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Measurement and regulation of oxygen content in gases using solid electrolyte cells. III. Oxygen pump-gauge *

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The technical problems of the conventional one-tube oxygen pump-gauge are reviewed. Several causes of error are shown: the semipermeability of the electrolyte tube, the electric coupling between the pump and the gauge, the existence of local cells due to electric leads deposited on the electrolyte, spurious zero-current voltages. A new set-up involving a microgauge is described. It is capable of producing and measuring within a few per cent accuracy, oxygen-inert gas mixtures with oxygen concentrations ranging down to a few 10^{-2}ppm.

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1. Introduction

Electrochemical pumping of oxygen through a solid oxide electrolyte such as stabilized zirconia has been extensively used for more than ten years, especially for changing the amount of oxygen dissolved in liquid or solid metals or oxides. Comprehensive papers and reviews [1–6] of the related techniques are available. Obviously the fuel cells and the H_2O or CO_2 reduction cells involving O^{2-} ion-conducting electrolytes can be also regarded as electrochemical pumps for oxygen. The scope of this paper will be confined to free-gaseous-oxygen pumping, oxygen being pure or diluted in an inert gas. To our knowledge, the idea was initially suggested by Weissbart *et al.* [7, 8] and Antonsen *et al.* [9]. The first quantitative study was due to Bullière [10]. This study was intended to check the validity of the Faraday law in the case of the oxygen electrode reaction on zirconia. The amounts of gaseous oxygen involved in the reactions occurring at the electrodes were measured volumetrically. It was observed that at low current densities the electrolysis efficiency was equal to 1 both for oxygen uptake and evolution at the electrodes. At higher current densities the efficiency of oxygen uptake decreased, although the efficiency of oxygen evolution at the other electrode remained equal to 1, at least for a certain time. The results were put to use in our laboratory in a device where such an oxygen pump was associated with a conventional gauge on the same electrolyte tube. The device provided oxygen-inert gas mixtures of well-defined compositions for our own experiments [11] and it was later patented [12]. A few comments have been published [13] on its properties and the utilization procedure especially when used with mixtures of gases containing bound oxygen such as CO_2 or H_2O.

The pump-gauge device was also patented by Philip's N.V. Gloeilampenfabrieken [14] and studied in more detail by Kröger [15, 16].

More generally, pumping of oxygen through zirconia was proposed by Fisher [17] and Hickam *et al.* [18]. It has been used for gas analysis [19, 22], in an oxygen-pump die for hot pressing [20], for production of pure oxygen [21], for removal of oxygen from gases [23] and as a selective oxygen

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* Due to unforseen circumstances, Part II of this paper will appear in a later issue.

leak source [24]. Guillou *et al.* [25] suggested using a temperature gradient as the driving force for the oxygen ions in the electrolyte.

The electrode preparation and the cell assemblage in batteries have been improved [26–29].

The pumping-gauge device itself has recently been the subject of some papers [30, 31] dealing with several drawbacks and improvements. The main improvement is an electronic regulation of the pumping effect using the oxygen gauge as a probe. This regulation makes the pump-gauge capable of providing a constant oxygen pressure in a streaming gas carrier, a technique outlined by Beekmans *et al.* [31]. An adequate device has been patented and described in detail by Rapp [32]. An interesting feature pertinent to the oxygen pressure measurement is added in this device; the electronic measuring circuit is connected in such a way that the ratio of the gauge voltage to the absolute temperature (E/T) is used in the measurement of the oxygen pressure which is then independent of erratic temperature variations.

An obvious drawback of the conventional pump-gauge is caused by the oxygen semi-permeability of the electrolyte tube. This was mentioned by Hartung *et al.* [35]. To minimize this effect, Beekmans *et al.* [31] suggested reducing the operating temperature to 600°C while Besson *et al.* [34] proposed a differential system which eliminates the problem and which was used successfully in gauges [36].

In this paper we will report on the results of a more critical study of this now conventional oxygen pump-gauge device and we will describe a new combination of a pump and a gauge which obviates the main disadvantages of the initial design.

2. The pump-gauge device

The conventional pump-gauge is simply made up of metal coatings deposited on a solid-electrolyte tube as shown schematically in Fig. 1. Generally, the metal is platinum and the electrolyte is zirconia, stabilized either by calcia or yttria; the operating temperature is chosen between 600 and 800°C. The analyzed gas streams in the tube and ambient air is in contact with the external electrodes.

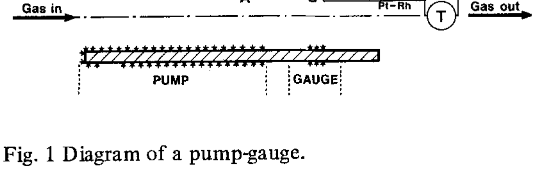

Fig. 1 Diagram of a pump-gauge.

A known current is passed through the electrolyte in the pump-zone by applying a suitable voltage between electrodes A and B (a positive sign is assigned to I for a current passing from the outside to the inside of the tube). If the electrolysis obeys the Faraday law the flow of oxygen J being pumped from the outside to the inside of the tube is equal to:

$$J = I/4F \qquad (1)$$

J in $\mathrm{mol\,h^{-1}}$, I in A, $F = 1$ Faraday.

The amount of oxygen is diluted in a volume of carrier gas equal to 0 [upstream gas flowrate in $1\,\mathrm{h^{-1}}$ – NTP)].

If C is the oxygen mole fraction in the upstream gas carrier, the resulting oxygen pressure PO is:

$$\mathrm{PO_2} = \frac{\dfrac{CD}{22{\cdot}4} + \dfrac{I}{4F}}{\dfrac{D}{22{\cdot}4} + \dfrac{I}{4F}}\, p \qquad (2)$$

where p is the total pressure (atm) in the pump-gauge.

When the amount of oxygen added to or extracted from the carrier gas is small, the term $I/4F$ in the denominator is negligible, and the expression is numerically:

$$\mathrm{PO_2} = (C + 0{\cdot}209\, I/D)p. \qquad (3)$$

The gauge electrodes C and D (cf. Fig. 1) are located in a zone where the temperature gradient is small enough for their temperatures to be well-defined. The gauge emf E is given by the Nernst law:

$$E = \frac{RT}{4F} \ln \frac{\mathrm{PO_2}}{P_{\mathrm{air}}} \qquad (4)$$

R = gas constant; T = absolute temperature; P_{air} = oxygen pressure in ambiant air in contact with the outside electrode.

Numerically:

$$E_{\mathrm{V}} = 4{\cdot}958 \times 10^{-5}\, T \log \frac{\mathrm{PO_2}}{0{\cdot}209\, P_{\mathrm{atm}}}, \qquad (5)$$

p_{atm} = ambient atmospheric pressure E in V.

By combining Equations 3 and 5 we get the relation between the pumping current I and the gauge-voltage E

$$E = 4{\cdot}958 \times 10^{-5}\, T \log\left(\frac{C}{0{\cdot}209}+\frac{I}{D}\right)\frac{p}{p_{\mathrm{atm}}}. \qquad (6)$$

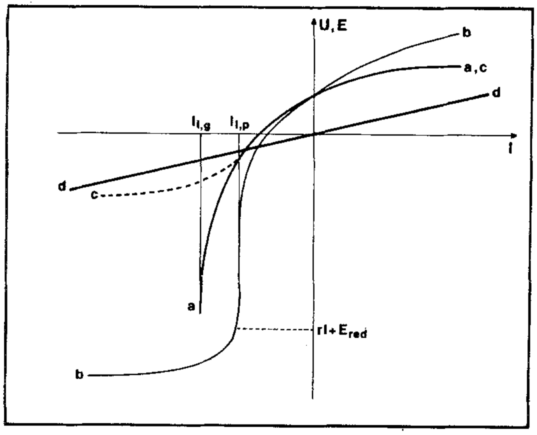

Fig. 2 Curve *a*: $E-I$ (theoretical characteristic with an oxygen-inert gas mixture); curve *b*: $U-I$ (pump characteristic); curve *c*: $E-I$ (experimental characteristic); curve *d*: ohmic drop in the pump.

The corresponding $E-I$ curve is plotted in Fig. 2 (curve *a*). It shows the existence of a limiting current I_{lg} equal to:

$$I_{\mathrm{lg}} = -4{\cdot}79\, CD. \qquad (7)$$

The relation between the pumping current I and the pump-voltage U is slightly more complicated. According to the more commonly accepted hypothesis the voltage U is related to I as a first approximation by:

$$U = rI + E_{\mathrm{p}} \qquad (8)$$

with

$$E_p = \frac{RT}{4F}\ln\frac{\pi}{\pi_{\mathrm{air}}}; \qquad (9)$$

r = ohmic resistance of the electrolyte in the pump-zone; π = oxygen pressure right at the triple contacts of the internal electrode; π_{air} = oxygen pressure right at the triple contacts of the external electrode.

In air, and with not too high a current I, it can be reasonably assumed that oxygen exchange is quite fast between the surrounding gas and the triple contact. So, as a first approximation, π_{air} is equal to P_{air}. On the other hand for the internal electrode, generally working under much lower oxygen pressure, the oxygen exchange rate is low and the local pressure π is smaller than P. The $U-I$ characteristic of the pump, as compared to the $E-I$ characteristics is shown in Fig. 2 (curve *b*). It shows the existence of a limiting current I_{lp} smaller than I_{lg}. The value of the parameter I_{lp} depends upon the operating conditions. It has been shown [37] that for vanishing gas flow rates, I_{lp} tends to be equal to I_{lg} and according to Equation 7 to be proportional to C. For high flow rate, I_{lp} is much smaller than I_{lg} and tends to be proportional to the square root of C.

In fact, when the variable E_{p} approaches a voltage E_{red} close to -1500 mV, a new electrode reaction occurs in the pump. Electrons are injected within the electrolyte [38], the conductivity of which becomes partly electronic. The Faraday law is no longer followed and we must use the following reaction instead of Equation 1 in the derivation of the relation between I and E.

$$J = \frac{If}{4F}, \qquad (10)$$

f = electrolysis efficiency. Under such conditions the $E-I$ characteristic is shaped as shown in Fig. 2 (curve *c*).

It is usually recommended to work with currents smaller than I_{lp}, Otherwise, electron injection in the electrolyte is supposed to increase drastically the brittleness of the tube and to shorten the pump life.

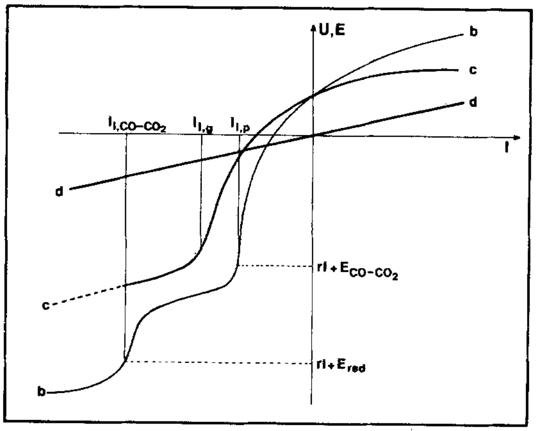

Fig. 3. Curve *b*: $U-I$ characteristic (with an oxygen-carbon dioxide inert gas mixture); curve *c*: $E-I$ characteristic; curve *d*: ohmic drop in the pump.

If carbon dioxide is present in the gas carrier, when the parameter E_p is larger than a value E_{CO-CO_2} the direct reduction of the CO_2 molecules is also possible in the pump [37]. The reaction occurs simultaneously with the oxygen molecule reduction. An example of a pump $U-I$ characteristic corresponding to this case is plotted in Fig. 3 (curve *b*). The $E-I$ characteristic can be easily deduced from this curve taking into account that for E_p smaller than E_{red} the electrolysis still obeys the Faraday law. The overall amount of oxygen being pumped remains that given by Equation 1, oxygen being extracted from the gas either as free molecules or by reduction of carbon dioxide molecules according to the overall reaction: $CO_2 \rightarrow CO + \frac{1}{2}O_2$. In Fig. 3, four zones can be considered:

$|I| < |I_{1p}|$: oxygen is directly pumped by oxygen molecule reduction;

$|I_{1p}| < |I| < |I_{1g}|$: oxygen and carbon dioxide molecules are reduced at the triple contacts of the electrode. Carbon monoxide molecules so produced are reoxidized in the gas by oxygen molecules in excess;

$|I| > |I_{1g}|$: same primary processes but carbon monoxide molecules are in excess;

$|U| > |rI + E_{red}|$: the Faraday law is no longer obeyed. In fact, the fourth condition can appear before the third one.

An interesting advantage of the presence of carbon dioxide in the gas carrier is evidenced by the comparison of Figs. 2 and 3, curves *c*. Above the limit fixed by the points $rI + E_{red}$ and under otherwise identical conditions the presence of carbon dioxide makes the pump capable of providing a gas with a lower oxygen content. The same effect is observed with water vapour.

3. Technical problems

3.1. *Gauge*

To avoid the difficulty of connecting a platinum wire to the inner gauge electrode, it has been proposed to use a metallic coating, generally strip-shaped, deposited on the electrolyte as an electric lead from the electrodes to the end of the tube. We have shown in a previous paper [40] that due to local thermocells, such a lead is likely to induce noticeable errors in the gauge emf measurements. The paper can be referred to for more experimental evidence.

Another constant problem of the gauges is the emf that is frequently observed when the same gas, air for instance, is in contact with both electrodes. To get an idea of the main parameter determining this emf we made measurements with air of different flow rates on both electrodes. Table 1 gives an example of the results so obtained. Several experiments of this type were carried out at different temperatures and for different directions of the gas fluxes. All these seem to indicate that the emf is mostly of thermoelectric origin, caused by small temperature differences (2–4°) between the electrodes that are more or less cooled by the gas streaming along them.

In the case of a thermocell:

$O_2(P_1, T_1)$, Pt / stabilized zirconia / Pt, $O_2(P_2, T_2)$,

the electrode reactions remain reversible [39–40] and consequently the cell emf can be written (at least for not too low oxygen pressures):

$$E = E_{hom} + \frac{1}{4F}\,[\mu_{O_2}(P_2, T_2) - \mu_{O_2}(P_1, T_1)]\,. \quad (11)$$

The electrolyte contribution E_{hom} appeared constant for fixed temperatures at the electrodes. For practical use we can deduce from this equation that the simple relation:

$$E = E_0 + \frac{RT_2}{4F}\ln P_2 \quad (12)$$

is valid. It is very similar to the Nernst relation for an isothermal cell:

$$E = -\frac{RT}{4F}\ln P_1 + \frac{RT}{4F}\ln P_2, \quad (13)$$

but here the local temperature T_2 must be used and E_0 includes a thermoelectrical homogeneous term E_{hom}. The parameter E_0 can be simply determined by measuring a pressure P_2 of a known value.

To check the validity of a thermal emf hypothesis and more simply of Equation 12, we have carried out measurements under such conditions that E_{hom} or E_0 was likely to induce noticeable errors if its effects were not correctly eliminated and particularly when E was in the range 1–10 mV. We have measured the oxygen pressures using Equation

Table 1.

$D\,\mathrm{lh}^{-1}$	0	2	4	6	8	10	12
emf (mV)	1·30	1·20	1·12	1·05	1·00	0·91	0·88

Temperature = 900°C.
Air inside the tube; flow rate = 0 lh^{-1}.
Air outside the tube; flow rate = $D\,\mathrm{lh}^{-1}$.

12 for different currents I passing through the pump and verified that the calculated pressures conform with Equation 3. Table 2 shows an example of the results. The calculated pressure variations are plotted in Fig. 4. The theoretical value of slope deduced from Equation 3 is 1·0 s x $10^{-2}\%\,\mathrm{mA}^{-1}$. It is in quite good agreement with the experimental value 1·0 x $10^{-2}\%\,\mathrm{mA}^{-1}$.

This result does not fully confirm the hypothesis of E_0 being a thermoelectric emf, but it clearly shows that under conditions where this spurious emf induces noticeable errors, the measurements can be easily corrected for its effects. Therefore a gauge can also be used for measuring very small oxygen pressure variations, for instance in air.

The main drawback of the conventional pump-gauge device is due to the gauge and the surrounding parts of the electrolyte tube being in contact with air. We have analyzed in a previous paper [36] the behaviour of a gauge used under such conditions for measuring low oxygen concentrations of the order of 1 ppm. It has been shown that due to low electronic conductivity of the electrolyte the tube wall is slightly permeable to oxygen. At a temperature higher than about 800°C the corresponding oxygen flux is high enough to modify the oxygen concentration in the gas carrier. At lower temperatures this effect is negligible, but the oxygen flux is still sufficient to induce departure from equilibrium values of the oxygen chemical potential right at the triple contact of the electrodes where the oxygen pressure is actually measured. To overcome this difficulty, a differential arrangement was proposed and successfully tested [36]. The differential arrangement for a pump-gauge simply, which consists of two concentric tubes on which pump and gauge electrodes are deposited facing each other, as shown in Fig. 5.

A reverse flux of a guard gas with low oxygen concentration prevents any oxygen from reaching and contaminating the analyzed gas. Experiments were carried out on such a differential arrangement. Similar results to those reported in our previous paper [36] were obtained. The measurement

Table 2.

I (mA)	−300	−250	−200	−150	−100	−50	−10	0	50	75	100	150	200	250	300
$(E-E_0)$ (mV)	−0·79	−0·66	−0·53	−0·40	−0·28	−0·15	−0·04	0	0·12	0·20	0·24	0·36	0·49	0·62	0·73
ΔP %	−3·1	−2·6	−2·1	−1·6	−1·1	−0·6	−0·16	0	0·48	0·8	0·86	1·4	1·85	0·45	2·9

Temperature: 890°C.
Air flushing the outside space in the gauge-pump direction, so that pumping of oxygen has no effect on its composition at the gauge level (this point was accurately checked).
Air inside the tube, flow rate: 160 cc mm^{-1}.
For $I = 0$, $E = E_0 = 1{\cdot}28$ mV.

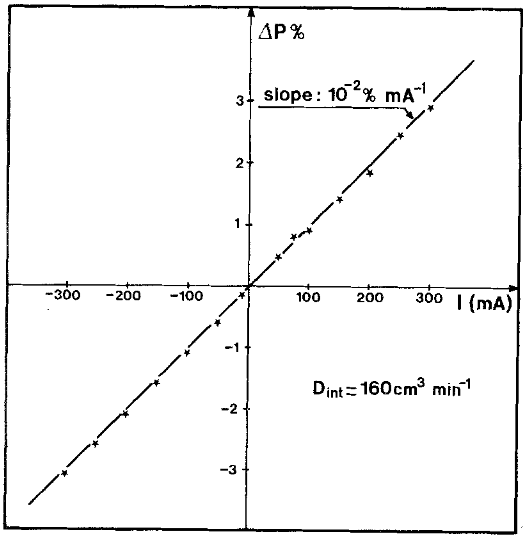

Fig. 4. Production and measurement of small variations of oxygen concentration in air with a pump-gauge. Theoretical slope calculated using the Faraday law: 1·05 X $10^{-2}\%\,\mathrm{mA}^{-1}$.

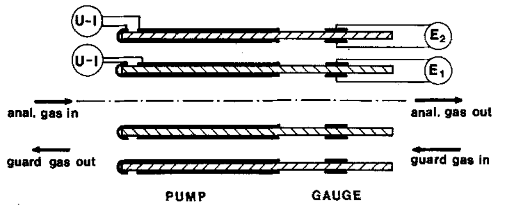

Fig. 5. Differential pump-gauge.

procedure described in this paper can be utilized with the differential pump-gauge, but unfortunately here, due to the geometry of the cell, the temperatures of the four electrodes of the two gauges are generally different and more unstable. It is then quite a tedious job to perform a measurement taking into account the effect of the corresponding temperature differences (as previously sketched in this paper for instance). In the later part of the paper we will describe another arrangement which allows us to overcome the oxygen permeation problem.

3.2. *Pump-gauge electrical coupling*

Another drawback of the conventional one-tube device results from a possible electric influence of the pump on the gauge. These two cells are in fact only separated by a part of the stabilized zirconia tube which is a conductor at the utilization temperature. To reduce the possible electric coupling, Hick *et al.* [33] proposed to heat the pump-gauge by two different furnaces, one for the pump and one for the gauge, separated by a cold zone. This coupling is likely to occur in pump-gauges where the internal or external gauge electrode is connected to the corresponding pump electrode either by a metallic coating of the electrolyte tube or through a common ground or an electronic device used for instance for regulating the system. Under these circumstances a part of the pumping current can, for instance, pass through the connected gauge electrode and induce a local ohmic drop which constitutes a spurious variation of the gauge emf. Such an effect has already been mentioned [41]. Rapp [42] also observed it. To estimate the magnitude of the corresponding error, measurements were made under such conditions that the error was maximized; that is to say with a pumping current of high density and an analyzed gas giving a small gauge voltage. In fact, the conditions and the measurement procedure were similar to those prevviously described when dealing with the parameter E_0. (The effect of this parameter was corrected as previously mentioned). Two sets of measurements were made: one with the external gauge electrode connected to the corresponding pump electrode and one with the gauge electrodes and the measuring electric circuit completely insulated from the pump circuit except for the electric contact due to the solid electrolyte. The verification of the Faraday law was also used as a test. The corresponding experimental results are given in Table 3 and plotted in Fig. 6. According to Equation 3 the theoretical value of the straight-line slope is 21 ppm mA^{-1}. The experimental value 20 ppm mA^{-1} obtained with an insulated gauge agrees quite well. When the external electrodes are connected the experimental value (95 ppm mA^{-1}) is very different. This comparison clearly demonstrates that the electric connection can induce tremendous errors.

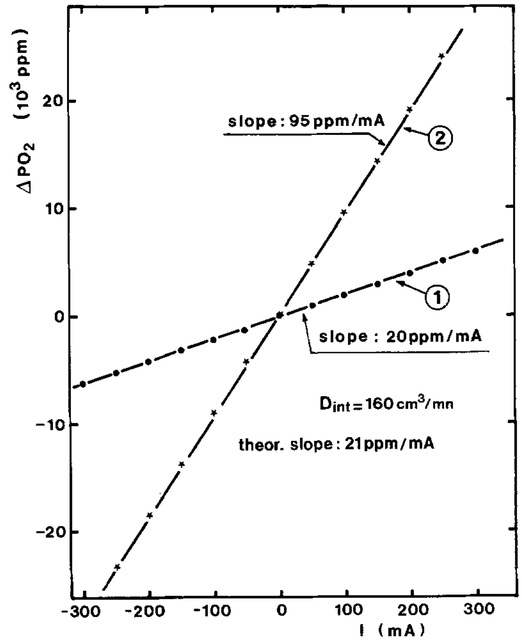

Fig. 6. Verification of the Faraday law: (1) Gauge electrodes and measuring electric circuit completely insulated from the pump circuit; (2) Connected external electrodes.

Another unfortunate consequence of the possible electric influence of the pump on the gauge concerns the regulation of the pumping-effect. Theoretically the time lag between the pump and the gauge is only determined by the time needed by the change in oxygen concentration imposed by the pump to reach the triple contact of the gauge electrode. The possible direct electric influence of the pump on the gauge, as previously sketched, is certainly characterized by a different time lag. Therefore, if the pump has a direct electric influence on the gauge, the response of the gauge will be determined by two, maybe very different, time lags. It is to be feared that under such circumstances quite unexpected behaviour of the regulated pump-gauge would be observed. The difficulties encountered in getting an accurate regulation [43] may have been of this nature.

Table 3.

I (mA)	−300	−250	−200	−150	−100	−50	−10	0	50	75	100	150	200	250	300
$E-E_0$ (mV) Insulated gauge	− 0·79	− 0·66	− 0·53	− 0·40	−0·28	−0·15	−0·04	0	0·12	0·20	0·24	0·36	0·49	0·62	0·73
ΔPO_2 10^3 ppm	− 6·3	− 5·25	− 4·2	− 3·18	−2·23	−1·2	−0·32	0	0·95	1·59	1·91	2·86	3·90	4·94	5·8
$E-E_0$ (mV) Connected external electrodes	− 3·10	− 2·91	− 2·32	− 1·72	−1·12	−0·56	−0·11	0	0·59	0·89	1·19	1·78	2·38	2·98	3·58
ΔPO_2 10^3 ppm	−24·7	−23·2	−18·5	−13·7	−8·9	−4·46	0·87	0	4·7	7·1	9·5	14·2	19	23·8	28·6

3.3. *Pump-microgauge*

In order to avoid the aforementioned difficulties, a new pump-gauge arrangement has been designed. It is schematically depicted in Fig. 7. In this assemblage, the pump and the gauge are entirely electrically independent from each other. The pump is formed of a closed-end tube of stabilized zirconia, the internal and external surfaces of which are almost completely metallized to constitute the electrodes. The gauge is held by an alumina tube which also serves to canalize the gas toward the gauge after passing along the pump internal electrodes. The gauge itself is a conventional gauge with a metal-metal oxide buffer system as a reference electrode, as shown in Fig. 8. Such gauges have already been used either in regular size (cf. the survey in reference [40]) or in small size (28-44-45). This one was initially designed for measuring oxygen pressures close to 0·2 atm under very high pressures of inert gas. It has been patented [46]. Its interest lies in the choice of the palladium-palladium oxide system. With this buffer mixture and at temperatures close to 600°C the oxygen pressure at the reference electrode is around 650 ppm. That is approximately the oxygen reference pressure for which the errors in the gauges caused by the oxygen semipermeability of the electrolyte are minimal. This point was clearly demonstrated [36, 41]. Therefore, we can expect that in such a micro-gauge, an error due to the semipermeability effects would be reduced to a negligible value. Its size is moreover small enough for its temperature to be uniform and the external electrode completely covers the surface of the electrolyte-tube; so the possible effects caused by thermoelectrical stray emf are also eliminated.

With a buffer system at the reference electrodes, the measured oxygen pressure PO_2 is deduced from the gauge voltage E through the usual relation:

$$E = E^{\circ}(T) + \frac{RT}{4F} \ln PO_2. \qquad (14)$$

The thermodynamic data for the palladium-palladium oxide system, (in common with all data regarding metal-metal oxide systems) are not accurate enough to permit an exact calculation of the parameter $E^{\circ}(T)$ and straightforward precise measurements of oxygen pressure. The microgauge requires a calibration and the main problem is the stability of such a calibration.

Table 4 shows an example of the calibration of a Pd-PdO reference electrode performed by measuring the voltage of the microgauge in contact

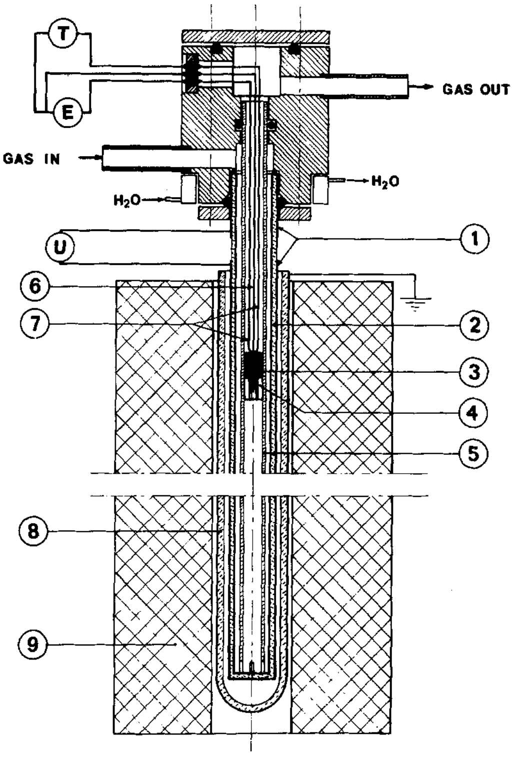

Fig. 7. Pump-microgauge: 1 – electrodes (pump); 2 – electrolyte tube (pump); 3 – microgauge; 4 – alumina holder; 5 – alumina tube; 6 – Pt lead; 7 – Pt-Pt 10% Rh Thermocouples; 8 – alumina tube; 9 – electric furnace.

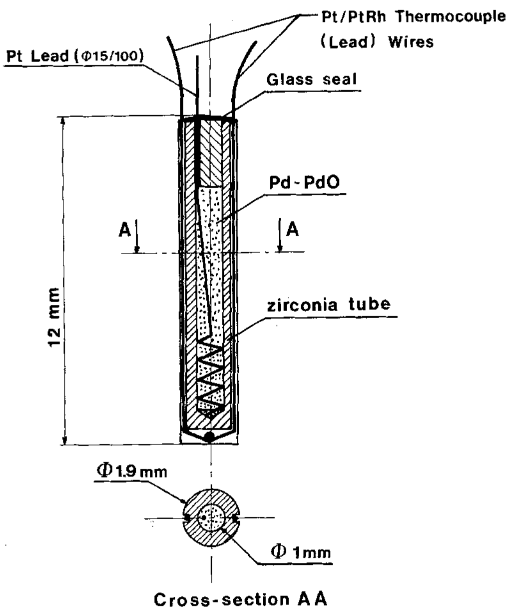

Fig. 8. Microgauge

Table 4. T micro gauge calibration

Air (PO_2 = 0·2 atm)			*Pure O_2 (PO_2 = 1 atm)*	
T (°C)	*E* (mV)	*E*° (mV)	*T* (°C)	*E*° (mV)
452	188	213·2	449	215·2
476	175·3	201·3	482	197·3
537	142·3	170·4	534	171·4
557	131·3	160·1	576	150·2
576	121·4	150·8	633	121·2
606	104·3	134·9	693	72·6
632	90·8	122·2	728	90·7
641	85·2	116·9		
673	68·2	101·0		
693	57·7	91·2		
702	52·9	86·7		
730	37·7	72·5		

with air and pure oxygen under 1 atm. The least square linear fit of all the experimental values gives:

$$E^\circ\,(\mathrm{mV}) = 444{\cdot}1 - 0{\cdot}5097\,T\,(^\circ\mathrm{C}) \qquad (15)$$

with an average error of 0·4 mV. The corresponding uncertainty in the measured oxygen pressure is about 1%. In order to estimate the stability of such a calibration, a microgauge has been kept at 480°C for seven months in contact with the surrounding air. During this period, variations of the reference electrode potential have always been smaller than 0·5 mV.

To verify that all aforementioned causes of error have been eliminated, we compared the results of measurements of different oxygen-argon mixtures by a microgauge and a differential gauge according to the measurement procedure described in a previous paper [36]. The oxygen pressures deduced from both measurements were identical within a few percent, which is the usual experimental scatter. This was verified for oxygen pressures ranging from 10^{-7} to 1 atm.

As a conclusion, we have shown in Fig. 9 a verification of the Faraday law performed at 610°C, with a pump-microgauge. The oxygen pressures were deduced from the microgauge emf using Equation 14 with E° given by Equation 15. The theoretical slope was calculated from Equation 3; for that, the gas flow rate D was measured with an accuracy of 1%. The experimental results lie on a straight line from 3×10^{-2} up to $3{\cdot}10^4$ ppm,

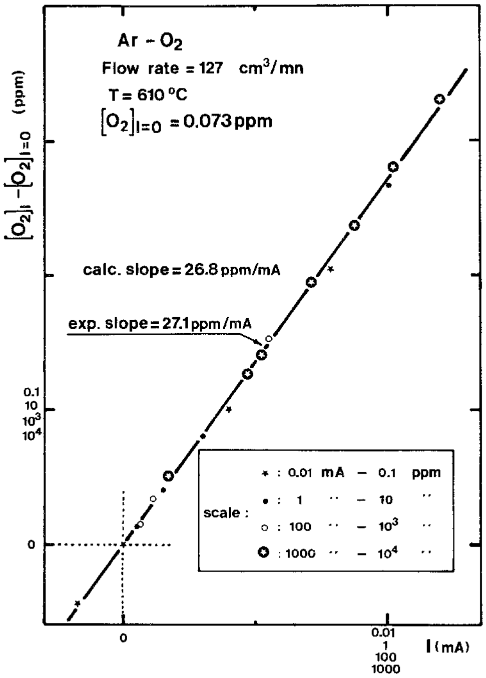

Fig. 9. Verification of the Faraday law with a pump-microgauge.

i.e. over 6 decades, and the range can be easily extended to 1 atm. There is no problem on this side with a pump and a gauge independent from each other as previously shown.

The experimental slope agrees with the calculated slope to within 1%.

We must mention a cloud in the blue sky! With an oxygen content smaller than 1 ppm, the response of the gauge is very slow in contrast with the results published by Mogab [47]. If such a difference is confirmed, it will indicate that the gas carrier, argon generally, plays an important part in the overall oxygen reaction kinetics, at least when the oxygen content is low.

References

[1] B.C.H. Steele in 'Mass transport in oxides'. (J.B. Wachtman Jr., A.D. Franklin, ed.) Nat. Bur. Stand. Special Publ. 296 (1968) p. 165.

[2] R.A. Rapp and D.A. Shores, *Tech. Metals Res.* 4 (1970) 123.

[3] K.S. Goto and W. Pluschkell in 'Physics of Electrolytes', Vol. II, J. Hladik, ed., Academic-Press, London (1972) p. 593.

[4] B.C.H. Steele and C.C. Riccardi, Proc. 1971 Metallurgical Chemistry Symposium H.M.S.O. London (1972) p. 1.

[5] V.F. Komarov and Yu. D. Tret'Yakov, *Zh. Fiz. Khim.* 45 (1971) 1740.

[6] A.V.R. Rao and V.B. Tare, *Q. Metallk.* 63 (1972) 70.

[7] J. Weissbart and L.S. Rowley, Electrochem. Society Meet., October 1964, Extended Abstract No. 31 of Battery Division Vol. 9.

[8] R.J. Ruka and J. Weissbart, *U.S.* 3, 400,054; 3 Sep. 1968.

[9] O. Antonsen, W. Baukal and W. Fischer, *Rev. Brown-Boveri* 53 (1966) 21.

[10] C. Bulliere, 'Etude du pompage électrochimique de l'oxygène dans une cellule à oxyde électrolyte solide', Diplôme d'Etudes Supérieures, Grenoble, July 1966.

[11] M. Kleitz, 'Réactions d'électrode dans les oxydes électrolytes solides', Thesis, Grenoble 1968.

[12] J. Besson, C. Deportes and M. Kleitz, *Fr.* 1, 580, 819; 4 Aug. 1969.

[13] M. Kleitz, C. Deportes and P. Fabry, *Re.. Gen. Therm.* 97 (1970) 19.

[14] N.V. Philips, *Gloeilampenfabrieken, Fr.* 1, 573, 618; 27 May 1969.

[15] D. Yuan and F.A. Kröger, *Amer. Ceram. Soc. Bull.* 47 (1968) 865.

[16] D. Yuan and F.A. Kröger, *J. Electrochem. Soc.* 116 (1969) 594.

[17] W. Fischer, *Swiss.* 445, 632; 31 Oct. 1967.

[18] W.M. Hickam and J.F. Zamaria, *Inst. Contr. System,* 40, (1967) 87.

[19] H.S. Spacil, J.F. Elliott, D.L. Schroeder and D.H. White, *U.S.* 3, 514, 377; 26 May 1970.

[20] A.L. Micheli, *Am. Ceram. Soc. Bul.* 52 (1973) 373.

[21] K. Petanides, E. Luehrsen and G. Heimke, *Ger. Offen.* 2, 061, 897; 6 Jul. 1972.

[22] R.E. Witkowski and A. Pebler, Electrochemical Society Meeting, Houston (1972) Abstract No. 186.

[23] C.B. Alcock and S. Zador, *J. Appl. Electrochem.* 2 (1972) 289.

[24] C.J. Mogab, *Rev. Sci. Instrum.* 43 (1972) 1605.

[25] M. Guillou, A. Lecante and M. Grunberg, *Rev. Gen. Therm.* 9 (1970) 27.

[26] W.A. Rocco, *Brit.* 1, 216, 024; 16 Dec. 1970.

[27] General Electric Co. *Fr.* 2, 048, 118; 23 Apr. 1971.

[28] R. Steiner, *Chem. Ing. Tech.* 44 (1972) 152.

[29] N.V. Philips 'Gloeilampenfabrieken', *Ger. Offen.* 2, 057, 835; 16 Jun. 1971.

[30] A. Hammou, S. Desagher and C. Deportes, *Mesures,* 36 (1971) 85.

[31] N.M. Beekmans and L. Heyne, *Philips Tech. Rev.,* 31 (1971) 51.

[32] R.A. Rapp, *U.S.* 3, 699, 032; 17 Oct. 1972.

[33] W.M. Hickam, R.E. Witkowski, *U.S.* 3, 650, 934; 21 Mar. 1972.

[34] J. Besson, M. Bonnat, C. Deportes and M. Kleitz, *Fr. Addn,* 2, 110, 620; 30 Jun. 1972.

[35] R. Hartung and H.H. Moebius, *Z. Chem.* 7 (1967) 473.

[36] J. Fouletier, H. Seinera and M. Kleitz, *J. Applied Electrochem.* (to be published).

[37] M. Kleitz, J. Besson, and C. Deportes, *Proceed. zèmes journées Internationales Etudes des Piles à Combustibles,* p. 354. Edit. Serai-Comasi, Bruxelles 1967.

[38] M. Kleitz, J. Besson and C. Deportes, Journées Intern. Etudes des Piles à Combustibles. Bruxelles 1965, *Rev. Energie Primaire (U.I.L. Bruxelles)* 3 (1966) 35.
[39] P. Fabry, Thèse de Spécialité, Grenoble, 1970.
[40] J. Fouletier, H. Seinera and M. Kleitz, *J. Applied Electrochem.* (1974) 305.
[41] 'Recent progress in solid-state oxygen pump and gauge', J. Fouletier and M. Kleitz, 24th Meeting of the I.S.E. Eindhoven, 10–14 September 1973.
[42] Y.K. Agrawal, D.W. Short, R. Gruenke and R.A. Rapp, *J. Electrochem. Soc.* **121** (1974) 354
[43] 'The electrochemical control of oxygen activity in flowing gases', R.A. Rapp and Y. Agrawal, *Fast ion transport in solids-solid state batteries and devices,* Belgirate, 5–15 September 1972.
[44] M. Sato, *Research Techniques for High Pressure and High Temperature,* Chap. 3, G.C. Ulmer, Edit., Springer Verlag, Berlin – New York (1971).
[45] B.C.H. Steele and Electronic Instruments Ltd, *Brit.* **1**, 328, 083; 30 Aug. 1973.
[46] C. Deportes, M. Hénault, F. Tasset and G. Vitter, *Fr.* **73**, 32671; 11 Sep. 1973.
[47] C.J. Mogab, *J. Vac. Sci. Techn.* **10** (1973) 852.