Evaluation of a Dispersed Cu_2O Getter for Oxygen Using a Solid Electrolyte Sensor

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OXYGEN monitors employing stabilized zirconia as solid electrolyte have been extensively used in several process metallurgical operations during the past decade. Detailed descriptions of such devices are available in the literature[1-9]. When two different oxygen partial pressures Po_2' and Po_2'' are maintained on either sides of a stabilized zirconia electrolyte tube, the resulting EMF, E is given by the equation

$$E = \frac{1}{4F} \int_{\mu''o_2}^{\mu'o_2} to_2 - d\mu o_2 \qquad (1)$$

If $t_{o2}-$ is unity over a range of values of $\mu''o_2$ to $\mu'o_2$ and a temperature range, then equation (1) reduces to the familiar Nernst equation

$$E = \frac{RT}{4F} \ln \frac{P'o_2}{P''o_2} \qquad (2)$$

By choosing a gas whose Po_2 is known precisely as the reference gas, the oxygen potential of an unknown gas is monitored from the measured cell EMF, When the oxygen sensor is used to monitor the oxygen potentials of buffer gas mixtures like $CO-CO_2$, Nernst equation is found to be valid down to P_{O_2} valnes of 10^{-18} atm at temperatures around 1300 K[1]. Deviations trom Nernst law and Faraday's law (while the sensor is used as an oxygen pump) become severe only for free oxygen sensing In inert gases in the ppm ranges. Ullmann et al[10] reported that the Nernst equation is not obeyed if the oxygen content of argon is below 2 ppm. Lindsay and Ruka[11] and Ullmann[12] found that the partial pressure measurements using solid electrolyte cells are accurate to within 2% when the oxygen pressures are higher than a few torr. Etsell and Flengas[1] obtained accuracies of the order of $\pm 4\%$ for Po_2 in the range $1-10^{-2}$ atm, $\pm 4\%$ in the range 10^{-4} to 10^{-5} atm and $\pm 30\%$ for 1 ppm range. Accuracies of these orders are confirmed by Sreedharan and Chandrasekharaiah [5,6] and by the present investigation for $A-O_2$ and N_2-O_2 mixtures. Strong flow rate dependence of the measured EMF and appreciable increase in step response time at low free oxygen content ($Po_2 < 10^{-4}$ atm) were observed earlier[1,5,13,14] which was attributed[13] to : oxygen permeability of the electrolyte ; slow oxygen reaction rate ; parasitic reactions at the electrode/electrolyte interface. According to Mari et al[13] oxygen permeability of the solid electrolyte could be overcome by increasing the gas flow rate ; slow oxygen reaction rate, by increasing the temperature of cell operation ; and elimination of parasitic reactions by purification of the gas from sources of H_2 and carbonaceous Impurities. Mari et al suggested an operating temperature of 750°C for the gauge which strikes a compomise between increasing oxygen reaction rates, with increasing temperature. Heyne and Beekmans([2]) have suggested an operating temperature of 600°C to reduce oxygen permeability. Oxygen permeability arising from 0.5% electronic conduction In stabilized zirconia was found to introduce a $\pm$ 1.5% error in measurements of Po_2 of the order of 1 torr at 700°C according to Fouletier et al([4]). Sreedharan and Chandrasekharaiah([5]) obeserved that the electrochemical semipermeability is greately reduced by replacing air with an inert gas having a Po_2 around 10^{-3} atm as the reference gas. This formed the basis of the differential guage devised by Fouletier et al. ([4]) for accurate monitoring of oxygen down to 1 ppm level. Mari et al. ([13]) used the simple pump-gauge itself at 750°C for accurate Po_2 measurement in the range up to 10^{-7} atm in combination with a chemical getter pump employing St-101 alloy (84 Z -16 A1) for the removal of all the trace impurities (along with liquid nitrogen trap, P_2O_5 trap and/or molecular sieves for moisture removal). The present investigation deals with the performance of an oxygen sensor when used with a commercial, dispersed copper oxide (reduced form of BASF R-3-11) getter for free oxygen removal in commercial nitrogen and argon gases with Po_2 of the order of few torr.

EXPERIMENTAL

Design details of the sensor are described elsewhere[5]. A 15 w/o calcia Stabilized zirconia (CSZ)

tube was employed. The temperature of the sensor was controlled with PID controller with an accuracy of ±0.5°C using a primarily calibrated Pt-10% Rh versue Pt thermocouple. The flow rate of the gas was varied with the help of a calibrated float type rotameter. Molecular sieves (equivalent to Linde-5A) used in this study was thoroughly outgassed at 200°C in a vacuum of 10^{-2} torr. Dispersed copper oxide pellets (type BASF R-3-11) were reduced gradually in a stream of N_2–H_2 mixture at 100 to 200°C. Starting with the flow of pure nitrogen, hydrogen was introduced into the gas stream gradually in order to avoid overshooting of temerature during the exothermic reduction of CuO (BASF). Po_2 of a commercial nitrogen gas checked with reduced BASF and molecular sieves singly and in combination and with reduced BASF and oxidised BASF (heated to 180°C) in sequence. Nearest test for argon and nitrogen gases containing oxygen impurity were done without passing the gas through any trap as their oxygen potentials lie in the range which is unaffected by traces of condensible or reducing impurities.

RESULT AND DISCUSSION

If the gauge is operated at a single constant temperature, its theoritical performance can be checked only by Faraday's law. Passing current can cause compositional changes in the electrolyte[15] which would require higher temperature to anneal out. On the other hand if Nernst test can be applied to flow-independent EMF's by varying the temperature of the cell in the range 800-1000 K it could unequivocally establish the theoretical or non-theoretical behaviour.

EMF—temperature plots for seven inert gas-O_2 mixtures are shown in Fig. 1. To verify the fact that these obey Nernst eqnation, the least square lines for these gases are extrapolated to the hypothetical absolute zero of temperature and they are seen to pass through the origin within experimental uncertainities bearing in mind that these uncertainity limits are valid only for the temperature range of actual measurements (Fig. 2). One of the seven gas mixtures shows a rather large intercept (about 6 mV) which is not explicable at present. The linear equations with the standard deviations computed for Po_2 of each of the gases are listed in Table 1. If equation (2) is rearranged and the

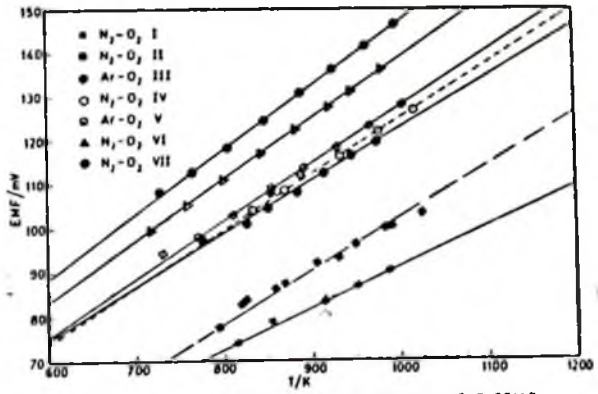


FIG 1. TEMPERATURE DEPENDENCE OF THE EMF FOR THE CELLS Pt, N_2-O_2 or Ar-O_2/ZrO_2-15 w/o CaO/O_2 (P_{O_2} = 0.21 Atm.), Pt

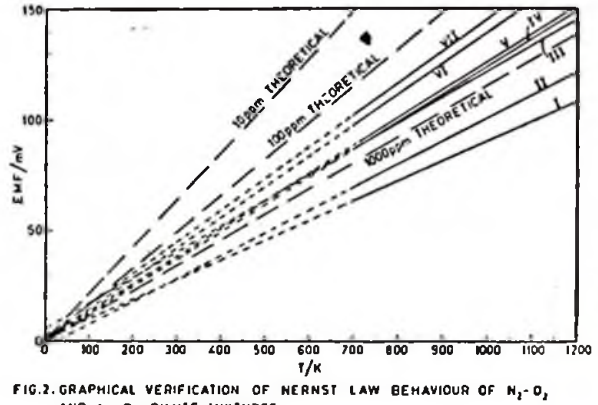


FIG.2. GRAPHICAL VERIFICATION OF NERNST LAW BEHAVIOUR OF N_2-O_2 AND Ar-O_2 DILUTE MIXTURES (LINES I TO VII CORRESPOND TO LINEAR EQUATIONS LISTED IN TABLE-1)

values of the constants are incorporated, it would read as follows when E is expressed in mV.

$$\log (P'o_2/P''o_2) = 20.16 \frac{E}{T} \qquad (3)$$

One of the sources of error in Po_2 measurements is the erratic temperature variation. RAPP[16] has made a device in which the electronic circuit is so connected that the ratio of $\frac{E}{T}$—is used in the measurement of oxygen pressure. Taking Po'_2 as the constant reference pressure, equation (3) can be differentiated to give the relation

$$\frac{dE}{dP''o_2} = -\frac{T}{20.16} \times \frac{1}{P''o_2} \qquad (4)$$

From the above relation, it is obvious that with decreasing partial pressure of oxygen the sensitivity increases. In terms of numbers, a one mV increase in E at, say, 973 K would mean a change of 47 ppm at 10^{-3} atm whereas the same variation of cell voltage would correspond to 0.5 ppm at a Po_2 of 10^{-5} atm.

TABLE I

Linear equations for EMF–T for N_2-O_2 and $Ar-O_2$ mixtures

	Gas Mixture	E/mV = A + BT/K (780 ≤ T/K ≤ 1000)	Standard deviation in E/mV	Po_2/ppm	Standard deviation in Po_2/atm
I	N_2-O_2	0.36 + 0.0905 T	0.35	3075	2.05 %
II	N_2-O_2	−2.93 + 0.1040 T	0.83	1972	2.75 %
III	$Ar-O_2$	6.42 + 0.1153 T	0.68	705	2.5 %
IV	N_2-O_2	−1.22 + 0.1256 T	0.21	655	0.5 %
V	$Ar-O_2$	1.20 + 0.1256 T	0.18	576	1.75 %
VI	N_2-O_2	0.70 + 0.1397 T	0.06	331	1.14 %
VII	N_2-O_2	1.93 + 0.1447 T	0.11	228	3.8 %

The least square equations for the lines in Fig. 1 correspond to EMF–T relations for the cell

$$\text{Pt, } \begin{matrix}Ar-O_2\\ \text{or}\\ N_2-O_2\end{matrix} \;\Big|\; \text{85 w/o } ZrO_2 - \text{15 w/o CaO} \;\Big|\; O_2\ (Po_2 = 0{,}2088 \text{ atm}) \text{ Pt}$$

The linear equations with standard deviations in Po_2 values are calculated taking into account deviations from Nernst equation,

Flow rate dependence of EMF of two inert gas oxygen mixtures each at three different temperatures is shown in fig. 3. As the volume flow rates are varied between 5 and 45 normal litres per hour at

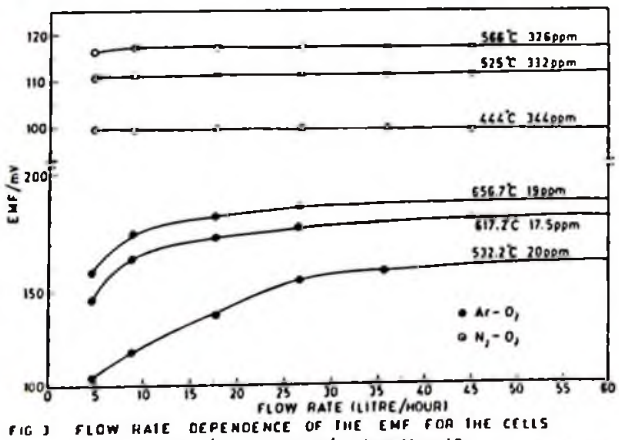


FIG 3 FLOW RATE DEPENDENCE OF THE EMF FOR THE CELLS Pt, N_2-O_2 or $Ar-O_2$ / ZrO_2 - 15 w/o CaO / O_2 (P_{O_2} = 0.21 Atm) Pt

25°C the linear rates vary between 3.5 to 31.5 cm per sec. For Po_2 of the order of 330 ppm, EMF is found to be independent of flow rate even at 444°C while a strong flow dependence is shown by the cell voltage up to linear velocities approaching 25 cm per sec or more for Po_2 in the region of 20 ppm. Constancy of Po_2 with temperature (within a few percent variation) verifies conformity to Nernst relation by the ges mixtures having Po_2 in the range of 10^{-5} atm. Constancy of Po_2 also shows the absence of erratic temperature variations, which is achieved by a good proportional power controller.

Drying of the gas by passing through activated melecular sieves has very little effect on the cell EMF. For a commercial nitrogen gas sample, cell EMF at 930 K and without molecular sieves were 89 and 88 mV respectively. The marginal increase in EMF should be due to the stoppage of oxygen consuming impurities in the gas stream since the temperature is controlled within ± 0.5°C which could result only in a change of about 0.1 mV. The effect of the reduced BASF R-3-11 pellets at room temperature or when heated to 180°C was checked on a commercial nitrogen gas and the results are presented in Table 2. When a commercial N_2 gas from a stock cylinder is passed directly through the sensor at 657°C a nearly flow independent EMF of about 94 mV was obtained corresponding to a Po_2 value of 1.92×10^{-3} atm. When the gas is passed through reduced BASF R-3-11 pellets at room temperature, surprisingly again a nearly flow independent EMF of 630-640 mV was recorded. This value corresponds to a Po_2 of $10^{-13.2}$ atm. Gas chromatographic analysis of a sample of gas passing through reduced BASF showed the presence of H_2 at 50-100 ppm level. Hence such low oxygen potentials could originate only from parasitic reactions at the electrolyte interface owing to the presence of reducing impurities like H_2. When the outcoming gas stream was purged through molecular sieves EMF tends to increase up to 800 mV. This chenge is EMF is in the expected direction since theoxygen ipotential

TABLE II

Dependence of EMF of the cell, Pt, N_2–O_2 (II)/15 CSZ/O_2 Po_2=0.21 atm), Pt at 657 °C on flow rate and BASF getters

Gas Train	EMF/mV					
	Flow rate (litre/hour)					
	4.5	8.7	17.5	26.6	36.7	45
N_2–O_2 gas (through) sensor	93.6	94.0	94.1	93.7	—	—
N_2–O_2 through reduced BASF	631	632	634	640	—	636
N_2–O_2 through reduced BASF and then oxidized BASF	116–134	164–168	185	213	—	—
N_2–O_2 through reduced BASF and Molecular Sieves (5A)			600–800			

has to decrease with the removal of moisture. To confirm that the low Po^2 was caused by reducing impurities like H_2 only, the gas stream from reduced BASF was again passed through a column of oxidized BASF R-3-11 maintained at 180°C. The result was that the EMF showed a strong flow rate dependence (Table 2) characteristic of free oxygen determination in the inert gases in the sub ppm level[10]. Further increase in temperature of the reduced BASF had no significant effect on the messured voltage. Before concluding it is necessary to state that the investigations with reduced BASF were carried out, when the "catalyst" was less than 50% consumed, and the highest flow rate employed here namely 45 litre per hour was within that recommended for maximum efficiency of the "catalyst" for one inch diameter columns.

CONCLUSIONS

Solid electrolyte monitors obey Nernst law down to 10^{-5} atm provided flow rate dependence was taken care of. Any temperature in the range of 800–1000K would be satisfactory for this purpose. When reduced dispersed copper oxide is used for oxygen gettering oxidized BASF and molecular sieves (or any othes drying agent) should also be used in the sequence given ; Otherwise the "inert" gas stream would be contaminated with reducing impurities. Outgassing of the reduced BASF could also be suggested (as it is only a logical extension of the above observations) as a measure to extend the life of oxidized BASF used in the subsequent column.

Acknowledgement

The authors express their sincere thanks to Dr. P. Rodriguez, Senior Metallurgist, RRC, Kalpakkam for his constant encouragement and support during the cousre of this work. The authors would also like to thank Dr. M. S. Chandrasekharaiah, Chemistry Divn., BARC, India for his helpful suggestions.

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