Electrode polarization at the Au, O₂(g)/Fe implanted yttria-stabilized zirconia interface

B.A. van Hassel, B.A. Boukamp and A.J. Burggraaf

*Laboratory for Inorganic Chemistry, Materials Science and Catalysis, Department of Chemical Technology,
University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

Received 16 December 1990; accepted for publication 4 March 1992

Ion implantation has been applied to modify the surface properties of yttria-stabilized zirconia (YSZ). A three-electrode cell was used for measuring steady state current-overpotential curves and for determining the electrode impedance. An increase of the equilibrium exchange current density at the Au, O₂(g)/yttria stabilized zirconia interface with a factor 10–50 has been observed after the implantation of 15 kV ⁵⁶Fe up to a dose of 8×10^{16} at. cm⁻². This increase results from a broadening of the active surface area due to an increase in the electronic conductivity of the Fe implanted YSZ surface and from an increase of the fraction of coverage of the adsorbed oxygen molecules. The double layer capacitance of the Au, O_{2,g}/YSZ interface increases with a factor 10–100 after the Fe implantation. This is most likely due to the variable oxidation state of the implanted Fe ions, thus providing an additional way for charge accumulation. In comparison with the not implanted Au, O_{2,g}/YSZ interface no changes in the rate-determining steps of the oxygen exchange mechanism occur after Fe implantation. Similar apparent charge-transfer coefficients have been determined. A slight decrease in the oxygen partial pressure dependence of I_0 is observed. The experimental results can still be explained with a reaction model where the charge-transfer process is in competition with the surface diffusion of molecular adsorbed oxygen species along the noble metal–solid electrolyte interface. At cathodic and anodic overpotentials inductive effects appear at low frequencies in the impedance diagram. The inductive effects result from a charge-transfer mechanism where a step-wise transfer of electrons to adsorbed oxygen species takes place.

1. Introduction

The surface modification of ceramic materials by ion beam techniques [1–3] is a topic which has recently attracted considerable interest. The changes in the chemical composition and microstructure of the ion implanted layer result in important variations of the electrical and catalytic properties of ceramics [4]. In this paper the influence of Fe implantation on the electrochemical properties of yttria-stabilized zirconia (YSZ) is studied.

YSZ is an oxygen ion conducting solid electrolyte with applications in oxygen sensors, oxygen pumps and fuel cells [5]. The transfer of gas-phase oxygen to the bulk (and vice versa) at the electrode/electrolyte interface is an important process in all those applications. This oxygen exchange is described by the following overall reaction:

where, in Kröger–Vink notation, O_O[×] is a normal O²⁻ ion in the yttria-stabilized zirconia lattice and V_O^{••} is an oxygen vacancy. The exchange reaction is geometrically limited to the three-phase boundary between the solid electrolyte, noble metal electrode and gas atmosphere. The surface of the solid electrolyte is known to have a pronounced influence on the rate of this oxygen exchange reaction [6–8]. It provides active sites for oxygen adsorption and may transport adsorbed oxygen species to the noble metal electrode, but it cannot participate in the electron transfer reaction as the electronic conductivity is too low. Besides properties of the solid electrolyte surface, the nature of the noble metal electrode also has a pronounced influence on the rate of the oxygen exchange reaction.

Mixed conducting oxides with a high ionic and electronic conductivity are expected to have considerable advantages as an electrode material in comparison with the presently used electronic conduc-

tors [7,9,10]. With good mixed conducting oxides the oxygen exchange would occur over the entire electrode surface.

This paper reports efforts to develop mixed conducting electrode materials by doping yttria-stabilized zirconia with transition metal oxides [11–14]. The doping takes place by the implantation of the corresponding transition metal ions into yttria-stabilized zirconia discs. It is shown that the implantation of a high dose of Fe ions results in an increase of the equilibrium exchange current density at the Au, O_{2,g}/yttria-stabilized zirconia interface.

2. Experimental

The preparation of the yttria-stabilized zirconia (YSZ, 13 cation% Y) discs has been discussed elsewhere [15,16]. The ion implantations have been performed at room temperature in a vacuum of 4×10^{-7} Torr. The YSZ discs were implanted perpendicularly to the sample surface at a beam current density of $2 \mu\text{A cm}^{-2}$ using the isotope separator of the Laboratory for General Physics (LAN) at the State University of Groningen. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck, p.a.) was used as feed material for the hot cathode ion source. The experiments presented in this paper have been performed on YSZ discs implanted with 15 keV ^{56}Fe up to a dose of 8×10^{16} at. cm^{-2} . Due to concurrent sputtering of the target surface during implantation a dose of approximately 3×10^{16} at. cm^{-2} Fe remains in the sample [18]. After implantation, the YSZ discs showed a brown metallic colour. Upon oxidation in air at 400°C the discs obtained an orange colour. An area of 8 mm^2 at the centre of the yttria-stabilized zirconia sample was protected against iron implantation by an aluminium mask.

Annular working and counter electrodes were made by sputtering 500 nm Au on both sides. The edge and centre of the pellet were protected against Au deposition by an aluminium mask. In the electrochemical cell the pellet was sandwiched by two annular Au foils with Au leads. The implanted discs were expected to exhibit electronic conduction in the near surface region. Hence the reference electrode was placed on the not implanted part of the sample in the centre of the annular working electrode in order to

Fig. 1. Geometry of the three-electrode electrochemical cell. The working (W) and counter (C) electrode have an annular symmetry. The reference electrode (R) is placed at the same side of the sample as the working electrode.

prevent possible electronic short-circuiting with the working electrode. The resulting three-terminal electrochemical cell is presented schematically in fig. 1.

The cell was heated in a tubular Hereaus furnace controlled by an Eurotherm Model 810 temperature controller in the temperature range of $500\text{--}800^\circ\text{C}$. The N_2/O_2 gas mixtures of desired ratio were obtained by a gas mixing system (Inacom instruments). Gas flow rates were kept at about 80 mL/min (STP). The ambient gas mixture was kept at atmospheric pressure. The Au electrode was conditioned by heating for 12 h at 820°C and for two weeks at 769°C in an oxygen atmosphere.

The electrode polarization measurements were performed under potentiostatic control using a Bank Pos 73 potentiostat. The actual electrode polarization was obtained by correcting the applied voltage for the voltage drop due to the uncompensated resistance between the working and reference elec-

trode. The uncompensated resistance was determined by impedance spectroscopy. Current densities were calculated by dividing the cell current by the geometric area of the working electrode (0.659 cm^2).

The electrode impedance was measured in the three-electrode cell over a frequency range of 10 mHz–100 kHz using a Solartron 1174 frequency response analyzer. An excitation voltage of 10 mV rms

was added to the dc polarization. The (differential-) dc electrode resistance, R_{el} , was obtained by varying the potential $\pm 5 \text{ mV}$ around the dc polarization used in the impedance measurements, and measuring the steady state current. The electrode resistance was determined from the slope of the steady-state current versus overpotential plot.

The electrode morphology of fresh and used samples was studied with scanning electron microscopy (SEM), see fig. 2. The apparatus for the ^{18}O exchange measurements has been described elsewhere [17]. The ^{18}O diffusion profile was determined by dynamic SIMS (IMMA of Applied Research Laboratories, supplied with a duoplasmatron ion source delivering a 20 keV $^{18}\text{N}^+$ ion beam with a beam diameter of $1.5 \mu\text{m}$ FWHM). Secondary ions were mass selected in a magnetic sector analyzer. SIMS measurements were performed at room temperature.

3. Results

3.1. Surface composition

The Fe depth profile [16,18], determined by Rutherford Backscattering (RBS), after oxidation at 400°C during 1/2 hour in air, is presented in fig. 3. A doped zone with a maximum Fe concentration of

Fig. 2. Scanning electron micrographs of porous Au electrodes on YSZ after approximately 40 days of varied history: (a) not implanted; (b) and (c) Fe implanted showing different areas on the same sample.

Fig. 3. Fe implantation profile in YSZ, determined by RBS, after annealing at 400°C in air for 1/2 h. The horizontal broken line indicates the equilibrium solubility of Fe_2O_3 (cation %) in YSZ at 1500°C in air [18].

Fig. 4. Schematic presentation of the distribution of Fe in YSZ after ion implantation and oxidation at 400°C in air.

50 cation% is created with a thickness of about 20 nm at the surface of the yttria-stabilized zirconia sample. The horizontal broken line represents the equilibrium solubility level of Fe₂O₃ in ZY17 at 1500°C in air [18]. XPS measurements showed that the implanted Fe ions are present in the Fe³⁺ oxidation state after the oxidation treatment [16,19]. Ion scattering spectroscopy (ISS) measurements [16,18] indicate that the outermost surface layer with an estimated thickness of less than 2 nm consisted mainly of Fe₂O₃. This is schematically presented in fig. 4. Due to the limited depth resolution of the RBS measurements this thin Fe₂O₃ layer is not observed in the profile of fig. 3. A more detailed discussion about the thermal stability and microstructure of the implanted layer has been presented in [16,18,19].

3.2. Steady state polarisation

Fig. 5 shows a current-overpotential curve of the

Fig. 5. Current-overpotential curve of the porous Au, O₂(g)/Fe-YSZ. For comparison the curve for the reference Au, O₂(g)/YSZ sample [15] is also given.

Fig. 6. Tafel plot presentation of the current-overpotential curves of fig. 5.

Au, O₂(g)/Fe-YSZ interface obtained at 769°C and $P_{O_2} = 1$ atm. The current-overpotential curve of the *not implanted* Au, O₂(g)/YSZ interface, measured under the same conditions, is shown for comparison. Comparison shows that modification of the YSZ surface by implantation with Fe ions results in a ten fold increase in the electrode current.

Fig. 6 presents the results of fig. 5 in the form of a Tafel plot. From this plot the apparent cathodic and anodic charge transfer coefficients are obtained: $\alpha_c = 0.60 \pm 0.01$ and $\alpha_a = 2.35 \pm 0.01$ for Fe-YSZ, which are slightly different from the values found for the not implanted sample: $\alpha_c = 0.66 \pm 0.01$ and $\alpha_a = 2.08 \pm 0.03$. The temperature dependence of the apparent charge transfer coefficients of the Fe doped sample is shown in fig. 7. The cathodic transfer coefficient is reasonably constant and has a mean value of $\alpha_c = 0.55 \pm 0.04$. The apparent anodic transfer coefficient is somewhat more temperature dependent and has a mean value of $\alpha_a = 2.28 \pm 0.08$. These mean values are again rather close to those of the not implanted sample [15,16].

The temperature dependence of the exchange current density of the Fe-YSZ sample is presented in the Arrhenius plot of fig. 8. Measurements have been performed on two identical samples (A and B). Initially sample B (denoted B_{init.}) showed a three times lower I_0 value than observed for sample A. After performing a series of cyclic voltammogram measurements [16,20] on sample B (denoted B_{final}) high I_0

Fig. 7. Apparent charge transfer coefficients of the Au, O₂(g)/Fe-YSZ interface as function of the reciprocal absolute temperature at $P_{O_2} = 1$ atm.

values, similar to those found for sample A, were obtained (see fig. 8). Apparently the cyclic voltammetric measurements caused some sort of ageing of the Au electrode.

The I_0 values of the reference YSZ sample [15,16] are also shown in fig. 8. These measurements were found to be reproducible within a factor 2. The results shown in fig. 8 represent a best case. From this

Fig. 8. Arrhenius plot of I_0 values for the Au, O₂(g)/Fe-YSZ interfaces in comparison with the I_0 value of the not implanted YSZ surface [15]: (□) $B_{init.}$, (△) $B_{final.}$, see text.

Fig. 9. I_0 as function of oxygen partial pressure at 769°C for the Au, O₂(g)/Fe-YSZ interface. Results for the Au, O₂(g)/YSZ interface [15] are presented for comparison: (□) $B_{init.}$, (△) $B_{final.}$, see text.

figure it can be concluded that the exchange current density for a porous Au electrode on YSZ increases with a factor 10–50 after implantation of Fe. The activation energy of I_0 for sample $B_{init.}$ is $E_{act} = 141 \pm 5$ kJ/mol, which is larger than found for the reference YSZ samples, $E_{act} = 112 \pm 2$ kJ/mol. Sample A showed, however, an activation energy of 115 ± 3 kJ/mol, similar to that of the reference sample.

Due to redox phenomena at the Au, O₂(g)/Fe-YSZ interface at low oxygen partial pressures ($P_{O_2} < 10^{-3}$ atm), the oxygen partial pressure dependence of I_0 could only be investigated in the range $10^{-3} < P_{O_2} < 1$ atm. In this range the logarithm of I_0 shows a positive dependence on the logarithm of P_{O_2} with a slope of $m = 0.51 \pm 0.07$, the mean value for the three measurements presented in fig. 9. This P_{O_2} dependence of I_0 is somewhat smaller than observed for the not implanted samples ($m = 0.60 \pm 0.02$). As for the YSZ reference sample the apparent charge transfer coefficients of the Au, O₂(g)/Fe-YSZ electrode exhibit little dependence on the P_{O_2} (fig. 10).

3.3. Impedance spectroscopy

3.3.1. Polarized interface

Impedance measurements have been performed as a function of frequency at the overpotentials indicated in fig. 11. The results are presented for the Fe

Fig. 10. Apparent charge transfer coefficients as function of oxygen partial pressure at 769°C for the Au, O₂/Fe–YSZ interface.

Fig. 11. Current-overpotential curve of the Au, O₂/Fe–YSZ interface measured at 769°C and $P_{O_2} = 1$ atm. The overpotential values where impedance measurements have been performed are indicated by a square.

implanted sample B_{init} (before cyclic voltammetric experiments had been performed). For the other Fe implanted samples similar results were obtained.

The measurements were analyzed with the computer program “Equivalent Circuit” [21]. The equivalent circuit presented in fig. 12 was found to reproduce most closely the measured impedance spectra. Values of the equivalent circuit parameters are summarized in table 1. The double layer capacitance, C_{dl} , and all other capacitive or inductive effects (CPE₁, CPE₂ and CPE₃) have been analyzed in terms of a constant phase element (CPE). The CPE

Fig. 12. Equivalent circuit used in the NLLS-fit analysis of the impedance diagrams presented in fig. 13.

impedance is given by: $1/(Y_0(j\omega)^n)$, where ω is the angular frequency and $j^2 = -1$. It is characterized by two parameters: Y_0 and n . The latter determines the dimension of Y_0 ($s^n \Omega^{-1}$). n will be referred to as the exponent value of the CPE.

At cathodic overpotentials, $\eta < -0.1$ V, an inductive loop appears in the impedance diagram at low frequencies. This is illustrated by the impedance diagrams shown in fig. 13a and b, which have been measured at $\eta = -0.614$ V and $\eta = -0.404$ V, respectively. At $\eta = -0.1$ V the inductive loop turns into a capacitive loop, see fig. 13c. The capacitive loop at low frequencies has been indicated by the drawn depressed semicircle. At equilibrium ($\eta = 0$ V) the contribution of this capacitive loop to the electrode impedance is small as shown in fig. 13d. This capacitive loop becomes more apparent when the overpotential increases towards $\eta = +0.1$ V, where it determines more than half of the dc electrode resistance (fig. 13e). At $\eta = +0.15$ V once again an inductive loop appears in the impedance diagram at low frequencies (fig. 13f).

The uncompensated resistance, R_u , in the equivalent circuit (fig. 12) is presented as a function of the overpotential in fig. 14. Taking into account the experimental uncertainty in R_u , it can be considered to be independent of the overpotential.

The resistance R_1 and the constant phase element CPE₁ could not be determined accurately as this combination provides, only at high frequencies, a minor but non-negligible contribution to the overall frequency dispersion. The physical significance will be discussed in section 3.3.3.

The polarization dependence of the double layer

Table 1

Values of the equivalent circuit element parameters (fig. 12) obtained from the NLLS-fit analysis of the electrode impedances presented in fig. 13. Resistances are expressed in ohms, the Y_0 parameters of the constant phase elements in $s^n \Omega^{-1}$, where n is the CPE exponent value.

Equivalent circuit element	Overpotential (V)						
	-0.614	-0.404	-0.202	-0.1	0	0.105	0.147
R_u	2.9	6.0	5.4	5.0	4.7	4.6	7.6
R_1	3.5	2.6	8.6	8.6	15.3		
CPE_1	6.0×10^{-4}	2.5×10^{-5}	1.6×10^{-4}	1.9×10^{-4}	6.7×10^{-4}		
n_1	0.46	0.98	0.75	0.74	0.6		
C_{dl} (CPE)	2.6×10^{-4}	7.4×10^{-5}	4.5×10^{-5}	6.3×10^{-5}	8.7×10^{-5}	7.3×10^{-5}	2.2×10^{-5}
n_{dl}	0.89	0.91	0.87	0.83	0.81	0.74	0.83
R_{ct}	23.4	121	487	702	293	12.9	10.4
R_2	3.6	8.0	119	168	55.1	24.4	9.2
CPE_2	9.72	0.861	1.64×10^{-3}	2.08×10^{-3}	5.75×10^{-3}	1.92×10^{-3}	7.23×10^{-3}
n_2	-0.94	-0.92	0.48	0.63	0.61	0.65	0.62
R_3	10.0	21.3	21.6	36.1		0.173	1.13
CPE_3	2.49×10^{-2}	6.92×10^{-3}	1.94×10^{-3}	5.04		0.846	0.112
n_3	-0.81	-0.68	-0.96	1.0		-1.0	-0.93

Fig. 13. Impedance diagrams (769°C, $P_{O_2} = 1$ atm) as obtained from the Au, O_{2,g}/Fe-YSZ interface as function of the overpotential: (a) $\eta = -0.614$ V, (b) $\eta = -0.404$ V, (c) $\eta = -0.1$ V, (d) $\eta = 0$ V, (e) $\eta = +0.105$ V and (f) $\eta = +0.147$ V. The drawn semi-circles indicate the contribution of the separate sub-circuits to the overall dispersion. Frequency is indicated in Hz.

Fig. 14. The uncompensated resistance, R_u , the charge transfer resistance, R_{ct} , and the electrode resistance, R_{el} , as function of the overpotential at $P_{O_2} = 1$ atm and 769°C , as obtained from the NLLS-fit analysis of the spectra of fig. 13. Values of the apparent charge transfer coefficients are indicated.

capacitance, C_{dl} of the implanted and the reference sample are presented in fig. 15. Comparison shows that C_{dl} increases one order of magnitude after Fe-implantation. The double-layer capacitance is assumed to be in parallel with the faradaic impedance of the electrode, which is presented by the circuit elements R_{ct} , R_2 , CPE_2 , R_3 and CPE_3 in the equivalent circuit of fig. 12.

The electrode resistance, R_{el} , is obtained by subtracting the uncompensated resistance, R_u , from the measured dc point in the impedance diagram. R_{el} depends exponentially on the applied overpotential (see

Fig. 15. CPE parameters (Y_0 , n) related to the double layer capacitances (C_{dl}) of the Au, O₂(g)/Fe-YSZ interface and the reference Au, O₂(g)/Fe-YSZ interface as function of the overpotential.

fig. 14). This behaviour follows directly from the partial differential ($\partial/\partial V$) of the Butler-Volmer equation. The apparent cathodic transfer coefficient obtained from fig. 14, $\alpha_c = 0.62 \pm 0.03$, is within experimental error equal to the cathodic Tafel slope presented in fig. 6: $\alpha_c = 0.60 \pm 0.01$. The apparent anodic transfer coefficient ($\alpha_a = 1.8 \pm 0.1$) deviates more seriously from the one of the Tafel plot ($\alpha_a = 2.35 \pm 0.01$), possibly due to the longer stabilisation time in the impedance measurements. Fig. 14 shows also that the major contribution to the electrode resistance is given by the charge transfer resistance, R_{ct} .

The parallel combination of the circuit elements R_2 , CPE_2 , R_3 and CPE_3 in fig. 10 will be called the concentration impedance of the adsorbed oxygen species, in order to facilitate the discussion of the results. This concentration impedance shows a complicated behaviour as function of the overpotential. At cathodic overpotentials the concentration impedance of the adsorbed oxygen species manifests itself in the impedance diagram as an inductive loop at low frequencies. At anodic overpotentials a capacitive loop appears in the low frequency part of the impedance diagram.

The behaviour of the measured impedances with respect to the overpotential is almost identical to what is observed for the Au, O₂(g)/YSZ electrode impedances [15,16]. The major difference is the much smaller dc electrode resistance observed after Fe implantation, as shown in fig. 16. This corresponds to the measured increase in the equilibrium exchange current density.

3.3.2. Unpolarized interface, temperature dependence

Impedance measurements have been performed at zero overpotential as a function of the temperature and oxygen partial pressure. The equivalent circuit which describes the measurements in a mathematical way is similar to the one shown in fig. 12, but the parallel combination of R_3 and CPE_3 is not present when the interface is at equilibrium. Below results are presented for sample B_{init}. For the other Fe-implanted samples similar results were obtained.

The uncompensated resistance, R_u , is temperature dependent with an activation energy of $E_{act} = 103 \pm 3$ kJ/mol (fig. 17), which is equal to that of the ionic

Fig. 16. Impedance diagrams of the Au, O₂(g)/Fe-YSZ and the Au, O₂(g)/YSZ interface measured under equilibrium conditions at 769°C and $P_{O_2} = 1$ atm.

Fig. 17. Arrhenius-plot of the resistances R_u , R_{ct} and R_2 of the equivalent circuit of fig. 12, determined for the Au, O₂(g)/Fe-YSZ interface at $P_{O_2} = 1$ atm.

conductivity of the YSZ sample. The same was observed for the Au, O₂(g)/YSZ interface [15,16].

The parallel combination of R_1 and CPE_1 gives a small contribution to the impedance diagram at high frequencies. R_1 is temperature dependent with an activation energy of $E_{act} = 98 \pm 3$ kJ/mol, which is about equal to the activation energy of R_u . The Y_0 value of the constant phase element CPE_1 decreased from $Y_0 = 9 \times 10^{-5} \text{ s}^n \Omega^{-1}$ at 770°C to $Y_0 = 2 \times 10^{-5} \text{ s}^n \Omega^{-1}$

Fig. 18. CPE parameters (Y_0 , n) related to the double layer capacitance (C_{dl}) of the Au, O₂(g)/Fe-YSZ interface and the reference Au, O₂(g)/YSZ interface as function of the reciprocal absolute temperature at $P_{O_2} = 1$ atm.

Ω^{-1} at 520°C with exponent values of $n = 0.72$ and $n = 0.78$, respectively.

The temperature dependence of the double layer capacitance is shown in fig. 18. In comparison with the double-layer capacitance of the reference YSZ sample the capacitance is one order of magnitude larger.

The charge-transfer resistance, R_{ct} , is temperature dependent with an activation energy of $E_{act} = 111 \pm 4$ kJ/mol (fig. 17), which is larger than observed for the not implanted sample ($E_{act} = 89 \pm 2$ kJ/mol).

The temperature dependence of resistance R_2 , which is related to the concentration impedance of the adsorbed oxygen species, is also presented in fig. 17. From this figure an activation energy of 130 ± 6 kJ/mol is obtained. The temperature dependence of the corresponding constant phase element, CPE_2 , is given in fig. 19. The value of the exponent of this CPE_2 is in the range $0.5 < n < 0.7$. The large scatter in the data reflects the small contribution of this part of the equivalent circuit to the total electrode impedance under equilibrium conditions.

3.3.3. Unpolarized interface, P_{O_2} dependence

Because of the redox phenomena at low P_{O_2} mentioned above, all P_{O_2} dependent measurements were restricted to the range $10^{-3} < P_{O_2} < 1$ atm. All these measurements were performed at 769°C. As the uncompensated resistance, R_u , is determined by the

Fig. 19. Parameters of CPE₂ (see equivalent circuit, fig. 12) as function of the reciprocal absolute temperature at $P_{O_2} = 1$ atm.

Fig. 20. Oxygen partial pressure dependence (at 769°C) of the resistances R_u , R_{ct} and R_2 of the equivalent circuit of fig. 12 (Fe implanted sample).

ionic conductivity of the YSZ sample, it is also independent of the oxygen partial pressure (fig. 20).

The resistance R_1 and the constant phase element CPE₁ too are independent of the oxygen partial pressure. For CPE₁ a mean value of $Y_0 = 9 \times 10^{-5} \text{ s}^n \Omega^{-1}$ and $n = 0.70$ was obtained. This P_{O_2} -independence suggests that this sub-circuit is not involved in the oxygen exchange reaction. Most likely it results from the interface between the Fe implanted layer and the solid electrolyte. Further research is required to clarify this point.

The double layer capacitance, C_{dl} , depends only weakly on the P_{O_2} (fig. 21) and is one order of mag-

Fig. 21. CPE parameters (Y_0 , n) related to the double layer capacitance (C_{dl}) of the Au, O₂(g)/Fe-YSZ interface as function of the P_{O_2} ($T = 769^\circ\text{C}$).

nitude larger than observed for the not implanted sample, which is in line with the comparison of the results from the temperature dependent measurements.

For Fe-YSZ the $\log R_{ct} - \log P_{O_2}$ plot shows a linear dependence with a slope of $m = 0.25 \pm 0.03$ (fig. 20). The order of this dependence is smaller than found for the not implanted sample ($m = 0.53 \pm 0.01$).

The concentration impedance related resistance R_2 of the Fe implanted sample strongly depends on P_{O_2} (fig. 20). The dependence order, $m = 0.80 \pm 0.07$, is larger than the dependence observed for the reference YSZ sample ($m = 0.67 \pm 0.02$). The Y_0 value of the constant phase element CPE₂ is somewhat larger than for the not implanted sample. It also depends strongly on P_{O_2} as shown in fig. 22. A decrease in Y_0 with two orders of magnitude is observed when the oxygen partial pressure is changed from 1 atm to 10^{-3} atm. The value of the exponent of the CPE₂ is in the range $0.54 < n < 0.58$. Hence this CPE resembles a semi-infinite diffusion impedance (Warburg).

3.4. ¹⁸O exchange measurements

The effect of the Fe implantation on the oxygen exchange rate of the YSZ solid electrolyte in absence of an Au electrode was studied by ¹⁸O exchange measurements in combination with dynamic SIMS. The samples were exchanged for 60 min at 750°C in ¹⁸O enriched oxygen gas with an isotope ratio

Fig. 22. Parameters of CPE₂ as function of P_{O_2} ($T=769^\circ\text{C}$).

Table 2

Mean values of ^{18}O ratios over the first 2 μm of YSZ and Fe-implanted YSZ solid samples. The exchange was carried out at $P_{O_2}=0.25$ atm at 750°C . Gas-phase ^{18}O ratio, R_g^{18} , was 0.92

Sample	Time (min)	^{18}O ratio, R_b^{18}
YSZ	60	$(2.9 \pm 0.7) \times 10^{-3}$
Fe-impl. YSZ	60	$(3.1 \pm 0.3) \times 10^{-2}$

$R_g^{18} = ^{18}\text{O} / (^{18}\text{O} + ^{16}\text{O}) = 0.92$. The results are summarized in table 2. The dynamic SIMS analysis of the Fe-implanted sample indicated a flat ^{18}O isotope profile up to 2 μm deep with a mean isotope ratio, R_b^{18} , of $(3.1 \pm 0.3) \times 10^{-2}$. Under identical conditions a value of $R_b^{18} = (2.9 \pm 0.7) \times 10^{-3}$ was measured for the not implanted sample. This is only slightly higher than the natural background ratio ($R^{18} = 2 \times 10^{-3}$).

4. Discussion

With respect to a reference YSZ sample the equilibrium exchange current density was found to be increased by a factor 10–50 after Fe-implantation (15 keV Fe, with a dose of 8×10^{16} at. cm^{-2}). The current densities were obtained by dividing the exchange currents by the respective macroscopic gold-electrode areas. This normalisation procedure is only allowed when the electrode morphologies are com-

parable. A scanning electron microscopy study of the (used) electrodes showed some differences in morphology, see fig. 2. The 500 nm thick Au electrode on the reference YSZ surface agglomerated into islands with a mean particle diameter of 1.3 μm (fig. 2a) covering 25% of the solid electrolyte surface. The 500 nm thick Au electrode on the Fe implanted YSZ surface also agglomerated in islands but with a much larger mean diameter of about 5 μm (fig. 2b). A large part of the electrode surface consisted also of interconnected Au islands, as shown in fig. 2c. The Fe implanted YSZ surface was covered for 29% with gold. Hence the surface coverage of the YSZ surface with the Au electrode is about equal for the Fe- and the reference YSZ surface but for Fe-YSZ the interconnection between the Au islands is much improved. As the YSZ samples are sandwiched between two annular Au foils it is difficult to determine how well contact is made with all the individual Au islands. It should be noted, however, that the I_0 values for the not implanted samples could be reproduced within a factor of 2. In our view the differences in the electrode morphologies are too small to explain the increase in the exchange current density with a factor of 10–50.

The results obtained for both the steady state polarisation measurements and the impedance measurements indicate that the rate determining steps in the oxygen exchange mechanism do not change upon Fe implantation. The same apparent charge transfer coefficients have been determined for the Fe and not implanted YSZ sample. The oxygen partial pressure dependence of I_0 changes from $m=0.60 \pm 0.02$ for the reference YSZ sample to $m=0.51 \pm 0.07$ upon Fe implantation. This could be explained by an increase in the fraction of coverage of the adsorbed oxygen species at the electrode. When this fractional coverage is no longer negligible then a decrease in the oxygen partial pressure dependence of I_0 can be predicted. This increase in the fraction of coverage of the adsorbed oxygen molecules can be an important factor in determining the increase in the equilibrium exchange current density.

For sample B_{init.} an activation energy of 141 ± 5 kJ/mol is found for I_0 . This value is somewhat higher than found for the reference YSZ sample (112 ± 2 kJ/mol) and the Fe-implanted sample A (115 ± 3 kJ/mol). However, for sample B_{final} (after the cyclic

voltammetry experiments) also a lower activation energy of about 115 kJ/mol is obtained. The higher value for B_{init} may be attributed to a slow change in the active electrode area, which stabilized during or after the cyclic voltammetry experiments.

In the impedance diagrams obtained from the Au, O_{2,g}/YSZ interface [15,16] and the Au, O_{2,g}/Fe-YSZ interface inductive loops are observed at low frequencies at cathodic overpotentials more negative than $\eta = -0.1$ V. Those inductive loops turn into capacitive loops at anodic overpotentials. At anodic overpotentials larger than $\eta > 0.10$ V an inductive loop appears again at low frequencies. In previous studies [15,16,22] it was shown that the experimental results can be explained with an electrode mechanism where a competition exists between charge transfer and mass transport of molecular oxygen along the Au, O_{2,g}/YSZ interface. Analytical solutions for this mass transport problem were obtained following the work of Wang and Nowick [23], Nguyen et al. [24] and Robertson and Michaels [25]. The inductive loops at low frequencies in the impedance diagram indicate that a stepwise transfer of electrons to adsorbed oxygen species occurs. In [16,22] a charge transfer model has been formulated in order to explain the inductive effect. Within the frame of this model an inductive effect appears at cathodic overpotentials when the fraction of coverage of one of the adsorbed oxygen species increases when the cathodic overpotential becomes more negative.

The double layer capacitance of the Au, O_{2,g}/Fe-YSZ interface is about a factor 10–100 larger than that of the Au, O_{2,g}/YSZ interface. This increase in capacitance results in an increase of the response time of potentiometric oxygen sensors, which is an unwanted effect. Such an increase of the double layer capacitance implies that the implanted Fe ions provide an extra possibility of charge accumulation at the Au, O_{2,g}/YSZ interface. A change in the oxidation state of the implanted Fe ions can account for this:

In a separate investigation [20] this reduction reaction was studied in more detail using cyclic voltammetry. It was shown that in an ambient with a low oxygen partial pressure, oxidation and reduction

phenomena occur which are related to the redox reaction of eq. (2). The equilibrium potential (E^0) of this redox couple is $E^0 = -0.439$ V versus $P_{\text{O}_2} = 1$ atm at 775°C and is in close agreement with the thermodynamic potential of coexistent Fe₂O₃ and Fe₃O₄ phases. Hence if no overpotential is applied all implanted Fe ions will be in the Fe³⁺ oxidation state at an oxygen partial pressure of 1 atm in the studied temperature range. From the scan rate dependence of the peak current in the voltammogram it has been concluded that the redox reaction at the electrode is rate limited by the diffusion of reduced or oxidized electroactive species. Both the implanted Fe ions and the electrons or electron holes in the YSZ surface layer have been considered as the electroactive species. The diffusion of electrons or holes towards the implanted Fe ions was considered to be the most likely process limiting the rate of the redox reaction.

An increase of the double layer capacitance may also result from an increased contact area of the Au electrode with the solid electrolyte. From the micrographs of fig. 2, it can be calculated that the surface coverage of Au for the Fe implanted and not implanted YSZ samples are 29% and 25%, respectively, and hence no large increase of the double layer capacitance can be expected from the electrode morphology.

The diffusion of electrons or holes in the Fe implanted YSZ surface results in an increase of the active area of the electrode, as schematically indicated in fig. 23. The contribution of the oxygen exchange outside the direct vicinity of the Au electrode to the overall oxygen exchange rate will critically depend

Fig. 23. Schematic representation of the Au, O_{2,g}/Fe-YSZ interface showing part of the Fe implanted surface to be active in the oxygen exchange reaction if the electronic conductivity is sufficient.

on the number of charge carriers and their mobility, hence on the electronic conductivity of the Fe implanted layer.

The total conductivity of the Fe implanted surface layer has been studied by four-point probe conductivity measurements [26]. Those measurements have been performed with 60 nm thick YSZ films deposited on insulating Al₂O₃ substrates. This procedure has been followed in order to separate the conductivity of the implanted region from the ion conducting YSZ substrate. The implantation of 15 keV Fe up to a dose of 8×10^{16} at. cm⁻² resulted only in small changes in the total conductivity. As only the total conductivity of the implanted layer has been measured, it is difficult to draw conclusions about the electronic conductivity of the implanted layer. In the temperature range of 400–600 °C, however, the conductivity of the Fe implanted YSZ film was dependent on the oxygen partial pressure. This was ascribed to the electronic conductivity of the 2 nm thick Fe₂O₃ layer, schematically presented in fig. 4. Considering the electronic conductivity of pure Fe₂O₃ [27] the electronic conductivity of this surface layer is probably *n*-type below 800 °C. Above 600 °C the conductivity of the Fe implanted YSZ thin film was dominated by its ionic conductivity.

Hence the four-point probe conductivity measurements and the cyclic voltammetry measurements give some indication of electronic conductivity in the Fe implanted YSZ surface. Due to this electronic conductivity part of the Fe implanted surface outside the direct vicinity of the Au electrode can be involved in the oxygen exchange, resulting in an increase of the equilibrium exchange current density.

Until now the catalytic activity of Au in the oxygen exchange reaction was neglected and the electrode was considered primarily as a current collector. The catalytic activity of Au metal in the oxidation of CO and H₂ in air has recently been studied by Haruta et al. [28]. It is shown that the catalytic activity of Au metal depends markedly on the crystallite size and the supporting oxide. High catalytic activities were observed for the oxidation of CO in air if small Au crystallites (mean diameter < 10 nm) were supported on the oxides of group VIII 3d transition metals like Fe, Co and Ni. The interaction between the Au metal and the support resulted in a high catalytic activity in the oxidation of CO and H₂ in air. Au supported on oxides of transition metals like TiO₂ or

ZrO₂ appeared to be far less catalytic active. In view of these results, the high dose implantation of Fe, which turns the YSZ surface into an Fe₂O₃ surface, may result in an increased catalytic activity of the Au electrode in the oxygen exchange reaction.

The surface oxygen exchange rate measurements provide a means of studying the exchange of oxygen without the presence of electrodes. At 750 °C and $P_{\text{O}_2} = 1$ atm the regular YSZ surface shows very little oxygen exchange activity. For the Fe-implanted YSZ sample a significant increase in the bulk ¹⁸O ratio is obtained from dynamic SIMS measurements. Similar results were obtained from gas-phase analysis during isotope exchange [29]. The flat ¹⁸O profile in the first 2 μm of the Fe implanted YSZ surface indicates that the diffusion of oxygen within the solid is fast compared to the rate of the surface exchange. From the difference in the sub-surface isotope ratio between the Fe and not implanted sample, it can be calculated that the oxygen exchange rate for the Fe implanted YSZ sample is at least a factor 10 to 30 larger than for the not implanted YSZ surface. Hence the increase in the rate of the oxygen exchange process is also observed in absence of the porous Au electrode.

5. Conclusions

This study shows the important role of the surface properties of yttria-stabilized zirconia (YSZ) in the oxygen exchange reaction at the Au, O_{2,g}/YSZ interface. The implantation of 15 keV Fe ions up to a dose of 8×10^{16} at. cm⁻² in YSZ results in an increase of the equilibrium exchange current density at that interface with a factor 10–50.

From the results of the electrochemical measurements it can be concluded that the rate determining steps in the oxygen exchange mechanism have not changed after Fe implantation. A competition still exists between the charge transfer process and the mass transport of molecular adsorbed oxygen species along the Au, O_{2,g}/Fe–YSZ interface. Inductive loops are observed at low frequencies in the impedance diagram during cathodic polarisation. They result from a charge transfer process where a step-wise transfer of electrons to adsorbed oxygen species takes place.

The results from the electrochemical measure-

ments are supported by ¹⁸O exchange measurements where in the absence of an Au electrode an increase in the oxygen exchange rate with a factor 10 to 30 is also observed.

The increase in electronic conductivity of the YSZ surface after Fe implantation is an important factor determining the increase of the oxygen exchange rate. The availability of electrons outside the direct vicinity of the noble metal electrode results in an enlargement of the reaction zone. An increase of the fraction of coverage of the adsorbed oxygen molecules can also explain the increase in the oxygen exchange rate.

The implantation of Fe results in an increase of the double layer capacitance with a factor 10–100. Hence the implanted Fe ions provide an alternative way of charge accumulation at the Au, O_{2,g}/YSZ interface. For sensor applications this is undesired as it causes an increase of the response time of a potentiometric oxygen sensor.

Acknowledgement

The authors appreciate the cooperation with the Laboratorium voor Algemene Natuurkunde (LAN) of the State University of Groningen. They are grateful to J.J. Smit for the ion implanter facilities. They thank Dr. D.O. Boerma of the State University of Groningen for his supervision during the RBS measurements. The SGM foundation is thanked for putting their SIMS facility at our disposition. Especially D. Gras and A.P. von Rosenstiel are thanked for their assistance. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for Scientific Research (NWO).

References

- [1] O. Aucielli and R. Kelly, eds., in: *Ion Bombardment Modification of Surfaces; Fundamentals and Applications, Beam Modification of Materials 1* (Elsevier, Amsterdam, 1984).
- [2] P. Mazzoldi and G.W. Arnold, eds., in: *Ion Beam Modification of Insulators, Beam Modification of Materials 2* (Elsevier, Amsterdam, 1987) pp. 412–448.
- [3] C.J. McHargue, R. Kossowsky and W.O. Hofer, eds., in: *Structure-Property Relationships in Ion-Beam Surface-Modified Ceramics*, NATO ASI Series E: Appl. Sci. Vol. 170 (Kluwer, Dordrecht, 1989) pp. 231–252.
- [4] B.A. van Hassel and A.J. Burggraaf, *Appl. Phys. A* 49 (1989) 33.
- [5] E.C. Subbarao and H.S. Maiti, *Solid State Ionics* 11 (1984) 317.
- [6] E.J.L. Schouler, *Solid State Ionics* 9/10 (1983) 945.
- [7] M.P. van Dijk, K.J. de Vries and A.J. Burggraaf, *Solid State Ionics* 21 (1986) 73.
- [8] M.P. van Dijk, K.J. de Vries and A.J. Burggraaf, *Solid State Ionics* 21 (1986) 83.
- [9] M.P. van Dijk, Ordering, electrical conductivity and electrode properties of ceramics with fluorite related structures, Ph. D. Thesis (University of Twente, Enschede, The Netherlands, 1985).
- [10] Y. Takasu, T. Sugini and Y. Matsuda, *J. Appl. Electrochem.* 14 (1984) 79.
- [11] D. Scholten, Surface modification of yttria stabilized zirconia by ion implantation, Ph.D. Thesis (University of Twente, Enschede, The Netherlands, 1987).
- [12] D. Scholten and A.J. Burggraaf, *Surface Interface Anal.* 9 (1986) 467.
- [13] D. Scholten and A.J. Burggraaf, *Solid State Ionics* 16 (1985) 147.
- [14] A.J. Burggraaf, D. Scholten and B.A. van Hassel, *Nucl. Instrum. Methods B* 32 (1988) 32.
- [15] B.A. van Hassel, B.A. Boukamp and A.J. Burggraaf, *Solid State Ionics* 48 (1991) 155.
- [16] B.A. van Hassel, Transport and oxygen transfer properties of ion implanted yttria stabilized zirconia, Ph.D. Thesis (University of Twente, Enschede, The Netherlands, 1990).
- [17] B.A. Boukamp, I.C. Vinke, K.J. de Vries and A.J. Burggraaf, *Solid State Ionics* 32/33 (1989) 918.
- [18] B.A. van Hassel and A.J. Burggraaf, *Appl. Phys. A* 53 (1991) 155.
- [19] B.A. van Hassel and A.J. Burggraaf, *Appl. Phys. A* 52 (1991) 410.
- [20] B.A. van Hassel and A.J. Burggraaf, *Solid State Ionics* 51 (1992) 175.
- [21] B.A. Boukamp, *Solid State Ionics* 20 (1986) 31.
- [22] B.A. van Hassel, B.A. Boukamp and A.J. Burggraaf, *Solid State Ionics* 48 (1991) 139.
- [23] Da Yu Wang and A.S. Nowick, *J. Electrochem. Soc.* 128 (1981) 55.
- [24] B.C. Nguyen, L.M. Rincon-Rubio and D.M. Mason, *J. Electrochem. Soc.* 133 (1986) 1860.
- [25] N.L. Robertson and J.N. Michaels, *AIChE Symposium series*, No. 254, Vol 83 (1987) 56.
- [26] B.A. van Hassel and A.J. Burggraaf, Effects of ion implantation doping on electrical properties of stabilized zirconia thin films, *Solid State Ionics*, submitted for publication.
- [27] B.M. Warnes, F.F. Aplan and G. Simkovich, *Solid State Ionics* 12 (1984) 271.
- [28] M. Haruta, H. Kageyama, N. Kamijo, T. Kobayashi and F. Delannay, in: *Successful Design of Catalysts*, ed. T. Inui (Elsevier, Amsterdam, 1988) pp. 33–42.
- [29] B.A. Boukamp, B.A. van Hassel and A.J. Burggraaf, presented at the 8th Int. Conf. on Solid State Ionics, Lake Louise - Canada, Oct. 1991.