pressures of O_2 in Fig. 1. A test was carried out in one run if the input impedance of the Solartron 1268 electrochemical interface, which served as a programmable potentiostat, was sufficiently large. This turned out to be the case. A preamplifier with an input impedance of 10^{14} Ω was used in the latter experiment.

Steady-state I–E curve were taken from 0 to 0.1 V and back and then from 0 to −0.1 V at a constant partial pressure of O_2. It was assumed arbitrarily that a steady state was reached when the current at constant potential did not change by more than 1 mV/min. The computer program allows such choices. The measurements had to be taken on a Au paste electrode because the currents became too small on the point electrode. Linear plots were constructed in the vicinity of 0. The polarisation resistance

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

was determined from the slope of the linear I–E curves through 0. A semilogarithmic plot of R_p vs. 1000/T is given in Fig. 2. The experimental data for R_p were found to scatter more than those [7] for the Pt|YSZ interface.

Some experiments were carried out to obtain information about the oxygen layer after the pretreatment at 700°C. The working electrode was allowed to cool down at open circuit from 700°C to the desired temperature. A negative sweep was started at 50 mV/s from E^o to −0.7 V, followed a positive sweep back to E^o. Then cyclic sweeps were activated. The results of such an experiment at 450°C are shown in Fig. 3 as an example. Voltammograms similar in shape to that in Fig. 3 were obtained at other temperatures between 300 and 500°C.

Cyclic voltammograms which were measured under the same conditions on point electrodes of Au and Pt at 50

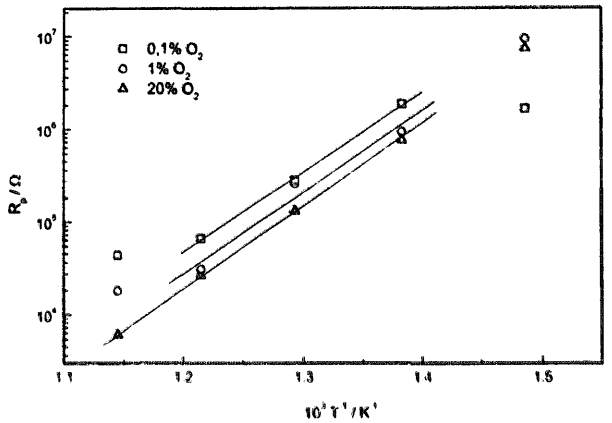

Fig. 2. Semilogarithmic plot of the polarisation resistance of the Au paste electrode versus 1000/T for different partial pressure of O_2.

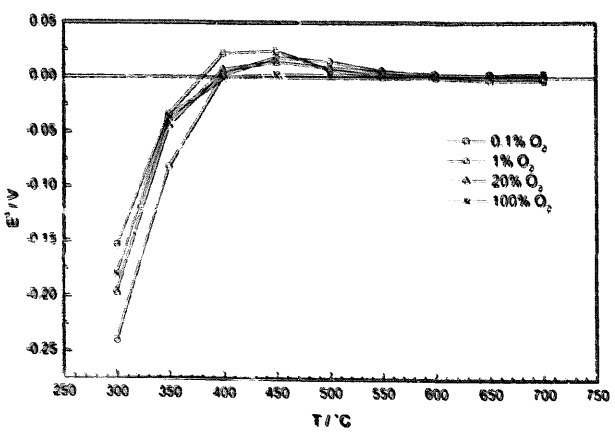

Fig. 1. Open-circuit potentials of a Au paste electrode, measured against a Pt foil in the same gas, as a function of temperature at different oxygen partial pressures.

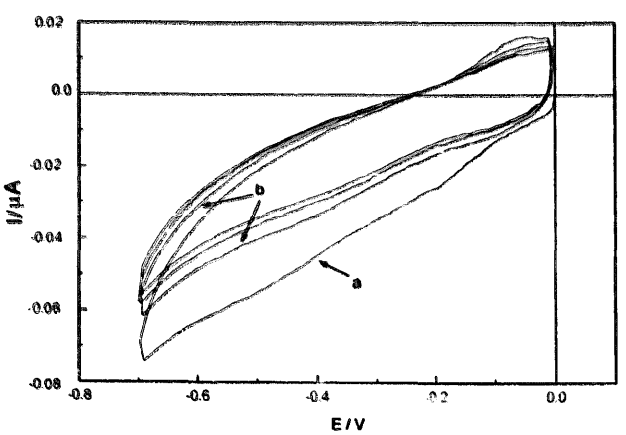

Fig. 3. Negative sweep at 50 mV/s from E^o to −0.7 V and positive sweep back to E^o (curve a) and subsequent cyclic sweeps (curve b) at 450°C and 100% O_2.

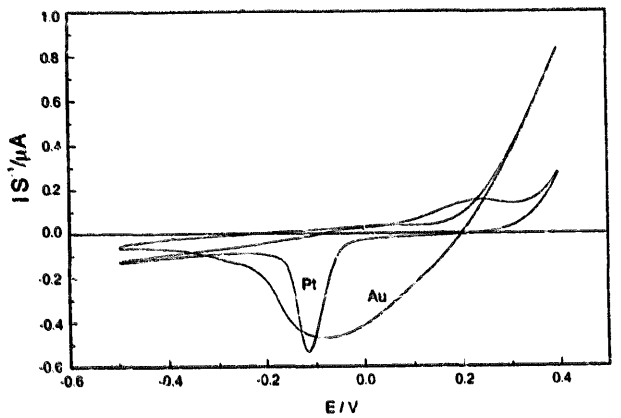

Fig. 4. Comparison of cyclic voltammograms on Au and Pt point electrodes, taken with 50 mV/s at 450°C and 1% O_2. $S = 1$ for Au and $S = 0.3$ for Pt.

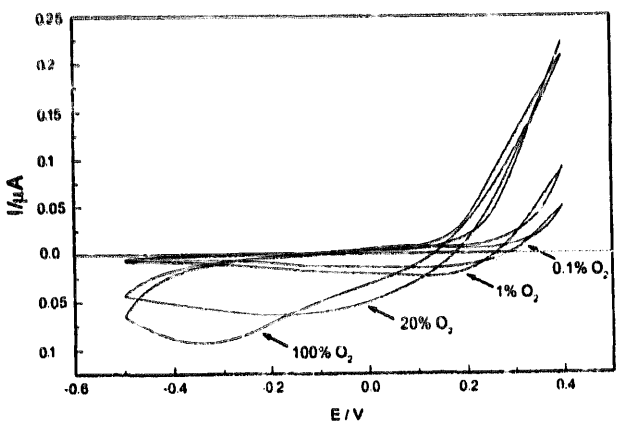

Fig. 5 Cyclic voltammograms on an Au point electrode, taken with 50 mV/s at 400°C under different partial pressures of O_2.

mV/s are shown in Fig. 4. Cyclic voltammograms obtained at 50 mV/s on an Au point electrode are presented for different partial pressures of O_2 at 400°C as an example in Fig. 5. The voltammograms had a similar shape at other temperatures between 300 and 500°C. A cyclic voltammogram measured at 600°C and 20% O_2 is shown in Fig. 6.

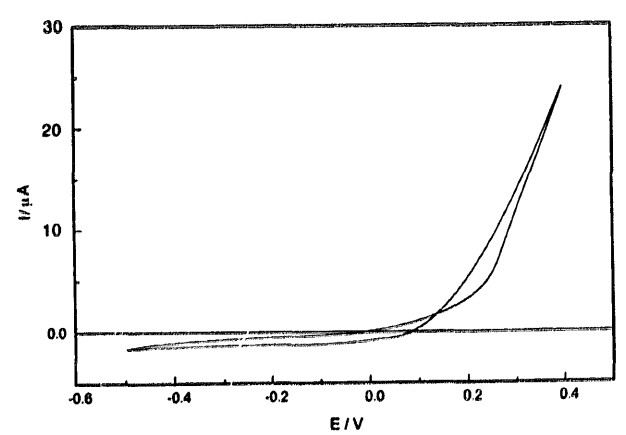

Fig. 6. Cyclic voltammogram with 50 mV/s at 600°C and 20% O_2 on an Au point electrode.

4. Discussion

Results concerning the establishment of the equilibrium of reaction 1 are discussed at first. Conclusions from the voltammograms are drawn next.

Fig. 1 demonstrates that the open-circuit potential between the Pt reference electrode and the Au paste electrode is practically equal to 0 for the different partial pressures of O_2 at temperatures above 600°C. The equilibrium of reaction 1 is established at both electrodes. Deviations which are positive at temperatures between 600 and 400°C are recognizable at lower temperatures. The absolute value of the deviations decreases with the partial pressure of O_2. At 100% O_2 a satisfactory agreement exists down to 400°C. The deviations become negative below 400°C. The latter results suggest that the equilibrium of reaction 1 does not exist below temperatures of about 450°C any longer. The change of the sign of the deviation has the effect that a voltage of nearly zero is also seen in a narrow temperature range between 400 and 350°C. However, this does not mean that the equilibrium of reaction 1 is established there.

The conclusion about the temperatures below which the equilibrium of reaction 1 is not established for a given partial pressure of O_2 is confirmed by the data in Fig. 2. The polarisation resistance assumes relatively large values at temperatures below 450°C. The exchange current density of the rate-determining step of reaction 1 becomes very small. Side reactions begin to have an influence. The open-circuit potential is a mixed electrode potential. The situation is similar to that found [7] on Pt.

The curves in Fig. 3 were taken under the maximum influence of the oxygen partial pressure (100% O_2). While the formation of gold oxides is not expected to occur at open circuit at 700°C [8], oxides might be produced at open circuit during the cooling to lower temperatures after the pretreatment, taking about 1 h in our set-up. However, the first negative sweep in Fig. 3 does not display a large cathodic peak due to the reduction of the oxygen layer. The shape of the subsequent cyclic voltammograms is mainly determined by capacitive currents and the ohmic potential drop. The influence of electrochemical processes remains small up to 450°C.

It should be pointed out that the R_p values at a given temperature and partial pressure of O_2 are larger by nearly one order of magnitude for Au|YSZ than those for Pt|YSZ. However, the contact area is probably larger for Au electrodes than for Pt electrodes. The extent to which a difference exists in the kinetic behavior of Au and Pt electrodes cannot be stated. For a similar reason the magnitude of the currents should be disregarded in a comparison of the cyclic voltammograms for Au and Pt which are

shown in Fig. 4. The important feature of Fig. 4 is the large difference in the shape of the voltammograms.

It was concluded previously [7] that a chemisorbed layer of oxygen atoms is formed on the Pt point electrode during the positive sweep before O_2 evolution starts. A narrow reduction peak results during the negative sweep. In contrast, there is only a small wave on the Au point electrode before the current increases rapidly with potential during the positive sweep. The rapid increase starts about 0.15 V earlier than on Pt. It is suggested that a chemisorbed layer of O atoms is formed on parts of the Au surface at potentials of the small anodic wave. This is followed by two simultaneous electrochemical processes occurring at a relatively large rate at more positive potentials: production of gold oxide and O_2 evolution. Both the chemisorbed oxygen and the oxide are reduced at potentials of the broad wave during the negative sweep.

It was already pointed out in an early paper [17] that the equilibrium potential for the formation of a bulk oxide is independent of the oxide thickness. If the overpotential for the oxide formation is not large, the current of a cyclic voltammogram becomes positive at potentials which are positive to the equilibrium potential during positive sweeps, started at a surface free of oxide. When the positive sweep is reversed, the current assumes positive values during the subsequent negative sweep until the equilibrium potential of oxide formation is passed. The reduction of the oxide takes place during the negative sweep at potentials which are negative of the equilibrium potential. The voltammogram on Au in Fig. 4 displays largely the behavior described in this paragraph.

The equilibrium potential becomes more positive with increasing coverage for chemisorbed layers. The sweep reversal leads to a rapid change from anodic to cathodic current. Such a behavior is seen on the Pt|YSZ interface.

The charge, due to anodic currents (Q_a), and that due to cathodic currents (Q_c), were obtained by integration from the voltammograms taken at 50 mV/s for various partial pressures of O_2 at a constant temperature between 350 and 500°C. The integration required a change of the voltammograms to current-time curves because the current remains positive during the first part of the negative sweep and negative during the first part of the positive sweep.

The ratio Q_a:Q_c is given in Table 1. The ratio is close to 1 at 350 and 400°C. It is nearly the same for the different partial pressures of O_2 at these temperatures. An influence of the partial pressure of O_2 does not exist. The anodic charge is slightly larger than the cathodic one because of the contribution of the O_2 evolution. However, most of the charge is used for the anodic formation and the cathodic reduction of the oxygen layer (small amount of chemisorbed oxygen and larger amount of oxide) at temperatures up to 400°C. The contribution of the O_2 evolution increases with temperature. Therefore the charge ratio becomes larger at 450 and 500°. The results in Table 1 confirm the conclusions about the behavior of Au on YSZ.

Table 1
Ratio of Q_a:Q_c for different temperatures and partial pressures of O_2

Temperature (°C)	350	400	450	500
0.1% O_2	1.08	1.24	1.39	1.72
20% O_2	1.22	1.15	1.31	1.89
100% O_2	1.11	1.18	1.38	1.72

The influence of the partial pressure of O_2 on the shape of the voltammograms in Fig. 5 results mainly from the shift of the open-circuit potential with the oxygen pressure into the positive direction at constant temperature. Therefore the anodic current at the potential of sweep reversal increases. Simultaneously the size of the cathodic wave becomes larger because more oxide is formed during the preceding positive sweep.

The cathodic wave which is mainly due to the oxide reduction remains recognisable at 50 mV/s up to a temperature of 550°C. At higher temperatures it cannot be recognised clearly any longer (compare Fig. 6). It is suggested that only a small amount of oxide is formed at temperatures above 550°C because the oxide begins to decompose. The respective curve for 750°C in Fig. 7 of Ref. [8] looks similar to the curve in Fig. 6. An indication of the small extent of oxide formation is also shown by the hysteresis between the positive currents during the last part of the positive sweep and the first part of the negative one. It is suggested that the O_2 evolution occurs at a slightly larger rate during the first part of the negative sweep because a small amount of oxide is present.

Acknowledgements

The research was financially supported by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung.

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