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PERFORMANCE OF ZrO_2 ELECTROLYTE CELLS FOR COULOMETRIC TITRATION AT HIGH VOLTAGE

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ABSTRACT

An experimental study was performed at 760 °C on the phenomena occurring during coulometric titration of oxygen from a gas phase with ZrO_2-based electrolyte cells at high voltage. The electrolyte does not act as an inert material at voltages up to 1600 mV, which is well below the dissociation voltage of ZrO_2 (2300 mV). The most drastic reduction processes are observed even in the 800–1200 mV range, involving large amounts of oxygen. The reaction kinetics in the final stage of the reduction processes are slow, and seemingly result in a permanent change in the condition of the electrolyte cell. The reversal of the reduction processes strongly influences the titration signal when oxygen passes through the cell. This reversal has also been studied by other means. It is suggested that a combination of the reduction of less stable impurities, the dissociation of ZrO_2, enhanced by formation of $ZrPt_3$ at the electrode interface, and the probable increase in oxygen vacancy concentration may be responsible for the phenomena. A special treatment of the cell has been developed, which involves driving large currents through the cell under air, followed by small currents. This treatment erases the history of any of the reduction processes and it also increases the porosity of the Pt electrodes. In addition, it increases the cell conductivity to the maximum theoretical value and defines the cell condition for optimal titration performance. Very complex phenomena occur in the electrolyte cell at high applied voltage, which are not fully understood. Nevertheless, practical conclusions can be drawn from the knowledge of these phenomena, which enable precise coulometric measurements to be made.

INTRODUCTION

Solid state electrolyte cells certainly constitute one of the major milestones in experimental thermochemistry and many excellent examples of application can be found in the classical book by Kubaschewski and Alcock [1]. The operation of these cells at near equilibrium conditions is nowadays a standard practice and possible sources of error have been extensively discussed [2]. However, not so much is known about irregularities that may

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Dedicated to Professor Oswald Kubaschewski in honour of his contribution to thermochemistry.

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occur during coulometric titration with these cells at high applied voltages. During our ongoing work on the further development of a new type of oxygen analyser, based on the idea suggested recently by Otsuka and Kozuka [3], we have observed such irregularities.

This prompted the present study, the purpose of which is to investigate experimentally these phenomena, to try to develop a better understanding of the processes that govern these phenomena and, finally, to extract practical hints on the design and operating conditions of the titration cell. We wish to obtain optimal performance for the titration of trace amounts of oxygen from a gas phase. This has to be converted to very low oxygen potentials, because in the actual oxygen analyser a metallic sample is reduced with the gas. This is why we need the high voltage.

In the following, we first present these experimental facts that demonstrate most clearly what is meant by "irregularities". This essentially non-inert behaviour of the electrolyte cell at voltages that are high, but that are still well below the decomposition limit for the ZrO_2-based material, is further explored by the measured oxygen release from the cell and the lowest oxygen potential that can be achieved with it. The history of the cell has a remarkable influence on the total cell resistivity. All of these individual aspects contribute to the actual performance of the cell as a titration unit.

EXPERIMENTAL SET-UP

The experimental set-up is depicted in Fig. 1. The electrolyte tube is part of a closed gas circuit which can be evacuated and filled with argon. The gas is circled at controlled speed with a hermetically sealed circulation pump. Small amounts of air may be injected through a specially selected diaphragm with an automated high precision syringe. The precision of the syringe in the 1–20 mm^3 range was checked by weighing the amount of ejected water. Dead space in the electrolyte tube was minimized by a solid quartz rod that forces the gas to flow close to the electrodes. A pair of titration electrodes, 75 mm in length, were prepared inside and outside at the centre of the tube using porous Pt paste and multiple 0.3 mm diameter Pt lead wires in intimate contact with the pasted area. An additional pair of probe electrodes were prepared similarly, isolated by a distance of 3 cm from the titration electrodes, for separate inspection of the oxygen potential. The titration electrodes are connected by four lead wires with the electrical circuit. One pair measures the voltage and feeds it back into the potentiostat which is preset to that voltage. The other pair drives the titration current from the potentiostat through the titration cell. This titration current I is measured in intervals of 250 ms by the voltage drop across a 1 $\Omega \pm 0.5\%$ resistor using an analog/digital convertor and a microcomputer for signal processing.

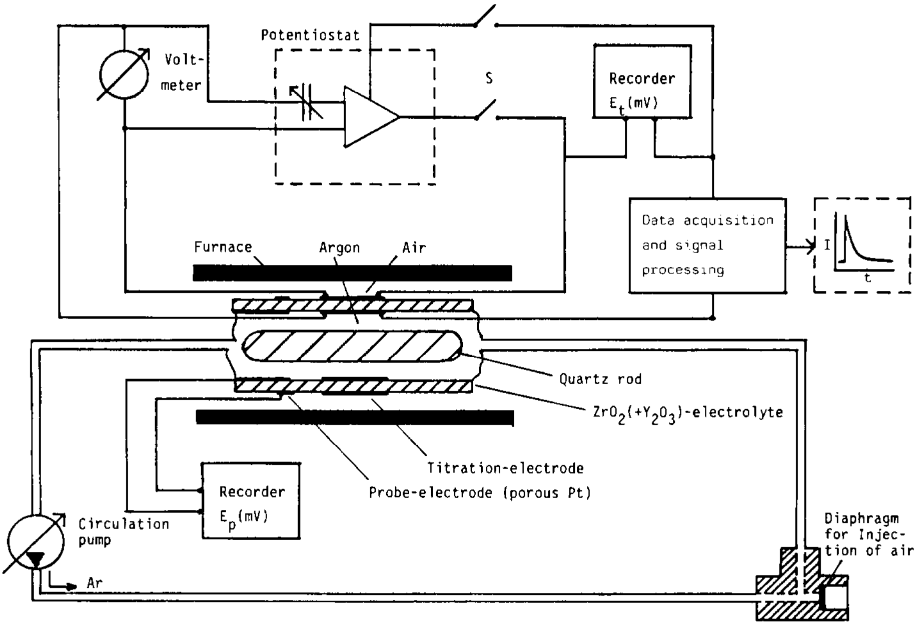

Fig. 1. Experimental set-up of the electrolyte cell in the closed gas circuit and the attached electrical circuit.

The electrolyte tube used was ZrO_2 + 8.5 wt% Y_2O_3 (Friedrichsfeld GmbH, type FZY) with i.d. 10 mm, o.d. 15 mm and length 450 mm. Some experiments were also carried out with a ZrO_2 + 13.6 wt% Y_2O_3 tube (Nippon Kagaku Togyo Co., type ZR-8Y) with i.d. 17 mm and o.d. 21 mm. However, the results obtained were similar. The lengths of the titration electrodes, which were changed from 70 mm to 350 mm (thereby extending out of the furnace into the cold part), were also of little influence. In preliminary experiments the thickness of the Pt paste was varied between 1 and 12 mg Pt cm^{-2}. There should be an optimum value for titration performance, since the thicker the paste, the better the electrical conductivity, but the worse the oxygen throughput. However, there is no clear optimum and any Pt-layer thickness in this range worked sufficiently well. An important part of the cell design is the reinforcement of the pasted area with an array of multiple Pt wires which have to be excellently connected to the paste. However, the most dramatic impact on the titration performance is exerted by a special treatment, described later.

Pure argon (99.998%) was used as the circulating gas for all the experiments reported here. The following schematic cell configuration was used.

$$\text{Pt, Ar}(+O_2)//ZrO_2(+Y_2O_3)//\text{air, Pt} \qquad (1)$$

In similar experiments Ar was substituted by an Ar + 0.1% H_2 mixture of the type used for the oxygen analysis in metal samples. This addition of hydrogen had a negligible influence on the observations.

The electrolyte cell was kept in a controlled furnace at 760 ± 1° C. The circulation pump was set to 200 cm^3 min^{-1}, except for the measurement of cell resistivity, where the pumping rate was increased until the data became independent of the pumping rate.

E.M.F. DROP WITH DISCONNECTED POTENTIOSTAT

Residual oxygen was pumped out of the Ar gas circuit by applying a voltage of 1400 mV with the potentiostat. After equilibration the e.m.f. at the probe electrode (E_p) was 1345 mV. According to Nernst's equation and its extension to electron and hole conductivity [4,5] this corresponds to a very low oxygen partial pressure p_{O_2}. The potentiostat was then disconnected by opening switch S in Fig. 1 and E_p was monitored as displayed in Fig. 2. Within the first 4 min only a very small voltage drop of 7 mV is observed. Then 15 mm^3 of air were injected into the gas circuit, containing a total volume of 35 cm^3. This corresponds to a drastic increase in p_{O_2} and, after homogenization, an expected drop in E_p below 200 mV. This drop, expected for a cell with inert behaviour, is shown by the dotted line in Fig. 2. In contrast, the observed value of E_p drops only slightly to 1280 mV and stabilizes again at 1320 mV, not far from the value extrapolated from the previous curve without any injection of air. The oxygen deliberately introduced into the closed system seems to have miraculously vanished.

The injection of 15 mm^3 of air was repeated (as labelled by the numbers 1–4 and 6 in Fig. 2) with very similar results. Even the repeated injection of 500 mm^3 of air (labelled by numbers 5 and 7–19) results in only very small

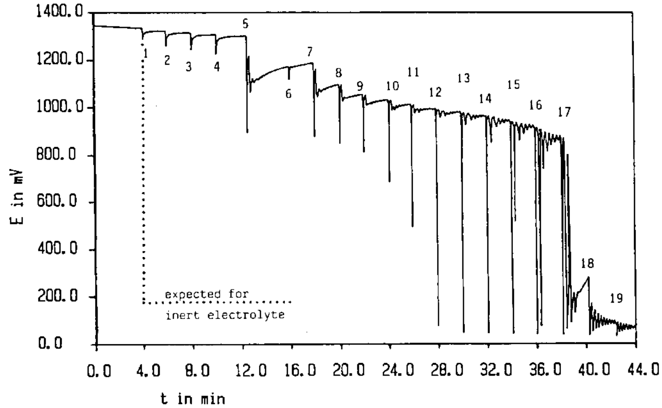

Fig. 2. Voltage drop at the probe electrode caused by the injection of air into the Ar gas circuit with the potentiostat disconnected. Signals labelled 1–4 and 6 correspond to 15 mm^3 injections, while signals 5 and 7–19 correspond to 500 mm^3 injections. The dotted line would be expected after the very first injection if the electrolyte was inert.

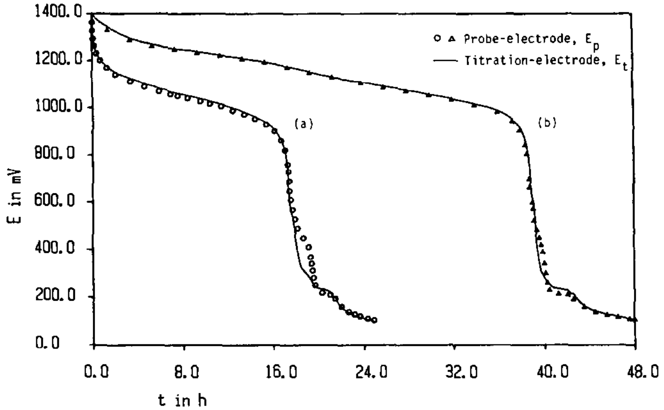

Fig. 3. Voltage drop at the probe and titration electrodes caused by the leaking of air into the Ar gas circuit with the potentiostat disconnected. Data are given for two different histories of the electrolyte cell: (a) 10 h at an applied voltage of 1400 mV from the potentiostat; (b) 120 h at an applied voltage of up to 1600 mV.

decreases in e.m.f. with subsequent stabilization at high e.m.f. values. However, after injection 17 (when the e.m.f. value is below approximately 800 mV) a drastic decrease in e.m.f. occurs.

For the next experiment the same starting point was chosen, namely equilibration at 1400 mV applied voltage and disconnection of the potentiostat at time zero. The voltage drop was monitored without any injection of air (similar to the first 4 min in Fig. 2) and the result is given in Fig. 3 for both E_p and the e.m.f. at the disconnected titration electrode (E_t).

Let us first focus on curve (a). This time the voltage drop is caused by oxygen diffusing through unavoidable leaks into the gas circuit. One might expect some sort of exponential drop, since, in the beginning, small amounts of O_2 should decrease p_{O_2} more drastically than at a later stage, and also since the driving force for oxygen diffusion gradually decreases. The data observed are very different from those expected. They are stabilized in the 1150–900 mV range for many hours and then drop markedly with some smaller stabilization effects around 300 and 200 mV. At the beginning of the smaller stabilization effects E_p is retarded relative to E_t.

In Fig. 3 data are also given for a second experiment (b), which corresponds to a different pretreatment of the cell. Before equilibration at 1400 mV the cell was exposed to applied voltages of up to 1600 mV for 120 h. This results in a marked effect on the first stabilization level, which is more than twice as long as that in (a) and is also shifted to higher voltages (1250–950 mV).

It should be emphasized that we have measured a number of curves which are very similar in shape to those in Fig. 3 using various electrolyte materials, electrode designs, etc., as stated in the previous section.

We will postpone the discussion until other relevant effects have been presented. One obvious conclusion should be given here. Although the type of experiment presented in Fig. 3 may look attractive for the determination of the leakage rate of the gas circuit, it would be completely misleading if interpreted in this way.

OXYGEN RELEASE FROM THE ELECTROLYTE AND OXYGEN POTENTIAL

In the following experiments the cell was equilibrated with the gas circuit at a preset voltage and then the voltage was increased by 200 mV. This results in a titration current signal that may be integrated to give the transferred charge. This charge, disregarding the contribution from the final residual current, is marked by the circles in Fig. 4 as a function of the applied voltage. Since the total amount of residual oxygen in the gas circuit, for any voltage above 250 mV, represents a possible charge of less than 1 mC, it is obvious that this has no effect on the titration of oxygen from the gas phase. The measured charge presumably represents oxygen released from the electrolyte material itself. For comparison, data measured by Otsuka and coworkers [6–9] in a similar way, but using liquid metals instead of the (Pt, Ar) electrode, and shown by triangles in Fig. 4. These data are independent of the kind of liquid metals used, e.g. Pb, In, Sn, Sb, Tl, Bi and Au.

In view of the phenomena which occur in the cell two questions can be posed. (1) What is the actual oxygen potential in the gas under a certain

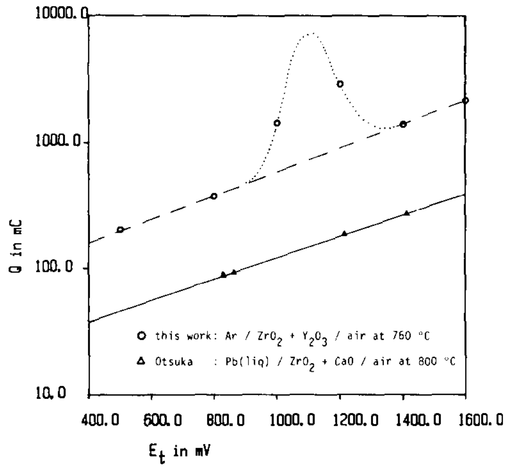

Fig. 4. The electric charge Q transferred after stepping the applied voltage from $E_t - 200$ mV to E_t. This stems from the oxygen released from the electrolyte. Data from similar experiments [6] using liquid metals instead of the (Ar, Pt) electrode are shown for comparison.

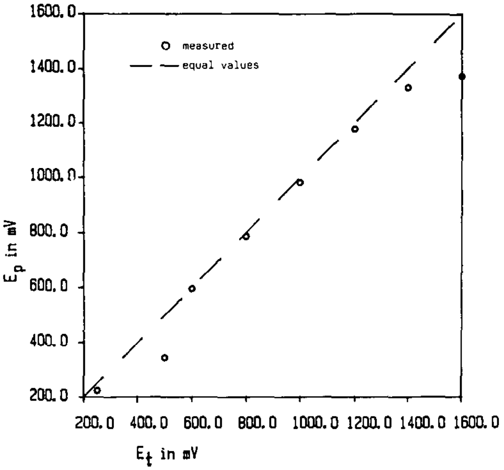

Fig. 5. The e.m.f. at the probe electrode (E_p) which follows rather closely the applied voltage at the titration electrode (E_t) up to 1200–1400 mV.

applied voltage? (2) Is there a lower limit to p_{O_2} that can be achieved by the pumping action of the titration electrodes? In Fig. 5 the e.m.f. at the probe electrode, after equilibration, is given as a function of the applied voltage at the titration electrode. Although the measurement of E_p is currentless its accuracy might be subject to polarization owing to the possible reactions between the gas and the inside electrode. The relationship between E_p and p_{O_2} will be addressed in the final discussion.

CONDUCTIVITY AND SPECIAL TREATMENT OF THE CELL

The current–voltage dependence at the titration electrode has been measured to quantify the possible throughput of oxygen through the cell. For this experiment the diaphragm unit, shown in Fig. 1, was completely removed, a sufficient stream of fresh air was blown through the inside of the cell and oxygen was titrated towards the outside of the cell. The two measured data sets, given in Fig. 6, were taken after different pretreatments of the cell. The lower set was obtained after the cell had been subject (for a long time) to an applied voltage of 1400–1600 mV with the gas circuit closed (low p_{O_2}) . The measurements were taken, initiated by a short application of $E_t > 2000$ mV as a starting point, not shown in Fig. 6. After completing the lower data set the cell was subjected to a special treatment described later in this section. The upper data set was then taken. This data set demonstrates that a marked improvement in the cell conductivity was achieved by the special treatment. This upper set consists of two subsets, which were taken with increasing/decreasing voltage.

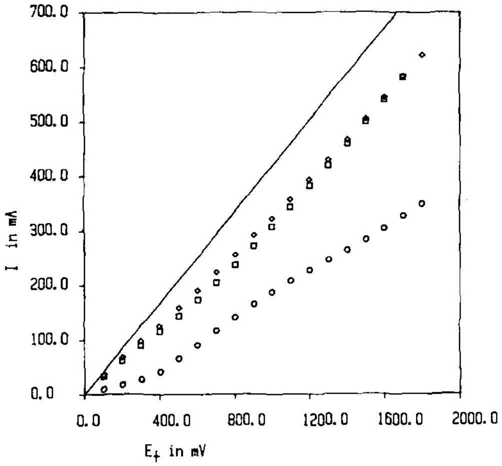

Fig. 6. Current I as a function of the applied voltage at the titration electrode (E_t) with air supplied at inner and outer electrodes. The measured data sets represent different histories of the electrolyte cell: (○) after operation at 1400–1600 mV and low p_{O_2} (inner electrode) for a long time; (◇ □) after "recuperating" the cell with a special current treatment. The straight line is calculated from the ionic conductivity quoted in the manufacturers data sheet.

The straight line shown for comparison in Fig. 6 was calculated from the ionic conductivity at 760 °C (as quoted by the manufacturer of the electrolyte) and the cell geometry. This line merges with the upper data set near zero voltages, indicating that the cell was in optimum condition for high conductivity. The deviation from the line at higher voltages may be explained in terms of the total resistivity of the actual cell, which includes two terms additional to the ionic resistivity of the electrolyte. These are the development of a diffusion layer for oxygen transport between the electrodes and the bulk of the convective gas flows on either side, and (to a lesser extent) the voltage drop along the Pt paste and lead wires.

The special treatment of the cell, responsible for the drastic improvement of the conductivity, was carried out as follows. The gas circuit was opened and fresh air was blown through the cell, as in the current–voltage measurement. Then, very large voltages of up to 7 V were applied at the titration electrodes for 10 min which drove currents of up to 1.5 A. This procedure was repeated several times with reverse polarity. Finally, oxygen was pumped with low voltage (100 mV) from the outside to the inside for about 12 h.

There are some hints in the literature [10,11] that the conductivity or "pumping capacity" of a cell may be considerably improved by driving large currents through it, or by applying an a.c. voltage. We found our procedure to be very efficient and we used it to recuperate the cell (optimum condition) before experiments on the coulometric titration of injected air were performed.

TITRATION OF INJECTED AIR

The set-up depicted in Fig. 1 with the closed gas circuit was used for the following experiments. After equilibration at an applied voltage of 250 mV from the potentiostat, 15 mm^3 of air were injected into the gas circuit and the signal of the titration current was stored. After equilibrium was re-attained (defined by a variation in the residual current of less than 0.005 mA) this single injection measurement was repeated twice. Then the applied voltage was increased in a number of steps up to 1600 mV. At each step at least 4 h were allowed for equilibration.

Typical current signals from the titrations at 800–1600 mV are displayed in Fig. 7. It should be noted that the maximum current at 1600 mV is lower than that at 1400 mV. The signals at 250, 500 and 600 mV, not shown in Fig. 7, are very similar to those at 1200 and 1600 mV. The signals at 800 and 1000 mV exhibit irregularities, such as very low current maxima and unusual signal shape, that are related to the phenomena in the electrolyte cell.

Integration of the residual-subtracted signals over 8 min (after that time the residual current attained the starting value in all cases) gives the measured charge. This is given as a percentage of the theoretical charge from the injection air in Fig. 8 for the various titration voltages. Results from additional measurements at 1400 mV (taken after the 1600 mV experiments) are also shown. They are clearly below the data previously taken at 1400 mV and are also below the ideal 100% line. Hence, operation at 1600 mV changed the condition of the cell and permanently reduced the accuracy of the measurements.

It should be noted that after very long operating times at 1400 mV the measured charge may decrease to 90% of the theoretical value. However, this deterioration can be cured by the special cell treatment described above.

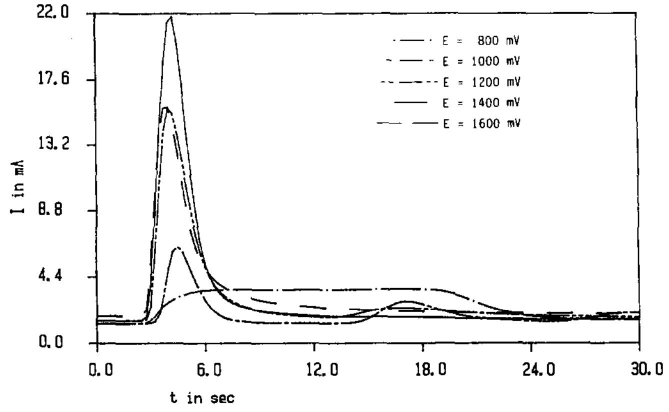

Fig. 7. Typical titration currents after the injection of 15 mm^3 of air at constant applied voltages in the range 800–1600 mV. The shape of the signals at 250–600 mV (not shown here) is similar to that at 1400–1600 mV.

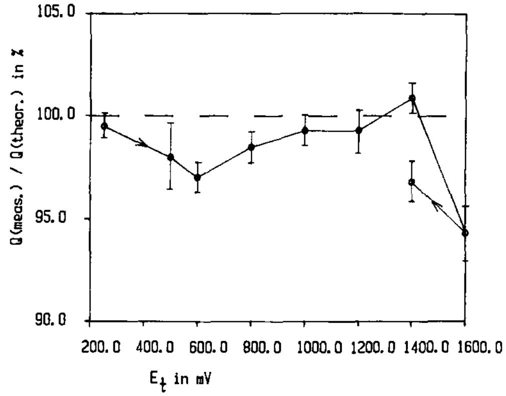

Fig. 8. Means and standard deviations of measured charge (after 8 min integration time) in percentage of theoretical charge calculated from the amount of injected air (15 mm^3). Data are taken after a special pretreatment of the electrolyte cell with different applied voltages in the order indicated by the arrows.

If the integration is terminated after 2 min a picture similar to that in Fig. 8 is obtained. However, the standard deviations decrease and the accuracy at 1400 mV is almost exactly 100%. A most notable change is observed at 1000 mV where only 80% of the charge is present after 2 min integration, compared with 99.3% after 8 min integration. This emphasizes the very long tail of the 1000 mV signal much better than could have been seen in any extension of Fig. 7.

Finally, we wish to investigate the lower limit of oxygen that can be measured in the gas phase. In our ongoing work, we analyse oxygen in metal samples that are heated in a furnace integrated into the gas circuit. In order to mimic this situation for the following experiments, the furnace (without a metal sample and with the furnace cold) was attached to the gas circuit between the diaphragm and the cell (see Fig. 1). This means that the injected air will be diluted in this additional dead space of 80 cm^3 before it reaches the cell to be titrated.

After applying the special treatment to the cell, titration was carried out at 1400 mV for various amounts of injected air. A comparison of measured and theoretical charges is given in Fig. 9. A corrected data set is also shown where a constant blank value, that arises from pushing the needle through the diaphragm and out again without injecting air, is subtracted. The range of the values given in Fig. 9 corresponds to the 1–20 mm^3 range of the syringe and it should be noted that the use of the syringe is recommended for high precision in the medium range. The agreement between measured and injected oxygen is good, only the lowest data point is somewhat high.

The lowest data point corresponds to 1 mm^3 of air or Q(theor) = 3.20 mC or a mass of 0.266 μg of oxygen. Its accuracy is certainly limited by the way air is introduced into the system. The needle of the syringe contains 0.9 mm^3

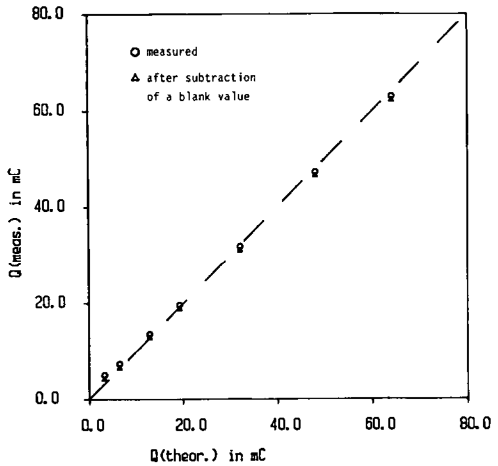

Fig. 9. Comparison of measured and theoretical charges obtained from titrating injected air (1–20 mm^3) from the circuit enlarged by an additional dead space. The lowest value corresponds to Q(theor) = 3.20 mC or 0.266 μg oxygen.

of air, and this could give an overshot of oxygen, considering the momentum transferred to the air during the injection. The titration signal was still very clearly resolved with a current maximum separated by 400 μA from the residual current, and the noise in the residual current was only ± 3 μA. This will not limit any attempt to measure oxygen contents below 1 p.p.m., which corresponds to 1 μg of oxygen in a sample mass of 1 g.

DISCUSSION

Oxygen release and uptake from the electrolyte

During the coulometric titration of oxygen using liquid metals, Otsuka and coworkers [6–9] observed the release of large amounts of oxygen from the electrolyte at high voltages as given in Fig. 4. The slope of the linear log Q vs. E (or log p_{O_2}) relationship is different from what may be expected if the oxygen release was due to an increase in oxygen vacancy concentration in the ZrO_2 ($+Y_2O_3$) crystal [8]. They concluded, therefore, that most of the oxygen was released from less stable oxidic impurities in the electrolyte.

It is remarkable that the slope of the log Q vs. E relationship is virtually independent of the liquid metal used. We observed the same slope in our measurements, with the exception of the range 800–1400 mV. In this range higher amounts of oxygen are released, as seen from Fig. 4. At the beginning of this range very flat titration signals were obtained. It is suggested that the titrated oxygen passing through the electrolyte is transiently trapped by oxidation processes which are the reverse of the processes responsible for the higher amount of oxygen released in this range. This agrees with the marked voltage drop after injection 17 in Fig. 2 and with the end of the major level of stabilization in Fig. 3. The extension of this level of stabilization depends on how long the cell has been subject to strongly reducing conditions, which simply reflects the amount of material involved. It also reflects the similar reaction kinetics of both the reducing treatment and the oxidation processes, as given in Figs. 3 and 4. The marked drop in both curves (a) and (b) of Fig. 3 after the 1400–1800 mV range is due to the continuing leakage of oxygen into the system, which causes a rapid increase in p_{O_2} since the oxygen sinks are almost filled up. The two minor stabilization levels at 200–300 mV involve a much smaller amount of material than the major level.

What kind of redox reactions could possibly be responsible for these phenomena? A list of the oxidic constituents of a commercial ZrO_2-based electrolyte is given ref. 5 as follows: Fe_2O_3, Na_2O, SiO_2, Al_2O_3, ZrO_2, HfO, MgO, ThO_2, CaO and Y_2O_3. The dissociation potentials at 760 °C can be calculated. They range between 1395 and 2764 mV with that of ZrO_2 being 2300 mV. However, this assumes that the constituents are pure phases, which is certainly not the case. Therefore they may not be excluded from reactions below 1400 mV. Even more likely is the reduction of Fe_2O_3 to Fe_3O_4 at 500 mV, continuing to FeO_n (890 mV) and Fe (960 mV) (again calculated for pure phases not dissolved in the matrix).

Another possible reaction that enhances the dissociation of ZrO_2, and thereby offers huge amounts of oxygen, is the formation of the intermetallic compound $ZrPt_3$ at the inner electrode according to

$$ZrO_2 + 3Pt = ZrPt_3 + O_2 \tag{2}$$

At 800 °C an oxygen potential of $p_{O_2} = 1.6 \times 10^{-25}$ atm or $E = 1280$ mV is given for reaction (2) by Worrell and Ramanarayanan [12]. This might explain the "bump" of additionally released oxygen in Fig. 4, compared with the straight line observed by Otsuka and coworkers [6,7], since in their experiments liquid metals other than Pt were used as the contact material.

The influence of the quartz rod, used to eliminate dead space in the cell, has also been considered. Reduction of SiO_2 to elemental Si would require too high a voltage (1840 mV). However, reduction according to

$$SiO_2(s) = SiO(g) + \tfrac{1}{2}O_2(g) \tag{3}$$

may occur at a lower voltage, depending on p_{SiO}. If we assume that SiO does not "condense" in the cold parts of the gas circuit by the reversal of reaction (3), the total amount of SiO formed at 1400 mV may be calculated at 760 °C using the data of Kubaschewski and Alcock [1] and the volume of the system, which gives $p_{SiO} = 9.4 \times 10^{-13}$ atm. The corresponding amount of oxygen released from the quartz rod, 6.1×10^{-14} μg or 7.4×10^{-13} mC is negligible compared with the measured oxygen release in Fig. 4. If SiO does condense in the cold parts of the gas circuit it should have been observed.

However it has not been detected. Moreover, there would be no reason for this reaction to stop after reasonable periods of time, in contrast with that observed in Fig. 4. In addition, this could not explain the observations in Fig. 3 and the oxygen uptake, which is obviously complementary to the release, as given in Fig. 4. Therefore, the quartz rod is a negligible source of oxygen.

Influence of the cell treatment

Takahashi et al. [10] concluded that the drastic improvement in the total conductivity of the cell, after passing high currents through the cell, was due to an increase in the porosity of the Pt layer as a result of oxygen gas being forced through it. This contribution is also important in our case, especially for the very first treatment. However, the solid state sintering of the porous Pt layer at 760 °C is not fast enough to cause the repeated deterioration of the cell conductivity, which depends more on the voltage than on the time of operation.

Therefore, after high voltage (low p_{O_2}) titration we have a second effect. The recuperation of the cell by the current/air treatment is not only due to the Pt porosity, but is also a result of the reversal of a number of partly sluggish reduction processes occurring in the electrolyte material.

This statement is not only substantiated by the measured variation in the cell conductivity as given in Fig. 6 (and similar data not shown here), but also by the titration of air performed with the same cell under different conditions. After the special current/air treatment virtually 100% of the injected amounts were titrated. After extensive use of the cell at 1400–1600 mV this decreased to about 90%, the titration current maxima were reduced by half and much longer integration times were necessary.

This means that a high cell conductivity or pumping performance is important for the titration of small amounts of oxygen. A lower conductivity does not only retard the titration. Some of the oxygen trapped transiently by oxidation processes as it passes through the cell is eventually released, but so sluggishly that it gets lost in the noise of the residual current. The poor titration performance at 800–1000 mV in terms of flat signals and long integration times is a direct consequence of this effect. The poor titration performance at 1600 mV compared with that at 1400 mV is due to two effects: (i) the reduction of the material proceeds even further and deteriorates the performance permanently, even after returning to 1400 mV; (ii) the electronic conductivity of the electrolyte seems to play a role, as discussed below.

Electronic conductivity of the electrolyte

The temperature dependence of the oxygen potential $p^{\star}_{O_2}$, at which ionic and electronic conductivities have equal values, has been reported by Iwase et al. [13] for a material similar to ours. From this we may calculate the ionic transfer number t_{ion} at 760 °C, t_{ion} is 0.99974, 0.9975 and 0.99 for $E = 1400$, 1600 and 1725 mV, respectively. These data do not indicate a significant electronic contribution at 1600 mV. However, a variety of impurities in ZrO_2 are known [14] to shift the ionic domain and to increase the electronic conductivity. This may also explain why the data reported [15] for $p^{\star}_{O_2}$ in ZrO_2-based material cover such a wide range.

In our case we infer from Fig. 5 that electronic conduction becomes important at 1600 mV and to a small extent at 1400 mV. In fact we expect E_p to remain constant for even higher values of E_t. At higher E_t values the electronic shortcircuit disables the titration electrode. It cannot produce lower values of p_{O_2} and consequently a constant value of E_p will be measured at the probe electrode. In addition, the value of E_p itself may be decreased by the partial shortcircuit and the corresponding flow of oxygen across the electrolyte. This latter effect will presumably not be dominant because the actual p_{O_2} value inside the electrolyte is inherently limited to the small electronic conductivity in the pumping electrode. This is in contrast with the well-known experiments where a decreasing p_{O_2} value is established by a metal–metal oxide mixture and no titration is involved. In which case the displayed e.m.f. becomes constant below the p_{O_2} values characteristic for the onset of electronic conductivity for the latter reason.

Despite the minor uncertainty regarding the e.m.f. reading at E_p it may be emphasized that very low values of $p_{O_2} = 10^{-27}$ bar or $E_p = 1330$ mV can be achieved with a pumping voltage of $E_t = 1400$ mV at 760 °C. This is the same optimum voltage that we observed for the titration of oxygen from the gas phase.

CONCLUSION

The phenomena occurring in the electrolyte cell during titration at high voltage are very complex and it cannot be claimed that all aspects are completely understood. However, the following conclusions can be drawn.

(1) The electrolyte is not inert when operated at voltages far below the dissociation voltage of the ZrO_2 matrix.

(2) Some of the reduction processes in the electrolyte are so slow that the cell performance becomes dependent on the cell history.

(3) With a special current/air treatment this history can be deleted, thereby converting the cell into the condition for optimal titration performance.

(4) An optimum value of the titration voltage is 1400 mV if a strongly reducing condition is required in the gas circuit. By making use of these conclusions, traces of oxygen far below 1 μg can be quantitatively titrated.

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