Use of air/platinum as the reference electrode in solid oxide electrolyte e.m.f. measurements

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Abstract

The electrode, air ($P_{O_2} \approx 21.222$ kPa)/Pt is often used as a reference electrode in numerous applications in oxygen gauges and coulometric devices which make use of zirconia based solid electrolytes. In recent years, a large number of thermodynamic measurements have been reported using the zirconia electrolyte based e.m.f. technique with this reference electrode. This review summarizes the merits, limitations, mechanistic aspects, precautions to be taken and the sources of error in the use of air/Pt electrode for thermodynamic measurements. In addition, a brief survey of recent applications of air/Pt electrode is presented, together with recommendations for the proper use of the omnipresent air as an oxygen fugacity standard. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrodes; e.m.f. Measurements; Pt; Thermodynamic measurements; ZrO$_2$

Contents

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1. Introduction

Atmospheric air and pure oxygen in conjunction with platinum have been increasingly used as the reference electrodes in numerous zirconia based e.m.f. and coulometric studies on the thermodynamic characterization of binary metal oxides, ternary oxides, metal-sulphur compounds and alloys. The air ($P_{O_2} \approx 21.222$ kPa)/Pt (hereafter referred to as air/Pt) combination has also been widely accepted as a 'primary' standard reference electrode in zirconia based oxygen gauges for accurate monitoring of oxygen partial pressure in the range 10^{-2} Pa to a few hundred kPa as revealed by a critical assessment of round-robin experiments conducted by the International Union of Pure and Applied Chemistry in 1984.[1] There is still a wide scope for popularising the use of this gaseous reference electrode in preference to condensed phase metal/metal oxide type coexistence electrodes in the accurate e.m.f. studies at high temperatures. However, many precautions are needed to exploit the better accuracy and precision of air/Pt electrodes as well as the exercise of discretion in the choice of test electrode systems which are adequately reversible.

In the light of the wide experience gained in this field, this paper presents the merits, disadvantages, limitations and precautions to be taken in the use of the air/Pt electrode in e.m.f. studies with zirconia based electrolytes. In addition, a brief compilation of the references on e.m.f. work (published during the past 20 years) is given in support of the increasing application of this electrode.

2. Earlier applications

Kiukkola and Wagner[2] demonstrated the use of calcia stabilized zirconia (CSZ) as a solid electrolyte (SE) in equilibrium e.m.f. measurements for the determination of thermodynamic properties of oxides at high temperatures. Subsequent to their pioneering work, a large number of galvanic cell studies were reported in the literature making use of Daniel type cells.[3–15] Most of these Daniel type cells essentially had a common inert environment, thereby limiting the reference electrodes to the realm of condensed phase metal/metal oxide buffers. Later developments in ceramic fabrication led to the commercial availability of stabilized zirconia in tube form. This permitted the use of O_2 (101.3 kPa)/Pt and air/Pt as reference electrodes in an effort to determine the standard Gibbs energies of formation, ΔG_f^o of oxides by 'absolute' means, free from the uncertainties in the thermodynamic data on condensed phase reference electrodes. The pioneering work in this aspect using the two compartment galvanic cell was by Tretyakov and Schmalzried.[16] They reported ΔG_f^o values for Cu_2O,

NiO, CoO, Fe_xO and Cr_2O_3 using the air/Pt reference electrode. Except for the anomalously more negative values for Cu_2O, the data were in good agreement with the values assessed in the literature[17] for the oxides of Ni, Co and Fe. However, the oxygen potential on Cr/Cr_2O_3 was less negative by more than 5 kJ at 1073 and 1273 K, presumably due to direct permeation of oxygen caused by the rather large difference in the log P_{O_2} values between the test and reference (air) electrodes. This had perhaps resulted in some of the earlier workers resorting to the use of condensed phase reference electrodes in two compartment cells with a closed end zirconia electrolyte. A typical example of such studies is that by Etsell and Flengas[18] who had taken additional precautions of individually sealing both the compartments under a static high vacuum to achieve true equilibrium in both the electrode systems. With the availability of better quality closed end zirconia tubes (which were produced as a result of the thrust in the development of commercial oxygen probes) and with a better understanding of oxygen permeability problems, a number of studies were reported in the literature using the air/Pt reference electrode in thermodynamic measurements[16,19–23] as well as in gauges.[24–30] Tretyakov and Muan[31] adopted a bielectrolyte arrangement consisting of concentric CSZ and yttria doped thoria (YDT) tubes extending the range of applicability of the air/Pt electrode to extend the electrolytic domain of CSZ to much lower values of P_{O_2}. Theoretical analysis of the lower electrolytic domain boundary of such a bielectrolyte system was reported by Shores and Rapp[32] for electrolytes of equal thicknesses and for making use of air/Pt as reference. Kleitz[33] made the next significant development to overcome the direct permeation of oxygen by resorting to a triple electrode arrangement wherein a conical CSZ electrolyte pellet with its vertex pressing against the flat platinum coated end of a CSZ tube was used. In this arrangement, the test electrode was pressed against the bottom of the CSZ cone and oxygen if any, permeating from the air/Pt electrode (from the inner compartment) through the tube would choose the least resistant path of discharging into the otherwise inert atmosphere of the outer compartment without causing polarization of the test electrode.

A similar combination of both bielectrolyte and point electrode arrangements was demonstrated to be useful in overcoming oxygen permeability by Mallika et al.[34] as shown in Fig. 1. These workers made use of a 15 wt.% YDT cone in conjunction with a 15 wt.% yttria stabilized zirconia (YSZ) tube to measure the eutectoid temperature of Fe_xO using air/Pt reference. In this arrangement, both the buffer and the measuring electrodes are exposed to a common gas phase which was pointed out as a disadvantage by Jacob and Sriram.[35] However, the merit in the bielectrolyte-triple electrode arrangement by Mallika et al. lies essentially in mini-
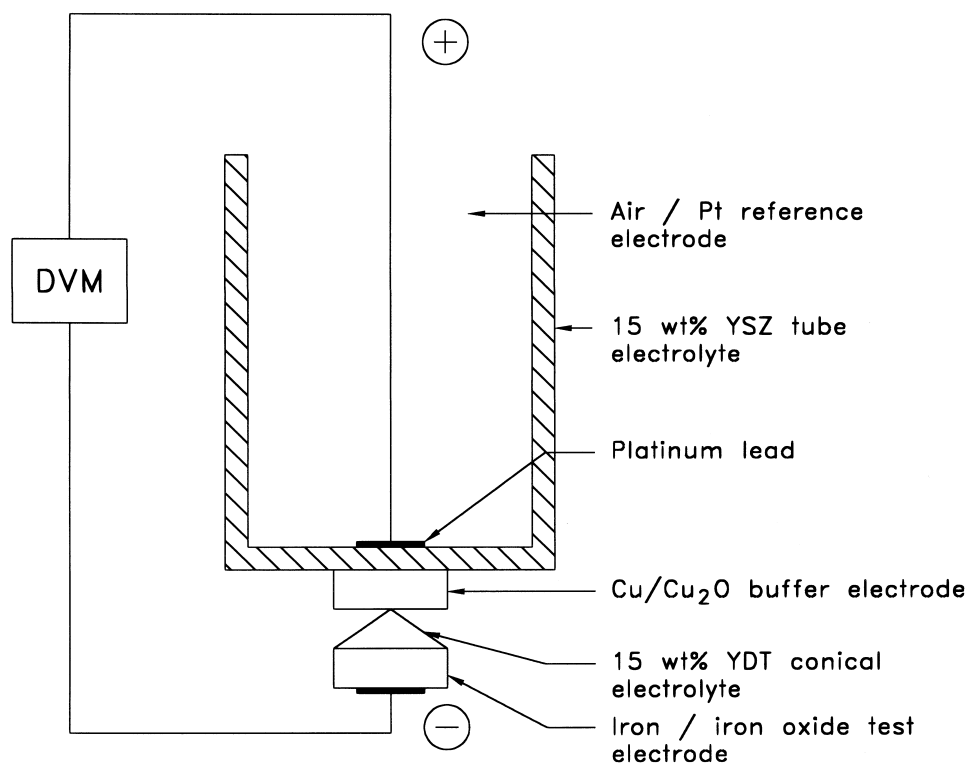
Fig. 1. Schematic of triple electrode–bielectrolyte arrangement.

mising the much larger oxygen flux from the air/Pt electrode by a point contact (though it does not deflect the O_2 flux from the measuring electrode[35]), besides overcoming the use of a tubular form of doped thoria. It is well known that the latter electrolyte tubes are highly prone to cracks during thermal cycling owing to very poor resistance to thermal shock. The oxygen flux caused by electrochemical permeability of YSZ and the errors so arising from this source could be minimized by three and four compartment cell designs.[35,36] In the last mentioned arrangement, the reference and measuring electrodes are separated from each other by reference buffer and measuring buffer electrodes which have the same P_{O_2} as their respective electrodes (reference and measuring). This design requires at least two coaxial tubes and a container crucible of YSZ in addition to an outermost crucible and envelope for enclosing the measuring electrode crucible. This is rather cumbersome to assemble as compared to the advantages claimed by the designers. To facilitate the use of zirconia based gauges for monitoring free oxygen in inert gases in the ppm range of concentration, two strategies were adopted. The first was by Sreedharan and Chandrasekharaiah[26] who made use of an inert gas such as N_2 or Ar bearing O_2 in the range of 1000 ppm as the reference gas instead of air/Pt. Such a reference gas was chosen after determining the precise oxygen concentration in the same gauge using air/Pt as the reference. For the second, Fouletier et al.[24] had patented a differential gauge which

was essentially identical in principle to the first, but with better operational convenience. It consisted of two coaxial stabilized zirconia tubes, the annular space between which could be flushed with an inert gas bearing O_2 in the 1000 ppm range. The inner and outer compartments could be used for air/Pt and the test gas respectively.

In thermodynamic measurements, at temperatures less than about 1300 K, a judicial choice of the solid electrolyte tube of high quality could minimise direct oxygen permeability from air/Pt and could be used advantageously for the study of especially those systems exhibiting a reasonable degree of reversibility. In the choice of systems for study, a lower limit of oxygen potential should also be fixed to minimise polarization. Some of these aspects will be considered after highlighting the merits of air/Pt reference.

3. Merits

A good reference electrode in solid electrolyte galvanic cell measurements using solid oxide electrolyte should possess the following characteristics:

(a) Materials used in reference electrodes should be readily available or should be easy to prepare. Air is omnipresent and Pt is the best established electrical lead in all types of galvanic cell studies. Even when a con-

densed phase reference electrode such as Cu/Cu_2O is used, Pt is invariably used as the lead wire.

(b) These should be highly reversible. This criterion requires them to be good electronic conductors with high diffusivity of oxygen over the temperature range of interest. Thus the reference electrodes have been ordered reversibility wise as follows[37] around 1000 K: $Cu/Cu_2O > Fe/Fe_xO > Ni/NiO > Cr/Cr_2O_3$. Air/Pt and O_2/Pt are considered to be much superior to even Cu/Cu_2O by Sato[30] and Sreedharan.[9]

(c) Inert gases bearing 'free' O_2 could in principle function as reference electrode materials in conjunction with appropriately prepared Pt lead. However, these electrode systems would show considerable flow rate dependence of cell voltage depending on the oxygen content of inert gas carriers.[23,25,26] The same is true with H_2/H_2O or CO/CO_2 buffer gas mixtures,[30] but O_2/Pt and air/Pt are nearly flow independent and the latter could even be static.

(d) These electrodes should be well characterised thermodynamically. In Daniel type solid electrolyte galvanic cells making use of displacement reactions in metal/metal oxide systems, it is necessary to know the ΔG_f^o of the metal oxide precisely as a function of temperature. The oxides Cu_2O and NiO satisfy this criterion quite well.[38] The ΔG_f^o of Fe_xO was well assessed by Giddings and Gordon[39] after an analysis of data from 63 papers published prior to 1973. However, Sjöden et al.[40] found sufficient scope for revising these data even as late as 1986. These investigators were able to discern the magnetic and phase transformations in Fe as breaks in the oxygen potential curve for Fe/Fe_xO against temperature. Further, the existence of the eutectoid temperature for Fe_xO limits the lower temperature of application of this electrode[34,41] to about 800 K. Even for the best metal/metal oxide reference electrode, an uncertainty of the order of ± 200 J would get added up in the derived value of ΔG_f^o of the oxide used in the test electrode. Nevertheless, the oxygen potential of air/Pt and O_2/Pt are associated with minimum uncertainty. Further discussion on the composition of air is given in the next section.

(e) These should have a smaller temperature dependence of oxygen potential. The M/MO_x type of reference electrodes would have a steeper temperature dependence owing to the significant value of $\Delta \overline{S}_{O_2}$ of oxygen. In addition, whenever the temperature of the galvanic cell is changed, the oxygen potential should readjust itself to a value closer to that of the phase boundary between the metal and its coexisting oxide. If the mutual solubility of the metal and its oxide changes rapidly with temperature, more time may be needed to ensure attainment of equilibrium during the thermal cycling. Fortunately, P_{O_2} of the air/Pt reference electrode is temperature independent and so no such readjustment of the composition of the phase boundary is involved in this electrode.

(f) The reference electrode material should be inert chemically, with respect to both electrolyte and electrical lead. The well known condensed phase electrodes generally have a higher temperature restriction with respect to their inertness towards Pt in contrast to the better compatibility of air with Pt.

(g) Wide temperature range of applicability is a highly desired characteristic of a reference electrode. Quite often, ΔG_f^o data obtained from e.m.f. measurements find acceptance but not so the entropy data [20]. This is caused by the large uncertainties in the temperature coefficient of e.m.f. studied over rather narrow temperature ranges. In the e.m.f. studies covering over wider temperature ranges, more reliable entropy data could be derived. Condensed phase reference electrodes are frequently restricted in the temperature range by (i) low temperature irreversibility, (ii) solid state transitions, melting or vapourization and (iii) high temperature chemical reactivity with the electrolyte and/or lead. In this respect air/Pt offers better scope of e.m.f. measurements over a span of a few hundred degrees.

(h) The reference electrode should not be readily polarizable. In coulometric studies, where there is a need to pass a calculated number of coulombs of electricity, the reference electrode should be highly reversible. Generally, solid phase reference electrodes get polarized irreversibly on passing macroscopic quantity of electric charge. For example, Markin and Bones[42] employed coulometric studies to derive isothermal $\Delta \overline{G}_{O_2}$ as a function of x in the non-stoichiometric oxide UO_{2+x} (where x is varied between 0.012 and 0.188) at different temperatures. They employed a split Ni/NiO pellet for this purpose. One half of this split pellet is used for passing electricity to change the oxygen stoichiometry of the UO_{2+x} pellet, while the other half was used to measure the open circuit e.m.f. after sufficient high temperature annealing subsequent to coulometric transfer of charge. The use of separate reference electrodes for the two purposes was necessitated due to the polarization of Ni/NiO. In this investigation, both the reference and measuring electrodes are made of solid phases which are bound to exhibit much lower reversibility at lower temperatures. If the measuring electrode happens to be a liquid metal such as in the studies on oxygen diffusivity, one could expect a high degree of reversibility at the electrolyte/liquid metal interface. Even for such studies, perhaps one should resort to split reference electrode if Ni/NiO were to be used. However, Mallika et al. successfully made use of Cu/Cu_2O as reference electrode for oxygen diffusivity studies in liquid Sn and Pb[43] using the cell configuration shown in Fig. 2. In this case, the same reference electrode was used for the determination of the limiting current caused by coulometric transfer of oxygen for measuring the oxygen diffusivity in liquid Sn and Pb in the temperature range 650–1000 K. The air/Pt reference elec-
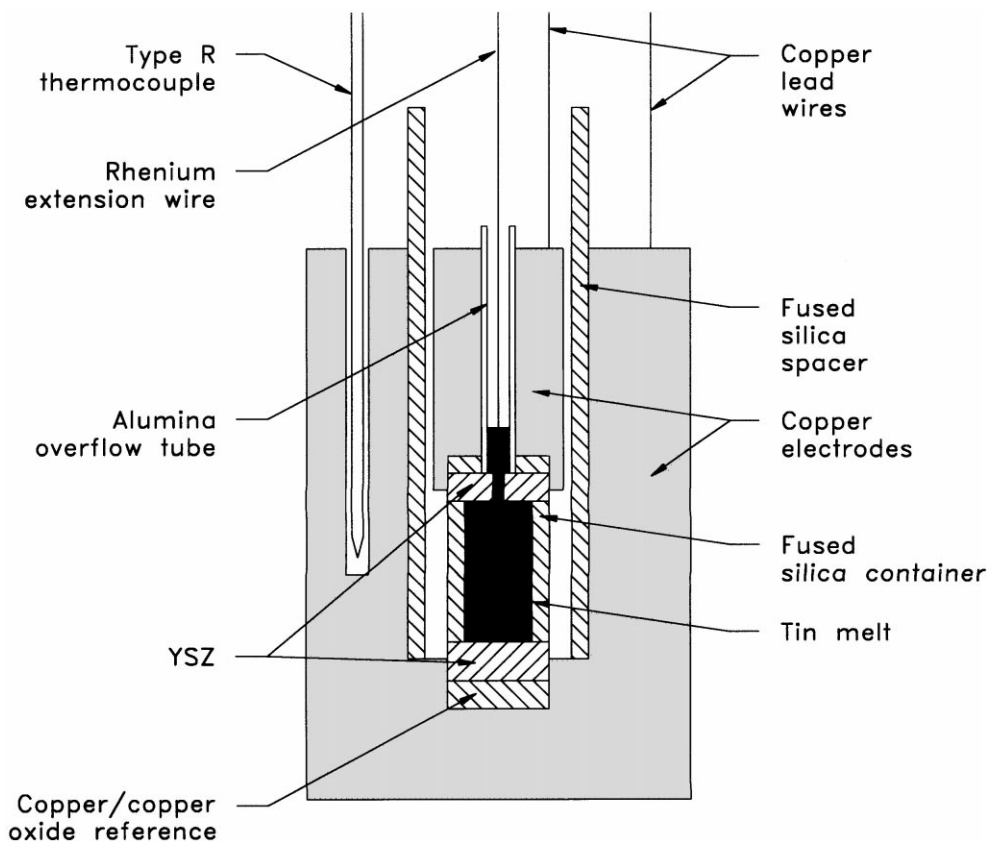
Fig. 2. Schematic diagram of the cell assembly for oxygen diffusivity measurements in liquid metals.

trode could be a better choice with respect to reversibility to detect flow profiles in liquid metals if one could minimize the direct electrochemical permeation of oxygen through stabilized ZrO_2 by suitable design. A typical arrangement used by Prasad et al.[44] is shown in Fig. 3. Thus, the ready reversibility of the air/Pt reference electrode could enable it to serve both the purposes simultaneously provided the oxygen potential monitored is in a suitable range.

4. Limitations

The limitations of the air/Pt electrode arise from 3 factors.

4.1. Uncertainty in composition

The factors affecting the composition of air[45] are: (i) Variation of atmospheric pressure of air with altitude; in the first few kilometres of altitude in the earth's atmosphere, pressure drop is estimated to be 1 kPa per 100 m of altitude according to Miller et al.[46] (ii) Typical pressure variations due to weather conditions amount to about ±2 kPa. (iii) The nominal composition of dry air according to Braker and Mossman[47] is given in Table 1 and is compared with that calculated for 100%

relative humidity at the standard temperature of 298 K for air at 1 atmosphere pressure. This shows a variation of about 1% of atmospheric pressure in the P_{O_2} of air caused by humidity conditions.

4.2. Irreversibility at lower temperatures

The lower temperature of operation of the air/Pt reference electrode was reported to be limited by the formation of a layer of either Pt_3O_4 or PtO_2[48] which would then give rise to some irreversibility. This lower limit was assumed to be in the range of 700 K. However, much depends on the method of preparation of the Pt-ceramic contact and porous deposition of finely divided Pt on the substrate. Measurements of e.m.f. could even be made at 540 K with the air/Pt reference in case the measuring electrode was not lacking in reversibility.[49] Nevertheless many other substitutes for Pt as electrical contacts for use with air as reference electrode material were reported in the literature. A comparison of the overpotential behaviour for the O_2/metal (metal = Pt, Ag or Au) electrodes in contact with oxide electrolyte was made by Fabry and Kleitz.[50] Though at higher P_{O_2} such as air/metal, the overpotential is proportional to $P_{O_2}^{-1/2}$ for all the three metals compared by them, at $P_{O_2} < 10^{-4}$ atm, the overpotentials vary in the proportion 50:10:1 for Pt, Ag and Au respectively. However, a
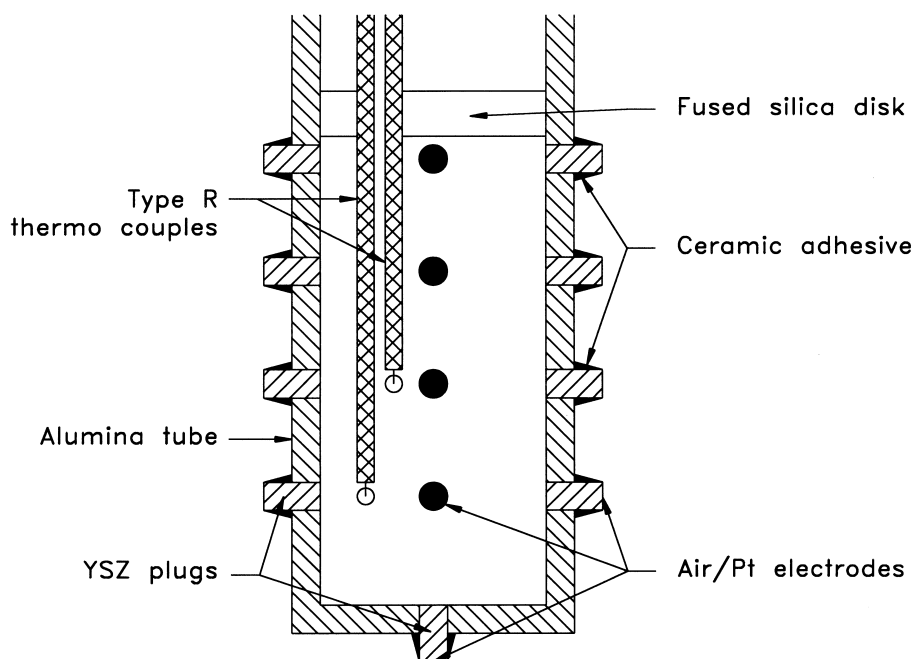
Fig. 3. Experimental cell for oxygen flow visualisation studies in liquid metals. Air/Pt electrodes are used for oxygen injection and as reference electrodes.

Table 1
Composition of dry and moist air[a] at a pressure of 1 atmosphere

Component	Composition (mol%)	
	Dry air[b]	Moist air[a]
N_2	78.084	75.640
O_2	20.946	20.290
Ar	0.934	0.905
CO_2	0.033	0.032
Rare gases	0.003	0.0029

[a] Calculated for a dew point of 298 K.
[b] Composition given by Braker and Mossman.[47]

compilation of the activation energies for oxygen diffusion through the metals by these authors revealed that much depends on the nature of the electrolyte such as the composition, rather than only on the characteristics of the metal for its reversible performance. Though Ag and Au would appear as better choices compared to Pt, the stability of Ag_2O would restrict its application in the air/Ag electrode. It is surprising that not much study is reported in the literature on the air/Au electrode though it appears to be much superior. Nevertheless, the advantage of Pt over the other metals could be mainly due to its much higher melting point which led to the development of composites of oxides with Pt as candidate materials for use with air or O_2 (1 atm) as reference. However, studies are still being carried out to assess the long term stabilities of metal electrodes for their use in device applications.[51,52] Bannister[53,54] reported the use of a solid solution of $(U_{0.38}Sc_{0.62})O_{2\pm x}$ with Pt powder in conjunction with air as reference in

oxygen sensors to operate down to 650 K. Badwal et al.[55] reported the use of semiconducting oxides as well as composites of these oxides with finely divided Pt as electrical contact materials between air and the ceramic in the sensors for oxygen monitoring in the range 573–873 K. These oxide compacts are made from PrO_{2-y}, TbO_{2-y}, CeO_{2-x}, NiO, $Fe_2O_3 + Fe_3O_4$, ZnO, MnO_2, SnO_2, V_2O_5, In_2O_3, $CrVO_4$, $CrNbO_4$, $(ZnO)_{0.97}(Al_2O_3)_{0.03}$, Sn doped In_2O_3, $LaNiO_3$, $(La_{0.8}Sr_{0.2})CrO_{3-x}$, $(Nd_{0.9}Sr_{0.1})CoO_{3-x}$ or $(Pr_{0.7}Gd_{0.3})O_{2-x}$ with Pt. Ruthenium dioxide, which is stable in air and could be obtained by the air oxidation of $RuCl_3$ solution painted over an electrolyte tube was found to be a good electronic conductor to serve as a reversible air electrode down to even 500 K. Jacob et al.[56] made use of a similar procedure of oxidising $RuCl_3$ solution painted on the electrolyte surface which was subsequently heated in air at 1073 K for 5 h to obtain a highly adherent thin film of RuO_2. This RuO_2/O_2 electrode was used as a reference to measure ΔG_f^o of $CuCrO_4$ over the range 590–760 K. On the other hand, the high volatility of RuO_2 in air ($P_{RuO_4} \approx 3 \times 10^{-3}$ Pa at 773 K) or pure O_2 [due to the formation of the rather stable RuO_4 (g)] seems to be a restriction. Periaswami[57] proposed the use of RuO_2 stabilized in the form of a perovskite for the air electrode in oxygen meters. The doped ternary compound $La_{0.8}Sr_{0.2}CoO_3$ was suggested as a good electrode material by Isaacs et al.[58] Alcock et al. reported that perovskite oxides offer better kinetics than noble metals such as Pt.[59] Investigations wherein Pt is substituted by binary and ternary oxides with high electronic defect concentrations in the air/Pt electrode are quite numerous and more discussion

on these materials is beyond the scope of this review. Nevertheless, a mention may be made of the use of La$_{0.8}$Sr$_{0.2}$MnO$_3$ by Kamata et al.[60] and Bi$_2$Ru$_2$O$_7$ and Bi$_3$Ru$_3$O$_{11}$ by Linquette–Mailley et al.[61] as substitutes for Pt in the air/Pt reference electrode. The latter electrode was reported to be suitable for use even below 500 K. Mallika[62] found that a carefully prepared Pt ceramic contact making use of a high quality Pt paste such as Demetron 308 A, Germany could help to obtain Nernstian behaviour for the air/Pt electrode down to 540 K. To achieve this performance, it was necessary to etch the zirconia tube with a 20% HF-20% HNO$_3$ mixture, followed by hot water leaching to remove the fluorides. Following this a porous, but smooth deposit of Pt was made on a larger area by the reduction of chloroplatinic acid in aqueous media. Even though a commercial platinum paste helped to give contacts at a few points only between the Pt foil and the ceramic substrate, a larger platinised area in the isothermal zone would be available for O$_2$/O^{2-} equilibrium. This was perhaps responsible for better performance of air/Pt electrode at lower temperatures as per certain reports in the literature.[17,49,62]

4.3. Direct oxygen permeability

This would be caused by the presence of micro cracks that allow permeation of molecular oxygen[63] through the solid electrolyte. This permeability would be higher, the higher the temperature and lower the P_{O_2} of the test electrode compared to that of air. It is therefore necessary to select solid electrolyte tubes of high quality with respect to low helium leak rates even at higher temperatures so that direct permeability of molecular oxygen is minimised. Electronic conduction (with an average transference number, t_e for the electrons) in solid electrolytes would contribute to 3 types of errors.[1]

(a) Lowering of cell voltage to the extent of $\bar{t}_e \times E_{th}$ where E_{th} is the theoretical e.m.f. as per Nernst equation.
(b) Changing of oxygen concentration in the test gas in case of oxygen gauges. This could be circumvented by increasing the flow rate of the test gas to the region of flow-independent voltage.
(c) Polarizing the test electrode giving rise to overpotential. The extent to which the above factors would contribute to the cell voltage is discussed in a later section.

5. Mechanistic aspects

It was well established that the electrode impedance and polarization depend on various factors including:

(i) The preparation procedure and heat treatment of the Pt electrode (electrode morphology).
(ii) The composition and surface treatment of the electrolyte.
(iii) The external parameters such as temperature and P_{O_2} of the surrounding gas and
(iv) The overpotential, η.

In order to understand the electrode kinetics i.e. the process taking place at the electrode/electrolyte interface, use of electrochemical impedance spectroscopy was mostly resorted to. The electrode conductivity, σ_E or in other words the reaction rate, is related to the exchange current density, I_o: $\sigma_E = I_o nF/RT$ where n is the number of electrons that take part in the charge transfer reaction and $\sigma_E = 1/R_E$ where R_E is the interfacial resistance. There are several reports in the literature on the kinetics of the electrode reaction at Pt, O$_2$/ stabilized ZrO$_2$ (SZ) interface.[64–69] A brief review of the earlier work is given in what follows.

5.1. Oxygen exchange at electrode/electrolyte interface

The P_{O_2} and temperature dependence of the exchange current I_o or the electrode interface resistance were studied by many workers and the mechanism of electrode reaction was predicted from the results so obtained.[70–78] The steps for the oxygen reduction at the triple-phase boundary, tpb (between Pt, gas phase and SZ) consist of dissociative adsorption of oxygen on the Pt surface, surface diffusion of atomic oxygen and a two-electron transfer near the tpb.

Some of the investigators predicted that the dissociative adsorption of oxygen molecules on the Pt surface to be rate determining step. Others suggested that the surface diffusion of adsorbed atoms on the Pt surface (O$_{ad}$) to the Pt/ZrO$_2$ interface to be the limiting step, while according to some others, it could be either the charge transfer reaction or mass transport in the gas phase. Most of the workers assumed the Langmuir type isotherm for the oxygen adsorption on Pt.[64,65,67–69,79–81] $\theta/1 - \theta = (P_{O_2}/P^*_{O_2})^{1/2} = (a_o/a^*_o)$; where θ is the coverage of O$_{ad}$ on Pt surface and a_o is the oxygen activity. $P^*_{O_2}$ and a^*_o are the P_{O_2} and a_o at which $\theta = 1/2$.

The application of the Langmuir adsorption isotherm to the P_{O_2} dependence of electrode conductance was also investigated by these workers and it was found that at lower P_{O_2} ($< 10^{-5}$ atm), the reaction rate at the tpb tends to be controlled by the diffusion of O$_2$ molecules in the gas phase or in the electrode pores to the tpb. It was shown by Mizusaki et al.[82] that at $T \leqslant 773$ K and $P_{O_2} \geqslant 10^{-4}$ atm, the reaction rate is controlled by the dissociative adsorption of O$_2$ molecules on the Pt surface close to the Pt/ZrO$_2$ contact. At $T \geqslant 873$ K, the surface diffusion of O$_{ad}$ on the Pt surface to the Pt/ZrO$_2$ contact is the rate determining step. They determined

the activation energy of the oxygen reaction to be 145 ± 5 kJ, which is independent of the surface coverage, θ. The activation energy for the surface diffusion of O_{ad} on Pt was determined to be 171.5 ± 10 kJ/mol and the heat of adsorption of O_{ad} on Pt to be 221.8 ± 17 kJ/mol.

Most of these investigations were carried out over a rather narrow range of P_{O_2} namely 1 kPa–1 Pa. But, Kuzin and Komarov extended the range from 1 Pa to 500 μPa.[83] Kleitz[84] and Sasaki et al.[85] found that there is no double layer existing at the electrode/electrolyte interface, which in turn obviated the building of electrical potential difference. This forms the basis of the inference made by Mizusaki et al. that the charge transfer reaction can not be the rate determining step of the oxygen exchange reaction between the gas-solid phases. On the contrary, Godickemeier et al. showed that the charge transfer is the rate limiting step during their studies on the effect of transport of electron and O_2 on the oxygen reduction kinetics.[86] There could be substantial shift in the mechanism depending on the P_{O_2} and temperature range employed by different workers in their electrochemical studies including complex impedance spectroscopy. For instance, in a very recent study using impedance spectra, Mitterdorfer and Gauckler[87] employed the P_{O_2} range $1–10^{-4}$ atm (101–0.1 kPa) at rather high temperatures, 975 and 1071 K. In this temperature range of around 1000 K, these authors found that ordinary Langmuir kinetics do not describe the oxygen adsorption on Pt accurately. They further observed the rate constant for oxygen adsorption, k_a, the rate constant for oxygen desorption, k_d and the Fickian surface diffusion coefficient, D depend on the surface coverage, θ. For high values of θ (0.2–0.75), k_a and k_d are found to vary exponentially with θ at around 1000 K. The value of $D(\theta)$ was found to vary from 2.8×10^{-11} to 4.3×10^{-11} m²/s for the values of 0.3 and 0.75 for θ respectively.

A new equivalent circuit for the Pt/YSZ was proposed by Nakagawa et al.[88] in order to understand the effect of morphological characteristics on the parameters R_E, C and Z (C is the capacitance and Z is the impedance).

The new circuit could be represented as shown in Fig. 4. Mizusaki et al. also proposed a model and simultaneously verified the same with the help of experimental results.[89] They observed that these results were consistent with the model proposed. According to this model, the oxygen atoms are supplied to the charge transfer reaction at the Pt/ZrO_2 interface either by the surface diffusion of O_{ad} on Pt or by the dissociative adsorption of O_2 molecules near the Pt/ZrO_2 boundary, as mentioned earlier. These two mechanisms can take place concurrently. Since diffusion occurs more easily at $T\geqslant873$ K, the oxygen atoms for the charge transfer process are supplied by surface diffusion whereas at $T\leqslant773$ K, the diffusion rate becomes rather slow and hence oxygen has to be supplied directly from the gas phase by adsorption. The σ_E at $T\leqslant773$ K is a constant which does not depend on P_{O_2} and is given by

$$\sigma_E = 16FAk(a_o^*)^2/RT \tag{1}$$

where $k(a_o^*)^2$ is the rate constant and A is the electrode area.

At $T\geqslant873$ K, σ_E is given by

$$\sigma_E = 4F^2BC\lambda\ a_o^* P_{O_2}^{1/2}/\delta(a_o^* + P_{O_2}^{1/2})^2 \tag{2}$$

where B is the length of the tpb, λ is a constant proportional to the surface mobility of O_{ad}, C is the surface concentration of oxygen adsorption site on Pt and δ is the average diffusion length of O_{ad} on Pt surface. Thus, from the mechanistic point of view, the reaction process taking place at the Pt/O_2 or air electrode is strongly dependent on temperature. However, no single study is yet reported in literature which covers a slightly wider temperature range (say even from 700 to 1100 K) to facilitate identification of any significant transition in the mechanism. Likewise, a comprehensive investigation of the transition in mechanism over a wider P_{O_2} range from 10^{-7} to 1 atm (or 0.21 atm) at a most frequently

R_E = Resistance

Z_d = Diffusion impedance

C = Capacitance
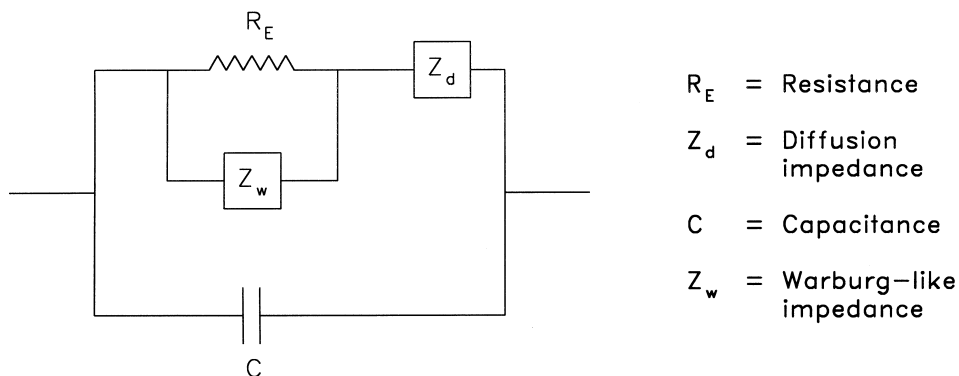
Z_w = Warburg–like impedance

Fig. 4. Equivalent circuit proposed for the O_2/Pt electrode.

used temperature of 900–1000 K is not available to unequivocally state as to below which P_{O_2} the mechanism is mass transfer controlled in gas phase, and above which P_{O_2} it is controlled by dissociative adsorption, surface diffusion of atomic oxygen or electron transfer at tpb.

6. Estimation of errors

6.1. Due to composition of air

The P_{O_2} of dry air is given to be 0.2095 atm by Braker and Mossman[47] whereas Sato[30] suggested a value of 0.2088 atm. For an estimation of error arising from uncertainty in air composition, Venkatraman et al.[45] made use of the Nernstian relation

$$E = (RT/4F) \ \ln \ [P_{O_2}(\text{air})/1] \tag{3}$$

for the galvanic cell

Pt, O_2(1 atm)|stabilized ZrO_2|$O_2(P_{O_2}$ (air)), Pt
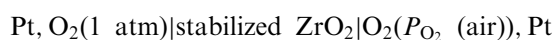
For a 1% variation in P_{O_2} (air) at 1400 K, either a 50 m increase in altitude from sea level, presence of moisture to the extent of 35% relative humidity or a 1% fluctuation in atmospheric pressure the error in measured cell voltage is estimated to be about 0.3 mV for each of the 3 sources. Thus, an overall loss of accuracy of about ±1 mV in the measured E could result if these errors are not recognised and corrected for. In air-conditioned laboratories (with temperature and humidity control) situated at sea level away from cyclone belt serious perturbations in P_{O_2} are not anticipated. Plugging in the values of 0.2095 and 0.2088 as per the composition after Braker and Mossman[47] and Sato[30] respectively, Eq. (3) would reduce to either −0.03367 T/K or −0.03374 T/K. The best way adopted to eliminate the uncertainty arising from that in the composition of air is to measure the actual e.m.f. of the cell I as a function of temperature and incorporate the results in correcting for the standard state of oxygen in thermodynamic measurements. The values of e.m.f. not differing by more than 0.5 mV throughout the year for the cell I was found for a P_{O_2} of 0.209 atm of air in all the thermodynamic measurements reported from this laboratory.

6.2. Due to oxygen permeability

Anthony et al.[1] discussed the errors in the measured cell voltage E arising from direct oxygen permeability through zirconia electrolytes in gauges while analysing the results of round-robin experiments in which 7 nations participated. The 3 contributions to the error are:

(a) The electronic conductivity of the zirconia electrolyte making the cell voltage, E to be lower by $\overline{t_e} \times E_{\text{th}}$ where $\overline{t_e}$ is the average electronic transport number. This aspect is mentioned earlier. However, the transference number, to^{2-} of the oxide ion in fully or partially stabilized zirconia electrolytes presently available is better than 0.999 up to the lower limit of the oxygen potentials corresponding to that of Fe/Fe$_x$O. Anthony et al. also concluded that error in the e.m.f. signal arising from electronic conduction is insignificant even for free oxygen monitoring in inert gases down to a level of 10 mPa. Hence, this contribution to error could be ignored since very reliable results even in ternary oxide electrode systems such as $LaMnO_3$|MnO|La_2O_3 could be reported using air/Pt reference electrode by Sreedharan[90].

(b) In the case of oxygen gauges, direct permeation of oxygen from the air side into the test gas in the measuring electrode compartment caused by either electronic conduction (as mentioned by Anthony et al.) or by some other means would result in a higher concentration of oxygen in the test gas. This error could be minimised by increasing the flow rate.[25,26] Triple electrode or differential gauge designs [26,33] could also be resorted to for minimising the error.

(c) Permeability of oxygen causes an overpotential at the test electrode which is difficult to eliminate. To assess the errors in cell voltage, temperature and reference oxygen pressure, the following Nernst equation (which is derived by assuming $to^{2-} = 1$)[2] should be differentiated:

$$E = RT/4F \ln P_{O_2}(\text{ref})/P_{O_2}(\text{test}) \tag{4}$$

$$\Delta P_{O_2}(test)/P_{O_2}(\text{test}) = 4F\Delta E/RT - 4FE\Delta T/RT^2 \tag{5}$$

The errors in temperature, e.m.f. and P_{O_2} (test) are thus interlinked. For example, an error of 3 K is equivalent to an error of 0.1 mV which in turn is equivalent to a possible error of 0.5% in the P_{O_2} (test). Errors in temperature measurement in excess of even 1 K are unlikely in well planned thermodynamic studies. Hence this contribution to the error in P_{O_2} (test) could be much less. Location of the head of the galvanic cell should be in an isothermal zone with a temperature uniformity of better than 1 K between both the sides of the electrolyte. Temperature gradience between the 2 electrodes represented as ΔT (equal to $T_{\text{air}} - T_{\text{test}}$) could give rise to thermoelectric contribution, $\alpha\Delta T$ where α (which is the Seebeck coefficient assumed to be independent of

Table 2
The use of an air/Pt reference electrode for the determination of ΔG_f^o of binary oxides

Sl. no.	Test electrode	Temperature range (K)	Remarks
1.	Ga/Ga$_2$O$_3$	823–1073	Ref. 97
2.	Te(l)/TeO$_2$	733–873	Ref. 98
3.	Te(l)/TeO$_2$	793–993	Ref. 99
4.	Cu/Cu$_2$O	798–1280	Ref. 100
5.	Pd/PdO	699–1063	Ref. 101
6.	Rh/Rh$_2$O$_3$	769–1263	Ref. 100
7.	Ir/IrO$_2$	762–1260	Ref. 100
8.	Ge/GeO$_2$	810–1180	For hexagonalGeO$_2$; Ref. 23
		800–1150	For tetragonalGeO$_2$; Ref. 23
9.	Sb(s or l)/Sb$_2$O$_3$(s or l)	773–1153	Ref. 102
10.	Te (s or l)/TeO$_2$	588–898	Ref. 103; 588–722 Kfor Te(s) as coexisting phase
11.	Co/CoO	873–1173	Published data prior to 1985 are listed in Ref. 104
12.	CoO/Co$_3$O$_4$	716–1095	Ref. 19
13.	MoO$_2$/Mo$_4$O$_{11}$	768–1058	Ref. 105
14.	MoO$_2$/MoO$_{3-x}$(l)	1075–1150	Ref. 105
15.	Sb$_2$O$_3$/Sb$_2$O$_4$	585–828	Ref. 106; platinum black added for better conduction and low temperature reversibility
16.	Cu$_2$O/CuO	1200–1323	Ref. 111
17.	Pb(l)/PbO	645–977	[Pt + (U$_{0.38}$Sc$_{0.62}$)O$_{2\pm x}$] used instead of porous Pt to ensure low temp.reversibility; Ref. 53
18.	Pb(l)/PbO	767–901	Ref. 187
19.	PbO/Pb$_3$O$_4$	696–812	Ref. 187
20.	Ni/NiO	760–1275	Ref. 116
21.	Sn(l)/SnO$_2$	673–1167	Ref. 54
22.	Tl/Tl$_2$O	780–1175	Oxygen potential determined; Ref. 119
23.	Ni/NiO	1073–1473	Ref. 122
24.	Fe/Fe$_3$O$_4$	727–794	Eutectoid temperature in Fe–O system determined; Ref. 34
	Fe/Fe$_x$O	779–834	
25.	TaO$_{2.5-\delta}$ single phase	1150–1400	activity versus composition derived; Ref. 126
26.	Pd/PdO	830–1023	Ref. 130
27.	Bi/Bi$_2$O$_3$	840–1030	Ref. 131
28.	MoO$_x$ single phase	880–1070	$x = 2.5, 2.7, 2.8$ and 2.85; Ref. 144
29.	Sb/Sb$_2$O$_3$	785–1014	Ref. 145
30.	Sn/SnO$_2$	923–1173	Ref. 146
31.	Fe/Fe$_x$O	750–1580	Ref. 171
32.	Ru/RuO$_2$	1005–1106	Ref. 96
33.	Fe/Fe$_x$O	862–1405	Ref. 172
34.	Fe/Fe$_x$O	1253–1385	Oxygen potentials derived; Ref. 174
	Fe$_x$O single phase		
	Fe$_x$O/Fe$_3$O$_4$		
35.	Ni(l)/NiO	1723–1823	Ref. 168
36.	Zn/ZnO	767–1007	Ref. 179
37.	Cd/CdO	723–850	Ref. 182
38.	In/In$_2$O$_3$	500–1060	Ref. 54
39.	CeO$_{2-x}$ single phase	823–1073	$x = 0.01$–0.0001; oxygen potential in the non stoichiometric oxide determined; Ref. 183
40.	Cu$_2$O/CuO	973–1373	Ref. 206
41.	Te(l)/TeO$_2$	748–898	oxygen potentials determined and phase equilibria in Te-Sb$_2$O$_3$-Sb$_2$O$_4$ evaluated, Ref. 207
42.	Sb$_2$O$_3$/Sb$_2$O$_4$	723–857	
	Sb$_2$O$_3$/Sb$_2$O$_4$/Te(l)	750–900	

temperature and P_{O_2}) is of the order of 100–200 μV per degree. Besides this effect, the error in E will be greater when the difference in P_{O_2} of the reference air and the test electrodes is larger as seen by the following equation derived by Anthony et al:[1]

$$\Delta E = [0.52 + 0.05 \log P_{O_2}(\text{test})]\Delta T \qquad (6)$$

In the above equation, the temperature is measured at the air/Pt reference electrode as in many of the equations and P_{O_2} (test) is the oxygen partial pressure at the test electrode and this expression is valid for temperatures around 1000 K. It could be seen that the error in e.m.f. is minimised to less than 1 mV when ΔT is insignificant (not more than 1 K) for values of the order of

Table 3
Application of air/Pt reference electrode for the thermodynamic characterization of ternary oxides

Sl. no.	Condensed phase electrode	Temperature range (K)	Salient features and remarks
1.	$NaCrO_2/Na_2CrO_4/Cr_2O_3$	784–1012	for ΔG_f^o ($NaCrO_2$); Ref. 107
2.	$LiCrO_2/Li_2CrO_4/Cr_2O_3$	626–721	ΔG_f^o ($LiCrO_2$) determined; Ref. 108
3.	$KCrO_2/K_2CrO_4/Cr_2O_3$	777–1200	for ΔG_f^o ($KCrO_2$) and threshold oxygen level in K(l); Ref. 108
4.	$FeCr_2O_4/Cr_2O_3/Fe$	1000–1700	To determine ΔG_f^o ($FeCr_2O_4$); Ref. 16
5.	$NiCr_2O_4/Cr_2O_3/Ni$	1000–1500	for ΔG_f^o ($NiCr_2O_4$); Ref. 16
6.	$La_2O_3/MnO/LaMnO_3$	1064–1308	ΔG_f^o ($LaMnO_3$) calculated; Ref. 90
7.	$La_2O_3/Co/La_2CoO_4$	973–1375	Gibbs energy data derived; Ref. 109
8.	$LaVO_3/LaVO_4$	1133–1373	oxygen potential measured; Ref. 110
9.	$CuLn_2O_4/Cu_2O/Ln_2O_3$	1173–1350	ΔG_f^o of double oxides calculated; (Ln = La, Nd, Sm, Eu and Gd); Ref. 111
10.	$Cu_2R_2O_5/Cu_2O/R_2O_3$	1173–1350	for ΔG_f^o of double oxides (R = Tb, Dy, Er, Yb, Y and In); Ref. 111
11.	$MgU_2O_7/MgU_2O_{6.67}$	826–1208	Oxygen potentials in the three systems calculated; Ref. 121
	$MgU_2O_{6.67}/MgU_2O_6$	779–1093	
	$MgU_2O_6/MgO. 2UO_{2+\delta}$	814–1294	
12.	$La_4Ni_3O_{10}/La_2NiO_4/NiO$	1203–1473	Gibbs energy data on $La_4Ni_3O_{10}$ and La_2NiO_4 calculated; Ref. 122
	$La_2NiO_4/Ni/La_2O_3$	1073–1473	
13.	$RECoO_3/RE_2O_3/CoO$	1073–1473	ΔG_f^o of $RECoO_3$ determined (RE = Sm, Eu, Gd, Tb, Dy or Ho); Ref. 125
14.	$Bi/(Bi_2O_3)_{0.78}(Nb_2O_5)_{0.22}$	840–1030	Thermodynamics of Bi_2O_3–Nb_2O_5 solid solutions evaluated; Ref. 131
15.	$UMoO_6/UMoO_5$	776–1127	ΔG_f^o ($UMoO_5$) calculated; Ref. 138
16.	$Sb/ZnO/ZnSb_2O_4$	850–972	ΔG_f^o of the ternary oxides determined; Ref. 145
	$Sb/MgO/MgSb_2O_4$	945–1117	
17.	$Cs_2Cr_2O_7/Cs_2CrO_4/Cr_2O_3$	797–874	ΔG_f^o ($Cs_2Cr_2O_7$,l) measured; Ref. 155
18.	$Na_2CrO_4/NaCrO_2/Cr_2O_3$	820–1006	ΔG_f^o ($NaCrO_2$) determined; Ref. 156
19.	$Rb_2U_4O_{12}/Rb_2U_4O_{13}$	1019–1283	ΔG_f^o of $Rb_2U_4O_{12}$ and $Cs_2U_4O_{13}$ derived; Ref. 157
	$Cs_2U_4O_{12}/Cs_2U_4O_{13}$	1033–1204	
20.	$BaMoO_3/BaMoO_4$	1053–1196	$\Delta G_{f,ox}^o$ ($BaMoO_3$) calculated; Ref. 158
21.	$Y_2BaCuO_5/Y_2BaO_4/Cu_2O$	717–1021	$\Delta G_{f,ox}^o$ (Y_2BaCuO_5) calculated; Ref. 170
22.	$LaRuO_3/La_2O_3/Ru$	1032–1256	ΔG_f^o ($LaRuO_3$) determined; Ref. 96
23.	$YBa_2Cu_3O_{7-x}$	620–930	Oxygen potential and phase transition on the single phase reported; Ref. 173
24.	$ZrO_2/MoO_2/ZrMo_2O_8$	986–1206	Oxygen potential in the system calculated; Ref. 185
25.	$BaBiO_{3-x}$ single phase	975–1300	$\Delta \bar{G}_{O_2}$ determined as a function of non stoichiometry and phase relations studied; Ref. 186
26.	$HfO_2/MoO_2/HfMo_2O_8$	982–1217	$\Delta G_{f,ox}^o$ ($HfMo_2O_8$) determined; Ref. 188
27.	$BaCuO_2/BaCu_2O_2/Cu_2O$	1003–1132	$\Delta G_{f,ox}^o$ ($BaCu_2O_2$) determined; Ref. 189
28.	$Ba_2CuO_3/BaCuO_2/BaCu_2O_2$	1175–1235	$\Delta G_{f,ox}^o$ (Ba_2CuO_3) determined; Ref. 189
29.	$Y_2O_3/YCuO_2/Cu$	1113–1255	$\Delta G_{f,ox}^o$ ($YCuO_2$) determined; Ref. 189
30.	$Y_2O_3/YCuO_2/CuO$	782–1122	Ref. 189
31.	$Y_2O_3/Cu_2O/Y_2Cu_2O_5$	1097–1292	$\Delta G_{f,ox}^o$ ($Y_2Cu_2O_5$) determined; Ref. 190
32.	$Rb_3CrO_4/Rb_2CrO_4/Cr_2O_3$	798–967	$\Delta G_{f,ox}^o$ (Rb_3CrO_4) determined;
		994–1189	$\Delta G_{f,trans}^o$ ($\alpha \rightarrow \beta$) Rb_2CrO_4 determined; Ref. 191
33.	$Rb_2Cr_2O_7(l)/Rb_2CrO_4/Cr_2O_3$	973–1153	$\Delta G_{f,ox}^o$ ($Rb_2Cr_2O_7$) determined; Ref. 191
34.	$Cs_2CrO_4/Cr_2O_3/Cs_3CrO_4$	1052–1098	ΔG_f^o (Cs_3CrO_4) determined; ΔG_{trans}^o ($\alpha \rightarrow \beta$) Cs_2CrO_4 determined; Ref. 192
35.	$Cs_2CrO_4(\beta)/Cr_2O_3/Cs_2Cr_2O_7(l)$	1025–1190	ΔG_f^o ($Cs_2Cr_2O_7$) determined; Ref. 192
36.	$K_2Cr_2O_7(l)/K_2CrO_4(\beta)/Cr_2O_3$	978–1149	ΔG_f^o ($K_2Cr_2O_7$,l) determined; Ref. 192
37.	$Na_2Cr_2O_7(l)/Na_2CrO_4(\beta)/Cr_2O_3$	960–1069	ΔG_f^o ($Na_2Cr_2O_7$,l) determined; Ref. 192
38.	$KCrO_2/K_3CrO_4/K_2CrO_4$	950–1134	Ref. 193
39.	$CaO/CaRuO_3/Ru$	971–1312	$\Delta G_{f,ox}^o$ ($CaRuO_3$) determined; Ref. 194
40.	$SrO/Sr_2RuO_4/Ru$	1044–1235	$\Delta G_{f,ox}^o$ (Sr_2RuO_4) determined; Ref. 195
41.	$Sr_2RuO_4/Sr_3Ru_2O_7/Ru$	926–1164	$\Delta G_{f,ox}^o$ ($Sr_3Ru_2O_7$) determined; Ref. 195
42.	$Sr_3Ru_2O_7/SrRuO_3/Ru$	991–1282	$\Delta G_{f,ox}^o$ ($SrRuO_3$) determined; Ref. 195
43.	$Cs_2O(l)/Cs_2RuO_3/Cs_2RuO_4$	946–1205	$\Delta G_{f,ox}^o$ (Cs_2RuO_3) determined; Ref. 196
44.	$Te(l)/NiTeO_3/NiO$	833–1104	ΔG_f^o ($NiTeO_3$) determined; Ref. 197
45.	$NiTeO_3/Ni_3TeO_6/NiO$	624–964	ΔG_f^o (Ni_3TeO_6) determined; Ref. 197
46.	$ZrO_2/ZrTe_3O_8/Te(l)$	874–1135	$\Delta G_{f,ox}^o$ ($ZrTe_3O_8$) determined; Ref. 198

Table 3 (*continued*)

Sl. no.	Condensed phase electrode	Temperature range (K)	Salient features and remarks
47.	$BaPbO_3/Ba_4Pb_3O_{10}/PbO$	756–968	ΔG_f^o ($Ba_4Pb_3O_{10}$) determined; Ref. 199
48.	$Ba_4Pb_3O_{10}/Ba_2PbO_4/PbO$	797–1097	ΔG_f^o (Ba_2PbO_4) determined; Ref. 199
49.	$Sm_2CuO_4/Sm_2O_3/Cu_2O$	968–1203	$\Delta G_{f,ox}^o$ (Sm_2CuO_4) determined; Ref. 200
50.	$Cu/Sm_2O_3/SmCuO_2$	967–1196	$\Delta G_{f,ox}^o$ ($SmCuO_2$) determined; Ref. 200
51.	$Sm_2CuO_4/SmCuO_2/Sm_2O_3$	619–1152	Ref. 200
52.	$CoO/CoSb_2O_4/Co_7Sb_2O_{12}$	790–1039	ΔG_f^o ($Co_7Sb_2O_{12}$) determined; Ref. 201
53.	$Co_3O_4/Co_7Sb_2O_{12}/CoSb_2O_6$	855–1035	ΔG_f^o ($CoSb_2O_6$) determined; Ref. 201
54.	$NiO/NiSb_2O_4/NiSb_2O_6$.	894–1061	ΔG_f^o ($NiSb_2O_6$) determined; Ref. 202
55.	$Bi_2CuO_4/Bi_2Cu_2O_5/Cu_2O$	772–950	$\Delta G_{f,ox}^o$ ($Bi_2Cu_2O_5$) determined; Ref. 203
56.	$RCoO_3/R_2O_3/CoO$ (R = Sm, Eu, Gd or Dy)	1080–1200	ΔG_f^o ($RCoO_3$) determined; Ref. 204
57.	$Nd_4Co_3O_{10}/Nd_2O_3/CoO$	1080–1220	Ref. 204
58.	$Nd_4Co_3O_{10}/NdCoO_3/CoO$	1100–1200	Ref. 204
59.	$Cu/CuYO_2/Y_2O_3$.	973–1323	ΔG_f^o of the ternary oxides, determined; Ref. 208
60.	$Cu_2Y_2O_5/CuYO_2/Y_2O_3$	973–1323	
61.	$Na_2MoO_4/Na_2Mo_2O_7/MoO_2$	758–843	To determine ΔG^o ($Na_2Mo_2O_7$); Ref. 209
62.	$Na_2MoO_4/Na_2Mo_3O_6/MoO_2$	858–921	ΔG_f^o ($Na_2Mo_3O_6$) calculated; Ref. 209
63.	$KUO_3/K_2UO_4/K_2U_2O_7$	941–1150	for deriving ΔG_f^o (KUO_3); Ref. 210
64.	$SrCrO_4/Sr_3Cr_2O_8/Cr_2O_3$	1073–1423	Gibbs energy data derived; Ref. 211
65.	$Cs_2U_2O_7/Cs_4U_5O_{17}/Cs_2U_4O_{12}$	1048–1206	ΔG_f^o ($Cs_4U_5O_{17}$) determined; Ref. 212
66.	$La_3Ba_3Cu_6O_{14+x}$.	823–1073	P_{O_2}-T-x diagram evaluated; Ref. 214

Table 4

Determination of ΔG_f^o of sulphides and sulphates using SEGC and air/Pt reference

Sl. no.	Test electrode	Temperature range (K)	Remarks
1.	$NiO/Ni_{3\pm x}S_2/SO_2(g)$(1 atm)	973–1173	ΔG_f^o ($Ni_{3\pm x}S_2$) derived; Ref. 112
2.	$M_2O_2S/M_2O_3/SO_2(g)$ or $M_2O_2S/M_2O_2SO_4/SO_2(g)$	1200–1500	Gibbs energy data determined (M = Nd, Gd or Y); Ref. 113
3.	Na_2SO_4 (molten)$/SO_3(g), SO_2(g)$	1173	Electrochemical behaviour studied; Ref. 114
4.	$REO_x/RE_2O_2S/Ag/Ag_2S$	1000–1100	ΔG_f^o (Ce_2O_2S) at 1068 K and ΔG_f^o (Y_2O_2S) at 1072 K calculated; RE = Ce or Y; Ref. 120
5.	$Co_3O_4/CoSO_4/SO_2(g)$	970–1050	Equilibrium constants calculated; Ref. 132
6.	[Cu, S] melt/$SO_2(g)$	1423–1623	Activities and phase equilibria in the melt studied; Ref. 133
7.	[Pb, S]/$SO_2(g)$	1223–1273	Sulphur potential measured; Ref. 142
8.	$Cu/Cu_2S/CaS/CaO$	1000–1350	Gibbs energy of formation of the oxysulphides and sulphates of Ca, Mg and La derived; Ref. 149
	$CaS/CaSO_4$	1050–1450	
	$Cu/Cu_2S/CaSO_4/CaO$	1050–1340	
	$Ag/Ag_2S/MgS/MgO$	1000–1150	
	$Cu/Cu_2S/La_2O_2S/La_2O_3$	1080–1350	
	$Ag/Ag_2S/La_2S_3/La_2O_2S$	950–1120	
9.	All possible sulphides and sulphates in Fe-Ni-S-O system co-existing with either NiO or Fe_2O_3	700–900 700–1100 700–1000 845–1040	ΔG_f^o of the following derived; Ref. $FeSO^{162}$ $NiSO_4$ $Fe_2(SO_4)_3$ Fe_4S_3
10.	Cu-S melts	1423, 1523	Activity coefficient of oxygen in the melts determined; Ref. 165
11.	$RE_2O_2S/RE_2O_2SO_4/RE_2O_3$	1000–1500	RE = (La, Pr, Nd, Sm, Eu, Gd, Tb or Dy); thermodynamics of oxidation of the oxysulphides studied; Ref. 166

−10 for log P_{O_2} (test). Hence, much of the accuracy and precision in e.m.f. for thermodynamic measurements depend on those of temperature measurement and on the location of the cell in a truly uniform zone (±1 K) of the furnace.

7. Recent applications

Tables 2–6 indicate the literature reports wherein the air/Pt reference electrode was used for thermodynamic property measurements. The literature sur-

Table 5

Measurements of activity, solubility and diffusivity of oxygen in liquid metals using air/Pt reference electrode material

Sl. no.	Liquid metal/binary alloy	Temperature range (K)	Remarks
1.	[O] in liquid (Pb + Tl)	1073	a_o over the entire composition range measured; Ref. 115
2.	(Ge + Sn) and (Ge + Sb)	—	Activity coefficient of oxygen measured; Ref. 117
3.	[O] in molten (Cu + Tl) and (Cu + In)	1423	Interaction parameters for In-O and Tl-O in Cu(l) derived; Ref. 118
4.	In-Sn liquid	1073, 1273	Activity of oxygen measured over the entire composition range; Ref. 123
5.	(Ge + Bi), (Ge + Pb) and (Ge + In)	1233	Activity coefficient of oxygen calculated; Ref. 124
6.	PbO-MgO-SiO$_2$ slag	1173–1273	Activity of PbO in the slag measured; Ref. 127
7.	In(l) and (In-Ga)	1023–1123	a_{As-O} in liquid metal and alloy determined; Ref. 128
8.	Te and [O] in Cu(l)	1373–1473	Interaction parameters calculated; Ref. 129
9.	Sn(l),(Ge-Sn) and (Ni-Sn)	1073–1223	Activity coefficient of oxygen derived; Ref. 134
10.	(In-Pb) and (In-Tl)	1073, 1273	Activity coefficient of oxygen in the alloys determined; Ref. 136
11.	(Cu-Sn)	1373–1573	Activity coefficient of oxygen calculated; Ref. 137
12.	Au-Co	1073–1673	Activity of oxygen in the alloy determined; Ref. 140
13.	In(l) and (In-Sb)	1000–1130 & 1083	Activity coefficient of oxygen in In(l) and ln-Sb alloy evaluated; Ref. 143
14.	(Pb-Sb)	1073, 1173	Activity coefficient of oxygen over the entire composition range at 1073 K and up to 0.5 at.% Sb at 1173 K; Ref. 148
15.	Sn, Pb, Cu, Ag, Ti, In, In-Sn, In-Pb, In-Cu and In-Ag liquids	1023–1223	Diffusivity, solubility, activity and the activity coefficient of oxygen studied; Ref. 150
16.	(As-Cu)	1373–1423	Interaction parameter measured; Ref. 152
17.	[O] in (Cu-As) and (Cu-Se)	1423	As-O and Se-O interactions on molten copper studied; Ref. 153
18.	Cu and Ag liquids	1373	Activity of oxygen in the liquid metals determined; Ref. 154
19.	(Bi-In)	1073	Activity coefficient of oxygen at infinite dilution for the entire composition range determined; Ref. 159
20.	(Cu-Pb)	1473	Activity of oxygen determined; Ref. 160
21.	(Bi-Sn)	1073, 1273	Activity coefficient of oxygen measured over the entire composition range; Ref. 161
22.	(Cu-Te)	1423	Activity of oxygen measured; Ref. 163
23.	(Bi-Pb) and (Bi-Sb)	1073	a_o in the liquid alloys measured; Ref. 164
24.	Bi, Sn and Ge liquids	973, 1073, 1173 1233, 1373	a_o in Bi and Sn and a_o in Ge(l) determined; Ref. 167
25.	(Ag-ln), (Ag-Sn), (Ag-Sb) and (Ag-Ge)	1273	Activity coefficients of oxygen in the liquid alloys measured; Ref. 175
26.	(Ag-Bi) and (Ag-Tl)	1273	Activity coefficient of oxygen measured; Ref. 176
27.	(Ag-Pb)	1273, 1473	Activity coefficient of oxygen determined; Ref. 177
28.	(Cu-Tl)	1373	Activity coefficient of oxygen determined as a function of alloy composition; Ref. 178
29.	(Tl-Te)	1073, 1223	Activity coefficient of oxygen measured; Ref. 180
30.	(Cu-In) and (Cu-Sn)	1373	Activity coefficients and interaction parameters calculated; Ref. 181
31.	[O] in Na(l)	473	a_o in Na(l) down to 473 K; Ref. 57
32.	(Ni-Ga)		Ref. 205
33.	Ga-In Ga-Sb In-Sb	973–1173	Activity coefficients of oxygen in the liquid alloys measured; Ref. 213
34.	Ga-In-Sb	973–1173	a_o in the ternary alloy determined; Ref. 213

veyed covered mainly the work reported during the last two decades, since most of the earlier work was included in the reviews and books.[30,37,91–93] The objective in making these tables is to list out some of the typical studies carried out in various laboratories around the world. This survey is by no means exhaustive or complete. Omissions if any are not intentional, but the contents of the tables are indicative of the variety of the systems rather than their details. The studies in recent years fall into roughly 5 groups namely those on (i) binary oxides, (ii) ternary oxides, (iii) sulphides and sulphates in controlled atmospheres such as SO$_2$ or pure

O$_2$, (iv) oxygen activity coefficient, its solubility and diffusivity in liquid metals as well as oxygen interaction parameters in dilute binary alloys and (v) activities of components in binary alloys and intermetallics. It is seen that wherever kinetics are not restricting the attainment of equilibrium in test electrodes, air/Pt reference can be universally employed. Quite a few studies are reported from this laboratory using carefully prepared an air/Pt electrode in which a substantially wide span of temperature below 800 K could be covered as seen from Tables 2, 3 and 6, without recourse to the novel electrode materials. The reason for the unattain-

Table 6
Use of an air/Pt electrode for the activity measurements in binary alloy

Sl. no.	Alloy bearing electrode	Temperature range (K)	Salient features and remarks
1.	Co-Sn/SnO$_2$	873–1323	Thermodynamic properties of CoSn and CoSn$_2$ determined; Ref. 135
2.	PdTe/PdTe$_2$/TeO$_2$	613–962	a_{T_e} in the miscibility gap region of Pd-Te determined; Ref. 139
3.	Au-Co/CoO	1073–1673	Phase equilibrium studies; Ref. 140
4.	Co-Zn/ZnO	873–1173	Thermodynamic properties calculated; Ref. 141
5.	Cu-Co(l)/CoO	1370–1730	Activities and thermodynamic properties derived; Ref. 147
6.	Mo-Te/MoO$_2$	728–1065	ΔG_f^o (MoTe$_2$, α) derived; Ref. 151
7.	Ni-Pd(l)/NiO	1673–1823	Activities of Ni in the liquid alloy over the entire composition range measured; Ref. 168
8.	Ni$_{0.595}$Te$_{0.405}$/NiO	963–1178	Activity of Ni measured; Ref. 169
9.	In-Sb/In$_2$O$_3$	873–1073	a_{In} measured; Ref. 184

ability of the same lower temperature limit of e.m.f. data in different measurements from the same laboratory is mostly due to the limitation from the measuring electrode rather than that of the reference electrode. Perhaps one more factor also contributed to the lower temperature capability of e.m.f. measurements. This was the gradual thinning of the flat YSZ surface by repeated lapping and polishing with carborundum and diamond paste in order to clean the surface for the next experiment. This factor was recognised when the need arose for the replacement of the tube caused by breakage. The new tubes were found to restrict the lower temperature limit under identical conditions of preparation of the platinum contact.

8. Recommendations for the use of air/Pt in e.m.f. measurements for thermodynamic data

The following practices may be adopted for obtaining reliable thermodynamic data on condensed phase coexistence systems by zirconia based e.m.f. measurements resorting to the use of an air/Pt electrode as recommended in the above discussions.

(a) Screening of fully stabilized zirconia electrolyte tubes for purity and for helium leak tightness (up to the maximum operating temperature) during e.m.f. measurements.

(b) Lapping and polishing of the flat closed end of the zirconia electrolyte tube in order to reduce the impedance of the ceramic in case e.m.f. measurements at temperatures lower than 900 K are envisaged.

(c) Etching and cleaning of the ceramic tube with HF and coating with a porous platinum layer over a large area near the closed end (of course within isothermal zone) and making point contacts between the Pt foil (attached to the lead) and the porous Pt layer.

(d) Temperature measurement to be made with Pt_10%Rh/Pt thermocouple calibrated to a precision of ± 0.1 K using freezing points of bismuth, zinc, antimony and silver[37,94,95] as standards. The temperature control should be better than ± 0.5 K at each temperature of measurement. Most important is the location of the galvanic cell in the isothermal zone of a bifilar resistance wound furnace. By isothermal zone, it is meant that the constancy of temperature should be better than 1 K over a length of at least 1 cm in which space of the furnace, the cell head comprising the tip of the measuring thermocouple, air/Pt electrode and the test electrode with its platinum disc are located.

(e) The e.m.f. of the galvanic cell with both sides containing air/Pt electrodes over the entire temperature range should be measured to confirm that the cell voltage is less than about 0.1–0.2 mV.

(f) The e.m.f. of cell I, where in the air/Pt electrode is measured against O$_2$/Pt as the test electrode, should be made in order to derive a linear expression for E in terms of T (K). This expression should have a negligible intercept (of the order of a couple of millivolts or less) and a slope close to -0.0337 for dry air ($P_{O_2} = 0.209$ atm). In case the slope is lower than -0.0337 (such as -0.0345[96]) cross-checking with the barometric pressure in the laboratory, ambient temperature and relative humidity should be done. This would confirm lower value of P_{O_2} (about 0.200–0.205 atm) prevailing in the atmospheric conditions of the laboratory.

(g) The reversibility of the test electrode system should be checked by micropolarization test. Care should be expended in the preparation of the test electrode to avoid polarization if any, caused by direct permeability of oxygen from the air/Pt reference electrode.

Acknowledgements

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