Forschungszentrum Karlsruhe

Technik und Umwelt

Wissenschaftliche Berichte

FZKA 6690

Measurement of oxygen activities in eutectic lead-bismuth by means of the EMF method

H. Muscher, J. Konys, Z. Voss, O. Wedemeyer

Institut für Materialforschung

Programm Nukleare Sicherheitsforschung

Forschungszentrum Karlsruhe GmbH, Karlsruhe

2001

Impressum der Print-Ausgabe:

Als Manuskript gedruckt

Forschungszentrum Karlsruhe GmbH
Postfach 3640, 76021 Karlsruhe

Mitglied der Hermann von Helmholtz-Gemeinschaft
Deutscher Forschungszentren (HGF)

ISSN 0947-8620

Abstract

Liquid lead and the eutectic lead-bismuth alloy (PbBi) are considered both as a spallation target and coolant of an accelerator driven system (ADS) for the transmutation of long-lived actinides from nuclear waste into shorter living isotopes. It is known that both, pure lead and PbBi, exhibit a high corrosion affinity against austenitic and ferritic steels, because of the high solubility of nickel and iron in PbBi.

Thermodynamic calculations and experimental results have confirmed, that the control of oxygen in lead or PbBi within a defined activity range can lead to acceptable corrosion rates. To control the level of oxygen dissolved in lead or PbBi, a sensor for measuring the oxygen activity is required. Within the *Sodium Fast Breeder Reactor Development*, an adequate technique was established for estimating oxygen in liquid sodium. This knowledge can be used for other metal/oxygen systems like oxygen in PbBi. For measuring the oxygen activity and calculating its concentration, the relevant thermodynamic and solubility data have to be considered. Reference electrode systems: Pt/air, In/In_2O_3 and Bi/Bi_2O_3 (all based on yttria stabilized zirconia as solid electrolyte) are investigated to evaluate their EMF-temperature dependency in saturated and unsaturated oxygen solutions. Results with all types of oxygen meters in PbBi at different oxygen levels were compared with theoretical calculations. The experimental data indicate that the design, construction and integration of an oxygen control unit in a large scale PbBi-loop seems to be very feasible.

A HGF Strategy Fund Project entitled “Thermalhydraulic and material specific investigations regarding the realization of an Accelerator-Driven System (ADS) to transmute minor actinides” is performed at Forschungszentrum Karlsruhe. The objective of this project is to develop new technologies and manufacture thermally highly-loaded surfaces, which are cooled by a corrosive lead-bismuth eutectic. The corrosion challenge for possibly structure, window and cladding materials (as vital components of an ADS spallation target for flowing lead-bismuth) must be solved. The beam window can be cooled by liquid Pb or PbBi in natural or forced circulation flow. Corrosion caused by liquid PbBi is generally, as for other liquid metal systems related to the solubility of oxygen.

The EMF method is used to measure the oxygen potential in lead-bismuth loops in order to control and prevent the corrosion of the materials used. The experimental investigations are performed in the KArlsruhe Lead LAboratory KALLA.

Messung von Sauerstoffaktivitäten in der eutektischen Blei-Wismut Schmelze mit Hilfe der EMF-Methode

Zusammenfassung

Sowohl flüssiges Blei als auch das Blei-Wismut-Eutektikum werden als Spallationstarget bzw. Kühlmittel für zukünftige ADS-Systeme erachtet, die der Umwandlung langlebiger minorer Aktiniden in kurzlebigere Isotope dienen sollen. Es ist bekannt, dass beide, reines Blei und eutektisches PbBi, eine hohe Korrosivität bezüglich austenitischer und ferritischer Stähle aufweisen, dies aufgrund der hohen Löslichkeit des Nickels und des Eisens in PbBi.

Eine Möglichkeit der Herabsetzung der starken Korrosion ist die in-situ Bildung stabiler Oxidschichten an der Oberfläche des Strukturwerkstoffes. Thermodynamische Berechnungen und experimentelle Ergebnisse haben bestätigt, dass die Sauerstoff-Regelung in Blei und/oder PbBi innerhalb eines definierten Aktivitätsbereichs des Sauerstoffs zu akzeptablen Korrosionsraten führen kann.

Um das Niveau des im Pb oder auch im PbBi gelösten Sauerstoffs zu regeln, ist ein Sauerstoff-Sensor zur Messung der Sauerstoff-Aktivität unentbehrlich. Eine entsprechende Messtechnik zur Bestimmung der Sauerstofflöslichkeiten im flüssigen Natrium ist im Rahmen der Entwicklung des Projektes “Schneller Brüter” ausgearbeitet worden. Dieses Know-how kann nun für andere Metall/Sauerstoffsysteme wie z.B. Sauerstoff in PbBi zur Anwendung kommen. Für die Messung der Sauerstoffaktivität und für die Berechnung der Sauerstoffkonzentrationen sind die notwendigen thermochemischen Daten sowie die entsprechenden Löslichkeitswerte in Betracht zu ziehen. Referenz- (Bezugs-) Elektrodensysteme: Platin/Luft, In/In_2O_3 sowie Bi/Bi_2O_3 (alle auf der Grundlage von yttriumstabilisiertem Zirkoniumdioxid als Festelektrolyt) wurden untersucht, um ihre EMK- vs. Temperaturabhängigkeit in sowohl sauerstoffgesättigten als auch -untersättigten Lösungen zu bestimmen. Die Ergebnisse mit allen Typen von Sauerstoffsonden in PbBi bei unterschiedlichen Sauerstoffpegeln sind mit den Berechnungen verglichen worden, die der Theorie entnommen sind. Die experimentell ermittelten Daten zeigen, dass der Entwurf, die Konstruktion und die Einbindung einer Sauerstoffregelungseinheit in einen PbBi-Kreislauf tatsächlich realisierbar ist.

CONTENT

1 Introduction

Lead and lead-bismuth alloys are considered as spallation target for a so-called accelerator driven system (ADS) in which long-lived actinides should be transmuted [Heu98][Rub95] [Bau99]. Lead and PbBi have a high neutron yield and are very transparent to neutrons of energies below 1 MeV. The molten metal could be used not only as a target but also as a coolant in this reactor system [Bena00]. But it is known from literature, that lead and bismuth are much more corrosive than e.g. alkali metals [Ber71][Tol66][Ash77]. Hence, an important issue of an ADS is the corrosion of the structural and window materials in the liquid PbBi target [IPPE98]. This corrosion process must be understood, controlled and reduced for safety and economic reasons [Rich80].

One way to reduce corrosion of metals in liquid Pb or PbBi would be the use of metals with very low solubility, e.g. tungsten or molybdenum [Week96][Tosh96][Week71] [Week70]. Another way is to form a stable oxide layer on the materials surface [Kof66]. Thermodynamic investigations of Al-Fe alloys showed the possibility that self-healing of the alumina scale can take place if the kinetics of the process is fast enough [Kley97]. Gromov et al. [Gro95] and Markov [Mar97] stabilized the oxide layer by maintaining an oxygen concentration of 10^{-6} at.-% in liquid Pb or PbBi with an oxygen control system.

In literature, corrosion problems with steel being in contact with lead and lead alloys are well known [Kon99][Rus00]. Since all the solubilities of gases and impurities vary with temperature, transport processes will take place which result in a dissolution of material at high temperatures and a precipitation at low temperatures [Kry74]. A temperature difference of 150°C is typical for technical lead loops [Roma63]. Therefore, even small solubilities can lead to heavy corrosion effects at high flow velocities, in the range of a few meters per second.

It is known and accepted that one should measure and control the oxygen concentration exactly to keep the conditions of the liquid lead in a range of low corrosion effects. After a certain period of time, oxygen in Pb or PbBi will be depleted by oxide formation on the surface of the structural steel and thus the conditions will shift to the region with low oxygen concentration and hence to strong corrosion effects, if there would be no oxygen control.

An oxygen control system in a PbBi loop requires the continuous measurement of the oxygen potential in the liquid alloy. A very suitable technique is the use of solid electrolyte oxygen sensors [Kon01]. Based on the experience in other liquid metal systems like sodium, lithium or lead-lithium [Bhat94] [Bor84][Bar88][McK74][Tay83], an adaptation to the specific conditions of the eutectic lead-bismuth alloy is necessary. Furthermore the thermodynamic database has to be established to allow theoretical calculations regarding the temperature and oxygen concentration dependency of the electromotive force (EMF) of such zirconia based oxygen sensors[Bock59] [West84] [Kudo90].

In the field of the PbBi-O system there is a need to establish a broader basis of understanding, knowledge and experience related to oxygen in heavy liquid metal coolants technology and to gain experience in the field of unique experimental techniques, physical model development and numeric analysis as well as in methods to measure and control impurities, caused by liquid metal corrosion within the cooling loops [Rus98].

The fundamental input to this research area comes generally from the basic work of oxygen in liquid alkali metals, such as Na or Li [Add84]. For instance oxygen in liquid sodium has been investigated extensively with the electromotive force (EMF) technique. Using this technique one can obtain more information in comparison to other techniques such as the classic Sievert's method, the gas equilibration, gas-transpiration, the coulometric and the calorimetric methods – all of them are described in the monograph of Fitzner and Chang [Fitz88].

The main objective of the present report is to review the data reported in the literature concerning particularly oxygen dissolved in liquid lead-bismuth eutectic with respect to a more general method of theoretical and experimental approach on the field "thermodynamic properties of gases dissolved in liquid alloys", as described originally in text-books and monographs of phenomenological chemical thermodynamics including the theory and practice of chemical equilibrium [Kort66] [Moor73][Pred82][Prig54]. Neither old nor new models work well for describing the physical properties and the thermodynamic behavior of oxygen dissolved in liquid lead–bismuth eutectic[Lupi72] [Mos73][Pred67]. The most important parameter, the dissolved oxygen activity data known to exist in the literature [Kaz83] and the thermodynamic description of the system PbBi-O is rather poor, especially for the set of parameters, such as the technological relevant and important temperature range (i.e. window) of 400°C – 550°C, where there are simply no reliable experimental data from measurements of oxygen solubilities are available up to now. It is therefore our aim to describe this system first of all qualitatively and then semi-quantitatively, to reach a better understanding of model-calculated values. Simple models do not take into consideration the solution behavior of the liquid alloys [Prin66]. Chang et al [Chan93] commented the existence of many quite different models describing the thermodynamic properties of gases in liquid alloys simply as a confusing impression of lack of understanding the in nature of such systems. It could be, that the suggested model assumptions and their key ideas are not appropriate even for oxygen dissolved in pure liquid lead [Ray72] [Ray71] or pure liquid bismuth [Ell65]. Binary alloys and higher order alloys are even much more complicated systems [Hill98][Rud67] [Mas90] [Froh80][Schm85]. From this discussion it becomes obvious that it is necessary to measure and control the oxygen concentration exactly to keep the conditions of the liquid lead in a range of low corrosion effects.

The rate-controlling step is here the uptake of oxygen from the gas phase. Hence, the long-term stability of the oxide layer can only be guaranteed, if two boundary conditions for the oxygen potential within the liquid lead-bismuth are fulfilled: the oxygen potential has to be high enough in order to prevent the dissolution of the oxides from the steel surface, and the oxygen potential has to be low enough to prevent the formation of large amount of lead oxide precipitation. This requires the continuous measurement and control of the oxygen concentration in a lead-bismuth loop.

The concentration of oxygen in lead that is necessary for the protective oxide scale formation on steel structures, may be controlled by solid electrolyte cells that measure and feed oxygen into the liquid lead or lead-bismuth. Such cells are sophisticated and require a special know-how to build them. To prevent PbO precipitation and to support Fe_3O_4 formation the following conditions for the oxygen potential must be established:

$$2\Delta G^0_{PbO} > RT \ln p_{O_2} > 0.5\Delta G^0_{Fe_3O_4} \ . \tag{1}$$

The standard values ΔG^0 of the Gibbs energies are well known for all relevant oxides and with these values the equilibrium oxygen partial pressure region that retains the stable conditions can be calculated. The oxygen partial pressure as a function of the H_2/H_2O or CO/CO_2 ratio can be calculated as follows [Schw65]:

$$p_{O_2} = \frac{p^2_{H_2O}}{p^2_{H_2}} \exp\frac{-2\Delta G^0_{H_2O}}{RT} = \frac{p^2_{CO_2}}{p^2_{CO}} \exp\frac{-2\Delta G^0_{CO_2}}{RT} \ . \tag{2}$$

If we choose a proper H_2/H_2O or CO/CO_2 ratio we will still form Fe_3O_4 but no PbO in the case of stagnant Pb in the concerned temperature range [Mül00]. If we consider a PbBi loop, there will be an equilibration across the temperature region through the oxygen dissolved in Pb (PbBi). So we have to consider the variation of the oxygen potential for a constant oxygen concentration throughout the temperature region between 400°C and 550°C.

Electrochemical oxygen meters used for the measurement of oxygen potentials in liquid metals have been developed in our laboratory over a long period of time for many liquid metal applications, e.g. Na, K, Pb-17Li, Borgstedt [Bor71] [Bor72][Bor74a] [Bor90] [Gan85] Bhat and Borgstedt [Bhat81][Per87]. Inherent problems associated with these meters were previously breakage of the ceramic electrolyte tube, non-theoretical response to oxygen activity and design related failures. For use of oxygen meters in Pb and/or PbBi, only rarely published data from Russian groups are available, Orlov [Orl98].

2 Thermodynamic background

EMF cells are used worldwide for that purpose since C. Wagner [Wag52] [Wag56][Kiu57] [Wag70] [Hau66] and G.W. Horsley [Hor61] have well published the principle of that method. The solid (oxide) electrolyte technique pioneered by them in the sixties has been rapidly developed since solid oxide electrolytes became better in quality and exhibited now a high extend of predominantly ionic character over a wide temperature range [Alc64] [Alc65][Ric69][Worr77][Worr73][Worr66][Stee65][Patt67][Dell78][Borg82][Patt71]. It is well known from the theory that this galvanic cells are suitable for activity measurements of oxygen dissolved in a great number of liquid metals and binary alloys [Rapp63] [Ots79][Ots75] [Rapp70] [Ste76] [Per88] [Ost65] [Haas56] [Chan81] [Stre52][Ots81] [Szw72] [Task79] [Ste82] [Ise76] [Con84] [Bhat87][Bhat88] [Borg87][Borg90] [Ric66] [Ric66a]. Detailed descriptions concerning the operating conditions are given in the review articles of Richardson, Rapp, Alcock, Hladik, Fischer, Goto [Rich68][Rich74][Alc68] [Goto72][Fis75] [Rama80] [Rapp70][Kom73]. The infinitesimal increment of inner energy U of a body results as a sum of the Pfaff-Caratheodory forms for work done on it and heat which it absorbs [Lew23] [Kuba58] [Sch73][Den71] [Bae00].

$$dU = \delta W + \delta Q$$

Entropy is a total differential in case of reversibility in regard to initial and final states, (equilibrium criterions).

$$dS = \frac{\delta Q}{T}$$

Putting the first and the second law of thermodynamics together one obtains:

$$dU = -pdV + TdS$$

the basic equation for a closed system, applicable only when volume change is the only form of (mechanical) work. By definition-the enthalpy is:

$$H = U + pV$$

and the Gibbs free enthalpy is:

$$G = H - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

For constant p, T:

$$dG = -pdV + TdS + pdV - TdS = 0$$

and for additional electrical work done in the system [Vett61][Skor79]:

$$dG = \delta W_{el} = -zFEdn$$

For constant p, T: $$dG = \sum \mu_i dn_i$$

Taking into account the chemical potential defined as a partial molar value [Barr71][Haas56],

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$$

a setup of model systems to which the behavior of real systems approximates under limiting conditions:

a) perfect gas b) perfect gas mixture c) an ideal solution

The gas is ideal, when (at constant T)

$$\mu = \mu^0 + RT \ln p / p^0$$

It is convenient to choose p° as unity in the same system of units as p itself, if so:

$$\left(\frac{\partial \mu}{\partial p} \right)_{T,n_j} = RT \frac{d \ln p}{dp} = RT / p = V_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_j}$$

Generally, in the case of the total differential dG one obtains:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

Let us concise discuss the reaction equilibrium:

The stoichiometry of a chemical reaction can be generalized as follows:

$$0 = \sum \nu_i M_i$$

This implies following equalities:

$$\frac{dn_a}{\nu_a} = \frac{dn_b}{\nu_b} = \cdots = \frac{dn_z}{\nu_z} = d\xi$$

Zero on the left side describes the condition for the chemical equilibrium of a chemical reaction.

$$dG = Vdp - SdT + \left(\sum \mu_i \nu_i\right) d\xi$$

$$\Delta G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \left(\sum \mu_i \nu_i\right) = 0$$

Let us now consider a perfect gas mixture, for each component (index i) of it we have:

$$\mu_i = \mu_i^0 + RT \ln p_i$$

where the first summand is a function of temperature only, substituting it in the equation above we obtain:

$$\Delta G = \sum \mu_i \nu_i = \sum \nu_i \mu_i^0 + RT \sum \nu_i \ln p_i = 0$$

Or in equivalent form:

$$\sum \nu_i \mu_i^0 = -RT \ln \prod_i p_i^{\nu_i} = -RT \ln K_p = \Delta G^0 (T/K)$$

This expression can be used to discuss galvanic cells (cell on open circuit, not performing work).

The electrochemical potential of each corresponding species is a linear function of the average local electrical potential called Galvani potential [Lang62] [Weis70] [Ham75][Kort57]:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln x_i + zF\varphi$$

An example is the reaction [DECH92] [Göp89] [Fou76]:

$$O_{2(g)} + 4\bar{e}\,(Pt) \leftrightarrow 2O^{2-}\,(YSZ)$$

which may be translated into:

$$4\tilde{\mu}_e + \mu_{O_2} = 2\tilde{\mu}_{O^{2-}}$$

When two phases, called I and II, can exchange a species under equilibrium, the electrochemical potential values in both phases are equal for this species:

$$\tilde{\mu}_c^I = \tilde{\mu}_c^{II}$$

The potential difference between two electric leads, I and II, made of the same metal is related to the difference between the electron electrochemical potentials of these leads. The electron concentrations being constant in the metal wire at constant T one can write according to:

$$\tilde{\mu}_e = \tilde{\mu}_e^0 - F\varphi$$

the following expressions:

$$\varphi^{II} - \varphi^{I} = -\frac{1}{F}\left(\tilde{\mu}_e^{II} - \tilde{\mu}_e^{I}\right) + \frac{1}{F}\left(\tilde{\mu}_e^{0\,II} - \tilde{\mu}_e^{0\,I}\right)$$

If the metals of the leads being the same in nature, the second term is zero.

$$\varphi^{II} - \varphi^{I} = -\frac{1}{F}\left(\tilde{\mu}_e^{II} - \tilde{\mu}_e^{I}\right)$$

The generation of a cell voltage at a zirconia oxygen sensor can be described as follows. Both at the measuring (I) and at the reference electrode (II) the same kind of equation is valid. One directly gets from these 2 equations:

$$-4\left(\tilde{\mu}^{II}{}_{e^-} - \tilde{\mu}^{I}{}_{e^-}\right) = \left(\mu^{II}{}_{O_2} - \mu^{I}{}_{O_2}\right) - 2\left(\tilde{\mu}^{II}{}_{O^{2-}} - \tilde{\mu}^{I}{}_{O^{2-}}\right)$$

which gives the cell voltage:

$$\varphi^{II} - \varphi^{I} = \frac{1}{4F}\left(\mu^{II}{}_{O_2} - \mu^{I}{}_{O_2}\right) - \frac{1}{2F}\left(\tilde{\mu}^{II}{}_{O^{2-}} - \tilde{\mu}^{I}{}_{O^{2-}}\right)$$

This equation shows two contributions: 1) a surface part (due to O_2) correlated to the surface specific conductivity and 2) a bulk part (due to oxygen ions)/electrolytic transmission line.

It is important to point out/discuss the difference between the Gibbs energy of solubility (better said: of solvation) and Gibbs energy of the oxide formation [Ond96] [Ond99].

Let us consider the thermodynamics of oxygen dissolved in pure lead (an unary system, activity of lead being in every case equal to unity $a_{Pb} = 1$). According to the general Hess scheme (1st law of thermodynamics) one obtains for the terminal solubility (saturation):

reaction 3 = reaction 1 + reaction2

Where reaction 1:

$$1/2\mathrm{O}_{2(g)} \Leftrightarrow [\mathrm{O}]_{\mathrm{Pb(l)}}$$

reaction 2:

$$\mathrm{Pb}_{(l)} + [\mathrm{O}]_{\mathrm{Pb(l)}} \Leftrightarrow \mathrm{PbO}_{(s)}$$

reaction 3: (the sum of reaction 1 and reaction 2):

$$\mathrm{Pb}_{(l)} + 1/2\mathrm{O}_{2(g)} \Leftrightarrow \mathrm{PbO}_{(s)}$$

For the reaction 1 we obtain:

$$\Delta G_{sol\,(1)}{}^{0} = -RT\ \ln \frac{a_{[O]}}{p_{O_2}^{1/2}} = 2F \cdot \left(E = E_{sol}\right)$$

For the reaction 2 (unary system) we obtain:

$$\Delta G_{2}{}^{0} = RT\ \ln a_{[O]} = 2F \cdot \left(E = E_{2}\right)$$

And in case of oxygen saturation in liquid lead:

$$\Delta G_{f}{}^{0} = RT\ \ln p_{O_2}^{1/2} = 2F \cdot \left(E = E_{sat}\right)$$

$$\Delta G_{sat}{}^{0} = \Delta G_{f}{}^{0} - \left(\Delta G_{2}{}^{0} = -RT\ \ln 1 = 0\right)$$

Or in equivalent description:

$$\lim_{a_{[O]} \to 1} \Delta G_{sol}{}^{0}\left(a_{[O]}\right) = \Delta G_{sat}{}^{0} = \Delta G_{f}{}^{0}$$

The case of unsaturated solutions it leads to:

$$\Delta G_{sol}^{0} = -RT \ \ln \frac{a_{[O]}}{p_{O_2}^{1/2}} =$$

$$= -RT \ \ln \ p_{O_2}^{1/2} - RT \ \ln \frac{x}{x^{sat}}$$

This explains the activity scale for dissolved oxygen in liquid metals according to the early works of Bhat, N. Rumbaut (on terminal i.e. saturation solubility data), H.U. Borgstedt and C.K. Matthews [Borg87a] [Rum83] [Rum82] which is based on:

$$a_{[O]}^{sat} = 1$$

For comparison see also [Ots80]. After saturating of the liquid lead with oxygen particles of PbO precipitate:

$$\mathrm{Pb_{(l,alloy)}} + 1/2\mathrm{O_{2(g)}} \Leftrightarrow \ \mathrm{PbO_{(s)}}$$

the Gibbs energy of lead oxide formation (from unary lead) can be written as:

$$\Delta G^{0} = -RT \ \ln \frac{a_{PbO}}{a_{Pb} \ p_{O_2}^{1/2}} = RT \ \ln \ p_{O_2}^{1/2}$$

A generalization of that equation for oxygen saturated binary alloys (like PbBi eutectic) leads to the following expression:

Reaction 1:

$$1/2\mathrm{O_{2(g)}} \Leftrightarrow \ [\mathrm{O}]_{\mathrm{PbBi(l)}}$$

$$\Delta G_{sol\ (1)}^{\ 0} = -RT \ \ln \frac{a_{[O]}}{p_{O_2}^{1/2}} = 2F \cdot \left(E = E_{sol}\right)$$

Reaction 2:

$$\mathrm{Pb_{(l,alloy)}} + [\mathrm{O}]_{\mathrm{PbBi(l)}} \Leftrightarrow \ \mathrm{PbO_{(s)}}$$

$$\Delta G_2^{\ 0} = -RT \ \ln \frac{a_{PbO}}{a_{Pb}\, a_{[O]}} = -RT \ \ln \frac{1}{a_{Pb}\, a_{[O]}}$$

$$a_{Pb} \neq 1$$

Reaction 3 (sum of reaction 1 and 2):

$$\mathrm{Pb}_{(\mathrm{l,alloy})} + 1/2\mathrm{O}_{2(\mathrm{g})} \Leftrightarrow \quad \mathrm{PbO}_{(\mathrm{s})}$$

For binary alloys the thermo chemical Hess scheme can be written similar as in case of unary systems:

$$\Delta G_{3(f)}{}^{0} = \Delta G_{1(sol,sat)}{}^{0} + \Delta G_{2,sat}{}^{0}$$

The basic thermodynamics of oxygen saturated liquid PbBi can be summarized as follows (in contrary to molten lead, which is a unary system, where $a_{[O]}{}^{sat} = 1$):

$$a_{[O]}^{sat} = 1/a_{Pb} \neq 1$$

(Under the assumption, that PbO and not Bi_2O_3 is the first precipitating oxide, which can be derived from the basic thermodynamic data [Cod72] [Otto65] [Otto66] [Bann84] [Kov81] [Kov79][Froh79][Froh76][Bie81][Du95][Du96][Kom62] [Du97][Du99][Fir60] [Boiv69][Boiv74] [Bord87] [Khar1][Khar2][Khar3][Khar4][Lev64][Geb54] [Ris98][Wri88][Alp70]).

It is known from experimental data published very recently, that the activity of lead (as well as the conjugated activity of bismuth) in PbBi is strong nonlinear dependent on the composition of the alloy – a_{Pb} as a function of analytical molar ratio x_{Pb} – but for the constant x_{Pb} = 0.45 value of the PbBi eutectic, there is no/or only a negligible effect on temperature and on pressure in the technical relevant ranges on a_{Pb} [Agar00][Task82].

$$a_{Pb} \cong 0.38$$

for very dilute oxygen solutions in PbBi melt (even in case of oxygen saturation) the system obeys both the Henry's and the Sievert's low and we get:

$$a_{[O]} = \frac{x_{[O]}}{x_{[O]}^{sat} a_{Pb}} = 2{,}6\,\frac{x_{[O]}}{x_{[O]}^{sat}} \neq \frac{x_{[O]}}{x_{[O]}^{sat}}$$

Sievert's law obeyed even at the saturation point [Dar53]

$$p_{[O]}^{1/2} = x_{[O]}\gamma_{[O]}^{0}$$

$$p^{1/2}_{[O],\,sat} = x_{[O],\,sat}\,\gamma^{0}_{[O]}$$

Henry s law obeyed even at the saturation point

$$p_{O_2,sat} = k_H(T)\,x_{[O],\,sat}$$

$$\mu^{PbBi}_{[O]} = 0.5\,\mu^{Gas}_{O_2}$$

By using the bismuth sesquioxide electrode with the following scheme one can measure the bismuth activity in liquid PbBi as follows:

$$(-)Mo, Bi_{(l)}, Bi_2O_{3(s)}\left|YSZ\right|PbBi_{(l)}, Bi_2O_{3(s)}, Mo(+)$$

$$\mathrm{Bi} \Leftrightarrow \mathrm{Bi}^{3+} + 3\mathrm{e}^{-}\cdots\left|\times 2\right.$$

$$3/2\mathrm{O}_2 + 6\mathrm{e}^{-} \Leftrightarrow 3\mathrm{O}^{2-}$$

$$\mathrm{Bi}^{3+} + 3/2\mathrm{O}^{2-} \Leftrightarrow 1/2\mathrm{Bi}_2\mathrm{O}_3\cdots\left|\times 2\right.$$

6 F charge passed for 2 Mol Bi, 4F charge passed for one Mol O_2.

With

$$2\mathrm{Bi} + 3/2\mathrm{O}_2 \Leftrightarrow \mathrm{Bi}_2\mathrm{O}_3\cdots\cdots K_1 = \frac{a_{Bi_2O_3}}{a^2_{Bi}\,p^{3/2}_{O_2}} = p^{2/3}_{O_2}$$

$$2\mathrm{Bi}_{\mathrm{alloy}} + 3/2\mathrm{O}_2 \Leftrightarrow \mathrm{Bi}_2\mathrm{O}_3\cdots\cdots K_2 = \frac{a_{Bi_2O_3}}{a^2_{Bi,alloy}\,p^{3/2}_{O_2}} = \frac{1}{a^2_{Bi,alloy}\,p^{3/2}_{O_2}}$$

and for $p^{(1)}_{O_2} = p^{(2)}_{O_2}$

the free energy of the reaction can be written as:

$$\Delta G = \Delta G_1 - \Delta G_2 = -RT\ln K_1 - (-RT\ln K_2) = RT\ln\frac{K_2}{K_1}$$

With

$$\Delta G = RT\ln\frac{a_{Bi_2O_3}}{a^2_{Bi,alloy}p^{3/2}_{O_2}}\cdot\frac{(a_{Bi}=1)^2 p^{3/2}_{O_2}}{a_{Bi_2O_3}} = RT\ln\frac{1}{a^2_{Bi,alloy}} = -2RT\ln a_{Bi}$$

$$\Delta G = -2RT\ln a_{Bi} = 6FE$$

the equation for the calculation of the bismuth activity can be so formulated as a final result:

$$a_{Bi} = \exp\left(-\frac{3FE}{RT}\right)$$

By using the Gibbs-Duhem-relationship (according to the partial molar properties),

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i = 0$$

at constant T and p

$$dG = \sum_i \mu_i dn_i = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i = 0$$

$$\sum_i n_i d\mu_i = 0$$

$$\sum_i x_i d\mu_i = 0 \qquad x_{Pb}d\mu_{Pb} + x_{Bi}d\mu_{Bi} = 0 \qquad a_i = f_i x_i$$

applied for our binary system PbBi. Generally, a differentiation of the equation for μ gives (since μ^0 is a constant):

$$d\mu_i = RTd\ln f_i$$

Rewritten in the corresponding mol fractions it leads to:

$$x_{Pb}\frac{d\ln f_{Pb}}{dx_{Pb}} + (1-x_{Pb})\cdot\frac{d\ln f_{Bi}}{dx_{Pb}} = 0$$

$$\frac{\dfrac{\partial \ln f_{Pb}}{\partial x_{Bi}}}{\dfrac{\partial \ln f_{Bi}}{\partial x_{Bi}}} = -\frac{x_{Bi}}{x_{Pb}} = \frac{\partial \ln f_{Pb}}{\partial \ln f_{Bi}}$$

After evaluating the activity coefficient of lead by means of a numerical or graphical integration the activity of lead can be calculated as:

$$\ln f_{Pb} = -\int_{0}^{x_{Pb}} \left(\frac{1-x_{Pb}}{x_{Pb}} \right) d \ln f_{Bi}$$

$$a_{Pb} = f_{Pb} \, x_{Pb}$$

3 Measurement of oxygen activity in liquid PbBi

The oxygen sensors that are well known from sodium and lead-lithium technology, are adapted to be used in liquid lead-bismuth. Thermodynamic calculations that give the theoretical correlation between the electromotive force EMF and the temperature for non-saturated and saturated oxygen in lead-bismuth, form the basis for the evaluation of the probe signals. Three reference systems are considered for the use in lead-bismuth:

- Platinum/air,
- Bi/Bi_2O_3,
- In/In_2O_3.

Schemes of the investigated galvanic cells

$$(-)\; SS, \left[Pb, PbO\right]_{PbBi} \left|YSZ\right| \left|O_{2(g)} p = 0.21\; bar, Pt\; (+)\right.$$

$$(-)\; SS, \left[Pb, PbO\right]_{PbBi} \left|YSZ\right| \left[Bi_2O_3, Bi\right], Mo_{(s)} (+)$$

$$(-)\; Mo, In, In_2O_3 \left|YSZ\right| \left[Pb, PbO\right]_{PbBi}, SS\; (+)$$

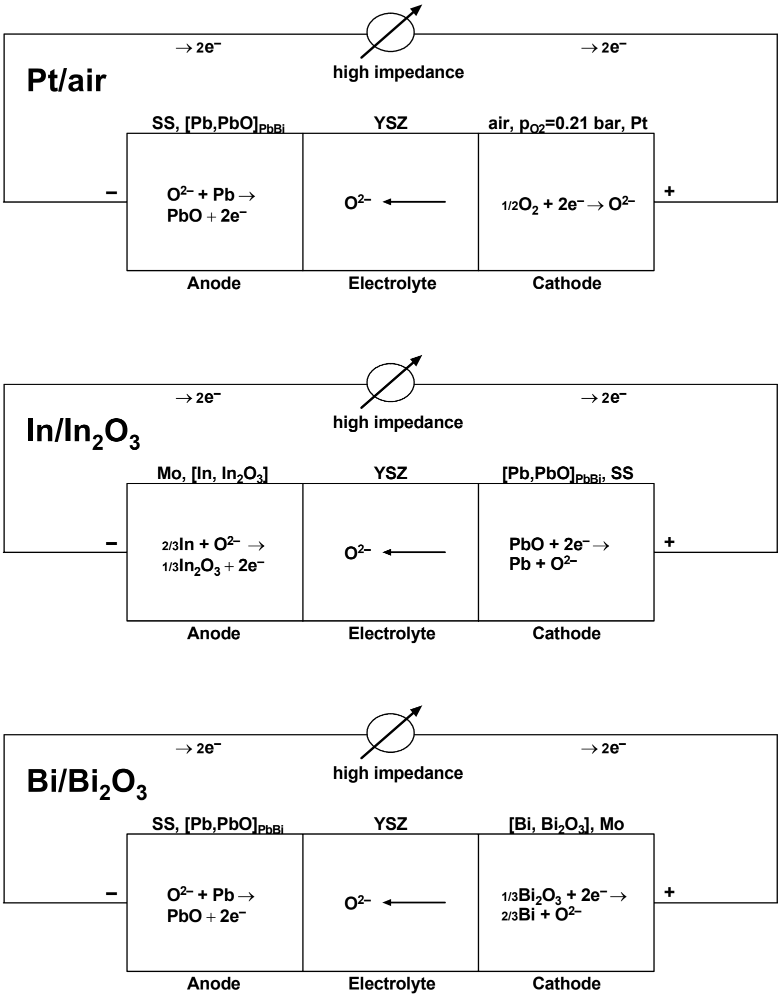

Figure 1: Modeling of the oxygen probes investigated

Notice the direction of the oxygen ionic flux in the YSZ if only the pO_2 of the reference is higher than the activity value of in PbBi dissolved oxygen. Oxygen probe under thermodynamical equilibrium produce an EMF value in accordance to the Nernst law.

The ionic transference number $t_{O^{2-}}$ of the zirconia solid electrolyte is defined as [Krö56]:

$$t_{O^{2-}} = \sigma_i / (\sigma_i + \sigma_e)$$

$$t_{O^{2-}} = [1 + (p_{O_2} / p^*_{O_2})^{-1/4}]^{-1}$$

which can be expressed as given above.

[Schm63][Schm66][Schm72][Kub62] [Hau56][Schm75].

The Nernst equation of the oxygen concentration cell can be obtained after the integration within the limiting partial pressure values, according to:

$$E = \frac{1}{4F}\left(\mu''_{O_2} - \mu'_{O_2}\right)$$

$$E = \frac{RT}{4F}\int_{p'_{O_2}}^{p''_{O_2}} t_{O^{2-}}\, d\ln p_{O_2}$$

The result is the well-known expression [Wag30]:

$$E = t_{O^{2-}}\frac{RT}{4F}\ln\frac{p_{O_2}^{\mathrm{Ref}}}{p_{O_2}^{\mathrm{Sample}}}$$

Typical values for $t_{O^{2-}}$ are 0.8-1.0.

Types of electrodes

All EMF measurements of galvanic cell reactions must be expressible in terms of a Nernst concentration cell.

A reversible electrode establishes by definition fixed activities of the potential relevant species. These activities maybe either invariant, constant (systems under equilibrium) or variable, in case of an unsaturation with respect to the component of interest, such as dissolved oxygen in liquid metals, or for a component of a binary alloy. An electrode of variable activities is reversible only if its composition is fixed and uniform throughout (x, y, z). By definition a small(est) throughput/passage of electric charge in either direction will not disturb the equilibrium. Such electrode with very well known activities is called reference electrode. The ability of an electrode to remain reversible depends upon the product of the concentration and diffusivity of the mobile species/ions in the electrode. In EMF measurements every electrode polarization should be prevented, both that kind of polarization which gives rise both to a step in activity across the phase border metal/ metal oxide and to a development of a gradient in activity across the electrode.

Direct electrodes

Direct electrodes are metals, alloys, gas electrodes and condensed phases containing solutes, which are an example for an alloy of a special kind.

The key point is, that the equilibration process is with respect to one component only between a single-phase (solid) electrode and the electrolyte.

Coexistence electrodes

Coexistence electrodes require an equilibration between two or more components in the electrode. Examples are mixed condensed phases or a gas mixture in equilibration with the electrolyte. They are particularly suitable for the determination of the standard Gibbs energies of formation, for example for oxides. The according expressions are easy, because the activities of each condensed phases are set equal to 1 (unity).

Precision and reliability of the experimental technique applied EMF data are about one order of magnitude better than calorimetric c_p-data.

Reference pO_2 values can be calculated from the knowledge of standard Gibbs energies of oxide formation. According to Kubaschewski et al and Schwerdtfeger et al, $H_2/H_2O_{(g)}$ gas mixtures can be used to fix the oxygen activity in the gas phase [Schw70]. The cell geometry/cell design should eliminate the possibility of occurrence of multiple ("mixed")/half-cell reactions.

Each electrode is isolated as good as possible from mutual contact with surrounding gas. EMF readings with high mV values, as indices for possible electronic transport through YSZ were avoided [Rie94][Rapp68]. To fulfill the electrode isolation requirement, the complete enclosure of the electrode in tube seemed for us to be the best solution. YSZ of sufficient purity is indeed an exclusive ionic conductor material [Stub77][Mont95][Kün94].

Sign convention. General considerations, basic formalism, formulae

In the metrology, where the circuit design of measuring devices and the topology of electric leads (branches and nodes) etc. - once fixed, and not changed anymore during the whole measuring cycle - are important topics and it is common, to measure a value with respect to a reference. Let us examine this subject in more detail. Taking into account the meaning of the idiomatic expression "to measure a (sample) value with respect to a reference (id est in German: *"bezüglich eines Referenzwertes")* we can point out a general hypothesis for every virtual global reaction of a potential - giving galvanic cell:

$$E_{global} = E_{sample} - E_{ref}$$

Both for "global", "reference" and "sample" parts of the whole-cell EMF the following expression, derived first by Helmholtz, holds [Bag93]:

$$\Delta G_i = -zFE_i = -RT \ln K_i$$

The indices “i” stands accordingly for 3 rows: “sample”; “reference”, “global”. Let us multiply the equation one with/ by the factor (-z F)

$$-zFE_{global} = \quad -zFE_{sample} - \quad (-zFE_{ref})$$

It means in other words, taking into account the two Gibbs energies of the oxide formation:

$$\Delta G_{global} = \Delta G_{sample} - \Delta G_{ref}$$

Hence:

$$-4FE_{global} = -RT \ln K_{sample}^{formation} - (-RT \ln K_{reference}^{formation})$$

After easiest manipulation we obtain:

$$4FE_{global} = RT \ln K_{sample}^{formation} - RT \ln K_{reference}^{formation}$$

So it is obvious that:

$$E_{global} = +\frac{RT}{4F} \ln \frac{K_{sample}^{formation}}{K_{ref}^{formation}}$$

z=4 is because the thermochemical table data are given for easy comparison in kJ/mol O_2. For an unary system (pure lead, a $_{Pb}$=1) we define the equilibrium constants of the first oxide formation according to the dimension of the free enthalpy of the oxide formation in kJ/mol O_2 as:

$$K_{ref}^{formation} = \frac{a_{In_2O_3}^{2/3}}{a_{In}^{4/3} \times p_{O_2}^{ref}} = \frac{1}{p_{O_2}^{ref}}$$

and for the sample as:

$$K_{sample}^{formation} = \frac{a_{PbO}^{2}}{a_{Pb}^{2} \times p_{O_2}^{sample}} = \frac{1}{p_{O_2}^{sample}}$$

Let us repeat (the equation given above generally holds):

$$\Delta G_{global} = \Delta G_{sample} - \Delta G_{ref}$$

$$-RT \ln K_{global} = -RT \ln K_{sample}^{formation} - (-RT \ln K_{reference}^{formation})$$

$$RT \ln K_{global} = RT \ln K_{sample}^{formation} - RT \ln K_{reference}^{formation}$$

Hence:

$$K_{global} = \frac{K_{sample}^{formation}}{K_{reference}^{formation}} = \frac{P_{O_2}^{ref}}{P_{O_2}^{sample}}$$

After simply manipulation (taking the logarithm of the left and right side of the equation with subsequent according multiplication by the factor minus RT) we obtain:

$$-zFE_{global} = -RT \ln K_{global} = -RT \ln \frac{P_{O_2}^{ref}}{P_{O_2}^{sample}}$$

and consequently, the final result is:

$$E_{global} = +\frac{RT}{zF} \ln \frac{P_{O_2}^{ref}}{P_{O_2}^{sample}}$$

$$E_{global} > 0 \Leftrightarrow \frac{P_{O_2}^{ref}}{P_{O_2}^{sample}} > 1 \qquad E_{global} < 0 \Leftrightarrow \frac{P_{O_2}^{ref}}{P_{O_2}^{sample}} < 1$$

As a consequence, the whole-cell EMF changes sign, depending on the above quotient. In case of our binary alloy with PbO as the first precipitating oxide the equilibrium constants of the oxide formation of PbO can not be simplified in the manner as described above and one obtains:

$$K_{sample}^{formation} = \frac{a_{PbO}^{2}}{a_{Pb}^{2} \times p_{O_2}^{sample}} = \frac{1}{a_{Pb}^{2} \times p_{O_2}^{sample}}$$

with a_{Pb} unequal to unity. The value of Agarwala and Jena for a_{Pb} for PbBi eutectic at our loop relevant temperatures (400°C to 550°C) remains as a nearly constant value of 0.38. According to this:

$$K_{global} = \frac{P_{O_2}^{ref}}{a_{Pb}^{2} \times P_{O_2}^{sample}}$$

and after simply algebraic manipulations one obtains:

$$E_{global} = + \frac{RT}{zF} \ln \frac{P_{O_2}^{ref}}{a_{Pb}^{2} \times P_{O_2}^{sample}}$$

As a consequence, the whole-cell EMF changes sign, depending on the quotient:

$$E_{global} \underset{<}{>} 0 \Leftrightarrow \frac{P_{O_2}^{ref}}{a_{Pb}^{2} \times P_{O_2}^{sample}} \underset{<}{>} 1$$

Taking for simplicity an a_{Pb} value of 0.5 for the whole temperature range of relevance, and knowing that firstly a_{Pb} strongly depends only on x_{Pb} (in our case x_{Pb} is a constant, however), and secondly the temperature effect on a_{Pb} remains negligible, we can state, that a positive shift of the recorded EMF data (plus 32,4 mV) for saturated oxygen in liquid PbBi eutectic should be observed in comparison with the same measurements for pure lead (as an unary system). Such comparison measurement has not been done until now.

Generally for unary systems one can declare, that if only the *shielded* electric lead wire from the reference electrode is connected with the plus (+) input of the voltmeter, the sign of the voltage on the display and/or at the GPIB output will be positive (plus) if only $p_{\text{ref}} > p_{\text{sample}}$, otherwise ($p_{\text{ref}} < p_{\text{sample}}$) a minus (-) sign is expected [Keith].

As mentioned above in our system (liquid PbBi eutectic), a positive +32,4 mV shift, according to the constant, but not equal one activity value of Pb in the alloy, should be observed, with the consequence, that the change of the sign at the voltmeter outputs from plus to minus and vice versa is expected for a quotient $p_{\text{ref}} / p_{\text{sample}}$ equal not to one but to exponent of (-1,8305) = 0.160. It is near one order of magnitude difference of the oxygen equilibrium partial pressures. Are these considerations concerning the sign of the whole cell-EMF correct and self-consistent or not? The answer gives us the careful analysis of the work of J. W. Gibbs and the worldwide-accepted Stockholm “Conventions Concerning the Signs of Electromotive Forces” from 1953 [Gibb31] [Lew61] [Ric78][Kir88] [Gugg49].

Formulae including the “de Donder” affinities

$$dG = -SdT + Vdp - Ad\xi$$

in case of an isothermal, isobaric process, when electric work is done by the cell one obtains [Dond36]:

$$dG = -Ad\xi = Edq$$

$$A = -E\left(\frac{dq}{d\xi}\right)_{p,T} = nFE$$

$$A = T\left(\frac{dS}{d\xi}\right)_{p,T} - \left(\frac{dH}{d\xi}\right)_{p,T} = T\Delta S_r - \Delta H_r = -\Delta G_r$$

We put the minus sign in front of the following partial derivative, because electrons are negative charged.

$$\left(\frac{dq}{d\xi}\right)_{p,T}$$

For the definition of the EMF both magnitude and sign are important [Ric77].

The **Stockholm Commissions** have ruled, that, as stated in Gibbs` treatment (1875-78), the direction of the (infinitesimal small) current fixes the loci of the anode (‘) and of the cathode (“) of a galvanic cell. Andre de Bethune [Beth55] comment to this - if one accepts as in Lewis and Randall’s work and in the Stockholm Commissions Convention, “ that a cell diagram shall always imply a flow of positive electricity through the cell from left to right, one may establish a correlation between their notation and Gibbs by writing for all possible cells: The whole-cell EMF is a difference of Galvani potentials of the cathode (right) and anode (left)” [Good87]. From the IUPAC convention of Stockholm one can conclude the following:

Primarily, the global (virtual, quasi stationary) cell reaction must be considered. The half–cell, where the reduction process takes place must be written down on the RIGHT side of the galvanic cell scheme. The half–cell, where the oxidation process occurs must be written down on the LEFT side of the galvanic cell scheme [Lew61].

The EMF is per definition the difference of the electrostatic Galvani potentials at the lead wire connected to the RIGHT-side-electrode with respect to the LEFT one.

$$EMF = \left(\varphi_{Right} - \varphi_{Left}\right)_{quasistationary}$$

If the affinity of the global (virtual, quasi stationary) cell reaction is greater then zero and

$$\left(\varphi_{Right} - \varphi_{Left}\right)_{quasistationary} > 0$$

the recorded EMF data should have a **+ sign**.

In the opposite case, the global (virtual, quasi stationary) cell reaction – in the meaning of Pfaff/Caratheodory infinitesimal expressions – goes in the opposite direction as in the postulated and written down reaction scheme (reaction substrates towards reaction products) known from above.

Besides, the same Stockholm convention is also adopted for the definition of magnitude and sign of half cell potentials of other systems, not only for solid electrolytes but also for water solutions, where the sample–half cell potentials are defined as the EMF of cells: on the left side of the galvanic cell scheme is the reference (the normal hydrogen electrode, NHE) and on the right side the sample electrode.

$$E = \left(\pi_{Right,\ sample} - \pi_{Left,\ NHE\ reference}\right)$$

Notice, that the π (pi) values, as EMF's measurable against the standard NHE, are not equal/ identical with the ϕ(fi) values, which have the physical meaning of the absolute (not measurable) Galvani potentials, each of them connected with the work, which must have be done by incorporating of an elementary charge from infinity into the bulk of another phase.

Implementing that knowledge of the Stockholm sign convention into our practice, we adopt it to both the systems In/In_2O_3 vs. Pb/PbO (oxygen saturated case) and Pt/air vs. Pb/PbO (oxygen saturated case, as well).

In the first case the virtual overall quasi-stationary, reversible reaction of the cell has the stoichiometry:

$$\frac{4}{3} In \quad + \quad 2PbO \quad \rightarrow \quad \frac{2}{3} In_2O_3 \quad + \quad 2Pb \qquad\qquad (\mathrm{charge} = 4\mathrm{F})$$

or equivalent:

$$2\,In \quad + \quad 3PbO \quad \rightarrow \quad In_2O_3 \quad + \quad 3Pb \qquad\qquad (\mathrm{charge} = 6\mathrm{F})$$

REDOX schemes:

The affinity of that unidirectional reaction (formation of indium sesquioxide) is A>0. What is exactly the RED and the OX parts of the global REDOX process here?

The oxidation (anodic process) –the left side of the galvanic cell scheme - is simply:

$$2In \longrightarrow 2In^{3+} + 6\,\bar{e}$$

The reduction (on the cathode) – and accordingly the right side of the galvanic cell scheme - is consequently**:**

$$3Pb^{2+} + 6\,\bar{e} \longrightarrow 3Pb$$

so the galvanic cell scheme becomes the form:

(-) Mo, In, In_2O_3| YSZ | Pb, PbO, SS (+)

Notice, that in this system oxygen ions as such have no influence on the potential, if only the liquid metal is saturated with dissolved oxygen.

Due to the convention adopted, the opposite sign must have been detected in the case of Pt/air reference:

In that first case the virtual overall (=global) quasi-stationary, reversible reaction of the cell has the simply stoichiometry of:

$$2Pb + O_{2(g)} \longrightarrow 2PbO \quad \text{ch arg e} = 4F$$

The affinity of that unidirectional reaction (formation of lead oxide) is A>0. What are exactly the RED and the OX parts of the REDOX couple in this process, which is quite different from the scheme previously discussed – see above?

The oxidation (anodic process) –the left side of the galvanic cell scheme - is simply:

$$2Pb \longrightarrow 2Pb^{2+} + 4\overline{e}$$

The reduction (on the cathode) – and accordingly the right side of the galvanic cell scheme - is consequently:

$$O_2 + 4\overline{e} \longrightarrow 2O^{2-}$$

The equimolar sum of the Pb(II) cations and O(II) anions is thermodynamically equal to the precipitated PbO oxide (1st law, Born–Haber cycle), so that in the end the galvanic cell scheme simplifies to:

(-) SS, Pb, PbO | YSZ | Pt, air pO_2 = 0,21 bar (+)

The main conclusion is here, that after taking care for the same (=identical) cell arrangement/ cell topology with respect to electrical leads etc**.** *In other words if only in both cases the same lead which was connected at one end with the reference electrode was plugged on the opposite side in to the plus input of the Keithley voltmeter,* different signs must have been recorded on the display when using Pt/air and In/In_2O_3 reference (this holds for oxygen saturated LM solutions): The different polarity is an obvious need, derived primarily from the thermochemical data tables/databases.

Notice if both lead wires are of the same kind, the difference of the (non-measurable) absolute Galvani potentials becomes measurable. Since 1953 as the Stockholm Commissions of the I.U.P.A.C. have fixed the invariant sign of electrode potentials in accordance to the work of J.W. Gibbs, erratic signs of thermodynamic functions in tables are excluded, as well. As one compares the numerical values for the temperature dependencies of the Gibbs free enthalpy of oxide formation of PbO (or Bi_2O_3) with that of In_2O_3 and - for comparison – with Na_2O, one can check, that both the straight lines for Bi_2O_3 and PbO are lying in/at the opposite side compared with the Na_2O line with respect to the reference: the In_2O_3 line [Bar73]– consequently, in that case using the same equipment. is it mandatory to obtain EMF readings of opposite sign if only oxygen saturated liquid metal solutions are examined. The same phenomenon, namely the opposite sign of collected EMF data is expected during a comparison of EMF values with respect to the Pt/air reference (positive sign) [Hans77] and/or to the In/In_2O_3 coexistence reference electrode (negative EMF values are expected after the analysis of thermochemical data gathered in tables) [JANAF].

Platinum/air reference electrode

Using data from Ullmann et. al. [Ull73], the following relationship between the resulting EMF and p_{O2}‘ was calculated:

$$E = -0.03369T - 0.021526T \ \ln p'_{O_2}$$

with

$$T \ln p_{O_2'} = \frac{2\,\Delta G^0_{PbO}}{R}$$

and

$$\Delta G^{\circ}_{PbO} = -436850 + 197.991T \quad (\mathrm{J/mol\,O_2})$$

and assuming the activity value of lead in PbBi to be ca. 0.5, the EMF for an oxygen-saturated solution of lead (if PbO is the first precipitating oxide) is as follows:

$$E(mV) = 1136.06 - 0.5762T \quad (K)$$

For unsaturated solutions of oxygen, one has to take into account the solubility of oxygen in PbBi, which is simply correlated with its thermodynamic activity value.

$$a = \frac{c_{[O]}}{c_{[O]\,sat}},$$

where c_0 is the oxygen concentration and c_{0s} the saturation concentration in the liquid metal. With the temperature-dependent solubility data of Orlov et. al.[Orl98]

$$\ln c^{sat}_{O,\,PbBi} = 11.969 - \frac{7827}{T(K)} \quad (\mathrm{wppm\ O})$$

and the above equation, one can calculate the dependency of the EMF on the oxygen concentration in PbBi as:

where $c_{O_{PbBi}}$ is in wppm oxygen (Fig. 2).

$$E(\mathrm{mV}) = 794.09 - 0.06085\mathrm{T} - 0.0431 \ln c_{O,PbBi}$$

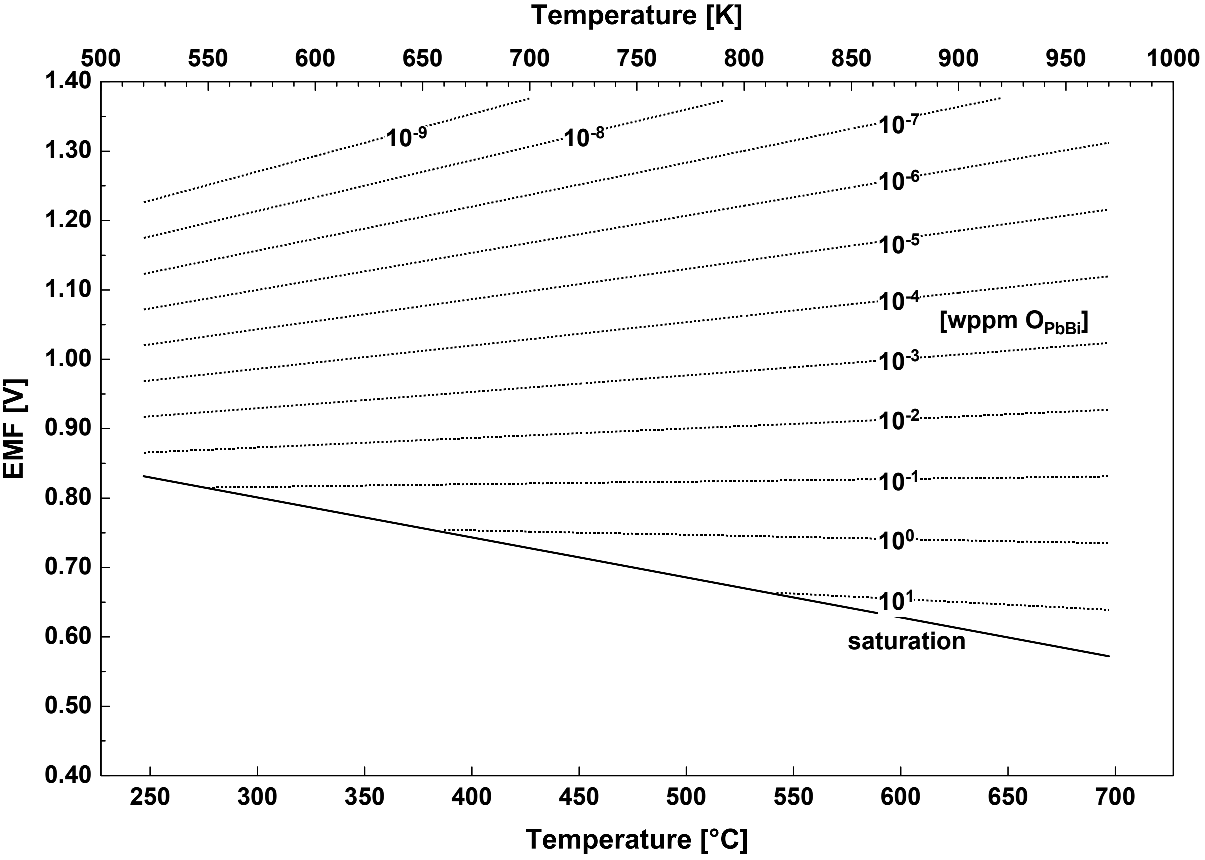

Figure 2: Calculated EMF's for saturated and unsaturated solutions of oxygen in PbBi for an oxygen sensor with Pt/air reference electrode

In/In_2O_3 reference electrode

According to the stoichiometry of the indium sesquioxide formation one obtains (dimension: J/ mol oxide) [And77]:

$$\Delta G^{O}{}_{\mathrm{ref}} = \mathrm{RT}\ln \mathrm{p}_{\mathrm{O}_2}^{\mathrm{ref}} = \frac{2}{3}\Delta_{\mathrm{f}} G^{O} In_2O_3 \ (J/mol\ oxide)$$

In case of oxygen saturated solution in PbBi

$$\Delta G^{O}{}_{\mathrm{sample}} = \mathrm{RT}\ln \mathrm{p}_{\mathrm{O}_2}^{\mathrm{sample}} = 2\Delta_{\mathrm{f}} G^{O} PbO - 2RT\ln a_{Pb}$$

and finally for the case of an oxygen unsaturated solution:

$$\Delta G^{o}{}_{\text{sample}} = \mathrm{RT}\ln \mathrm{p}_{\mathrm{O}_2}^{\text{sample}} = 2\Delta_{\mathrm{f}} G^{o} PbO \; - 2RT\ln a_{Pb} + 2RT\ln \frac{C_O}{C_O^{sat}}$$

The virtual overall reaction of the cell has the stoichiometry:

$$\frac{4}{3} In \quad + \quad 2PbO \quad \rightarrow \quad \frac{2}{3} In_2O_3 \quad + \quad 2Pb \qquad\qquad (\text{charge} = 4\text{F})$$

Using Gibbs free energy of indium oxide formation data (these of lead oxide are given above):

$$\Delta \mathrm{G}^{\circ}_{\mathrm{In_2O_3}} = -618365 + 216.3\mathrm{T} \qquad (\,\mathrm{J/mol\,O_2})$$

the EMF for oxygen saturated Pb can be calculated as:

$$\Delta G_{global} = \Delta G_{right} - \Delta G_{left}$$

$$E^{0} = +\frac{1}{4F}\left(\frac{2}{3}\Delta_{\mathrm{f}} G^{0}_{\mathrm{In_2O_3}} - 2\Delta_{\mathrm{f}} G^{0}_{\mathrm{PbO}}\right)$$

and assuming the activity value of lead in PbBi to be ca. 0.5, the EMF for oxygen saturated PbBi can be calculated in the same manner:

$$\mathrm{E(V)} \; = -0.4703 + 1.7567 \cdot 10^{-5}\mathrm{T}\ (K)$$

In case of unsaturated solutions of oxygen in PbBi, the EMF of the cell can also be estimated

$$E = +\frac{1}{4F}\left(\frac{2}{3}\Delta_{\mathrm{f}} G^{0}_{\mathrm{In_2O_3}} - 2\Delta_{\mathrm{f}} G^{0}_{\mathrm{PbO}} - 2RT\ln\frac{C_O}{C_O^{sat}} + 2RT\ln a_{Pb}\right)$$

by using the temperature-dependent solubility data from Orlov as (Fig. 3):

$$\mathrm{E(V)} = -0.80754 + 5.3324 \cdot 10^{-4}\mathrm{T} - 4.308 \cdot 10^{-5}\mathrm{T}\ \ln c_{\mathrm{O,PbBi}}$$

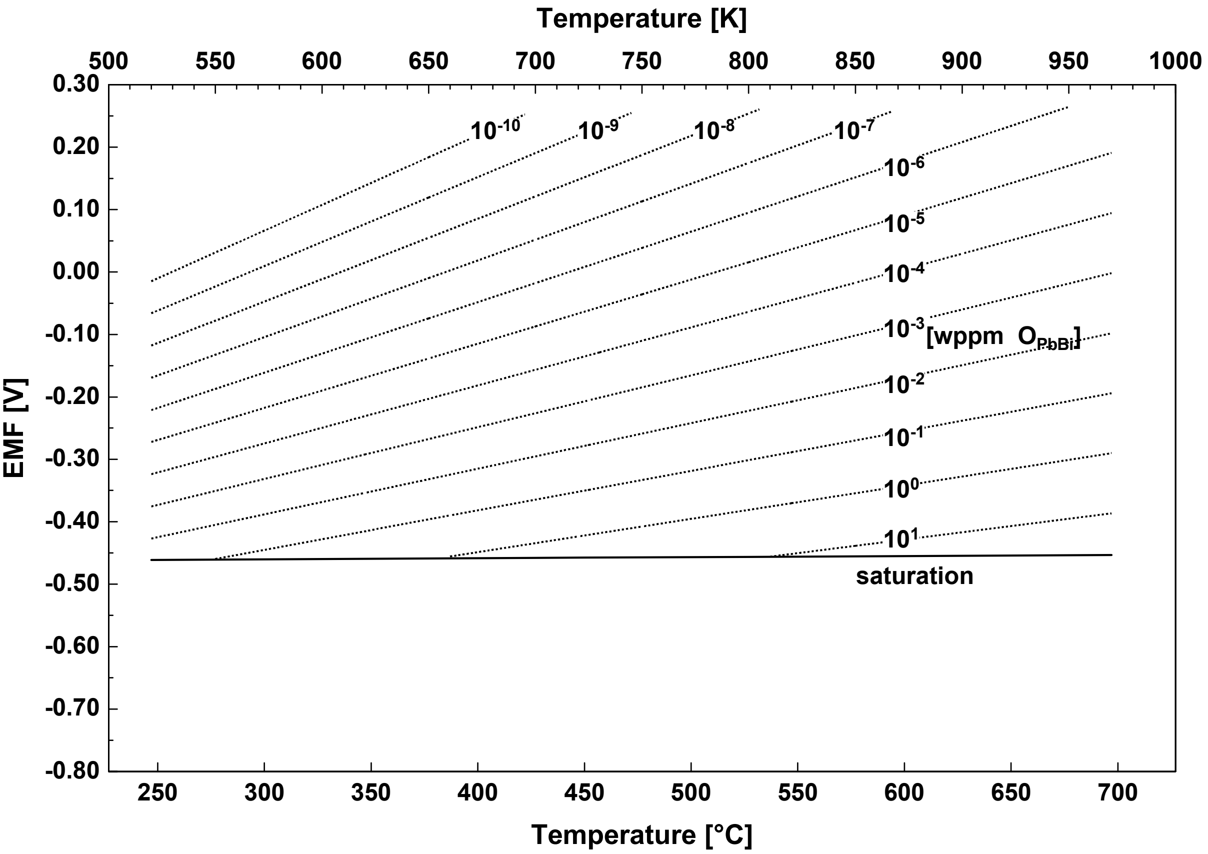

Figure 3: Calculated EMF's for saturated and unsaturated solutions of oxygen in PbBi for an oxygen sensor with In/In_2O_3 reference electrode

Bi/Bi_2O_3 reference electrode

The thermodynamic calculations for the reference system Bi/Bi_2O_3 [Ise79] [Chat73] were fulfilled in accordance to the scheme presented above in case of the In/In_2O_3. There is only one important difference: the reaction path (affinity A>0) is the following:

$$\frac{2}{3}Bi_2O_3 \quad + \quad 2Pb \quad \rightarrow \frac{4}{3}Bi \quad + \quad 2PbO \qquad\qquad (\text{charge} = 4\text{F})$$

The affinity of that unidirectional reaction (formation of lead oxide) is A>0. The RED and the OX parts of the global REDOX process are given below:

The oxidation (anodic process) –the left side of the galvanic cell scheme - is simply:

$$3Pb \longrightarrow 3Pb^{2+} + 6\bar{e}$$

The reduction (on the cathode) – and accordingly the right side of the galvanic cell scheme - is consequently:

$$2Bi^{3+} + 6\bar{e} \longrightarrow 2Bi$$

so the galvanic cell scheme becomes the form**:**

(-) SS, Pb, PbO | YSZ |, Bi, Bi_2O_3, Mo (+)

Notice, that in this system oxygen ions as such have no influence on the potential, if only the liquid metal is saturated with dissolved oxygen.

According to the stoichiometry of the bismuth sesquioxide formation one obtains (dimension: J/ mol oxide):

$$\Delta G^{O}{}_{\mathrm{ref}} = \mathrm{RTlnp}_{\mathrm{O_2}}^{\mathrm{ref}} = \frac{2}{3}\Delta_{\mathrm{f}} G^{O} Bi_2O_3 \ (J/mol\ oxide)$$

In the case of oxygen saturated solution in PbBi

$$\Delta G^{O}{}_{\mathrm{sample}} = \mathrm{RTlnp}_{\mathrm{O_2}}^{\mathrm{sample}} = 2\Delta_{\mathrm{f}} G^{O} PbO - 2RT\ln a_{Pb}$$

and finally for the case of an oxygen unsaturated solution:

$$\Delta G^{O}{}_{\mathrm{sample}} = \mathrm{RTlnp}_{\mathrm{O_2}}^{\mathrm{sample}} = 2\Delta_{\mathrm{f}} G^{O} PbO - 2RT\ln a_{Pb} + 2RT\ln\frac{C_O}{C_O^{sat}}$$

Let us repeat once again: the virtual overall reaction of the cell has the stoichiometry:

$$\frac{2}{3}Bi_2O_3 \quad + \quad 2Pb \quad \rightarrow \frac{4}{3}Bi \quad + \quad 2PbO \qquad\qquad (\mathrm{charge} = 4\mathrm{F})$$

Using Gibbs free energy of bismuth oxide formation data (these of lead oxide are given above):

$$\Delta G^{\circ}_{\mathrm{Bi_2O_3}} = -386790 + 188.95\mathrm{T} \qquad (\mathrm{J/mol\ O_2})$$

the EMF for oxygen saturated PbBi can be calculated as:

$$E^0 = -\frac{1}{4F}\left(\frac{2}{3}\Delta_{\mathrm{f}} G^0_{\mathrm{Bi_2O_3}} - 2\Delta_{\mathrm{f}} G^0_{\mathrm{PbO}}\right)$$

$$\mathrm{E\ (V)} = 0.1297 - 5.33\cdot 10^{-5}\mathrm{T(K)}$$

In case of unsaturated solutions of oxygen in PbBi, the EMF of the cell can also be estimated

$$E = -\frac{1}{4F}\left(\frac{2}{3}\Delta_\mathrm{f} G^0_{\mathrm{Bi_2O_3}} - 2\Delta_\mathrm{f} G^0_{\mathrm{PbO}} - 2RT\ln\frac{C_O}{C_O^{sat}} + 2RT\ln a_{Pb}\right)$$

by using the temperature-dependent solubility data from Orlov as Fig. 4):

$$\mathrm{E(V)} = -0.2075 + 4.62 \cdot 10^{-4}\mathrm{T} - 4.308 \cdot 10^{-5}\mathrm{T}\ln c_{O,PbBi}$$

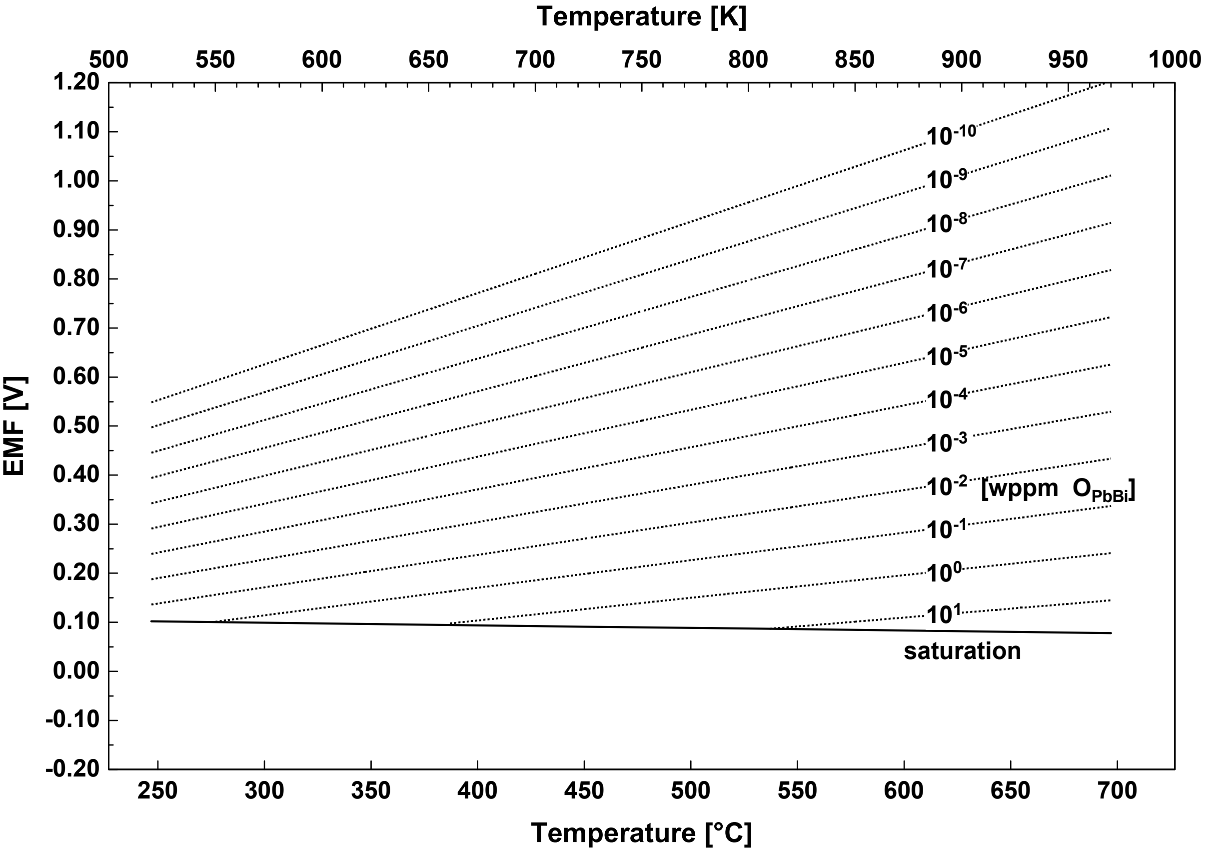

Figure 4: Calculated EMF's for saturated and unsaturated solutions of oxygen in PbBi for an oxygen sensor with Bi/Bi_2O_3 reference electrode

Design of the oxygen meter

The schematic design of the oxygen meter can be seen in Fig. 5. The photograph on the right presents the YSZ tube, the gas in– and outlet valves, the metallic wire and the outer test capsule, filled with PbBi.

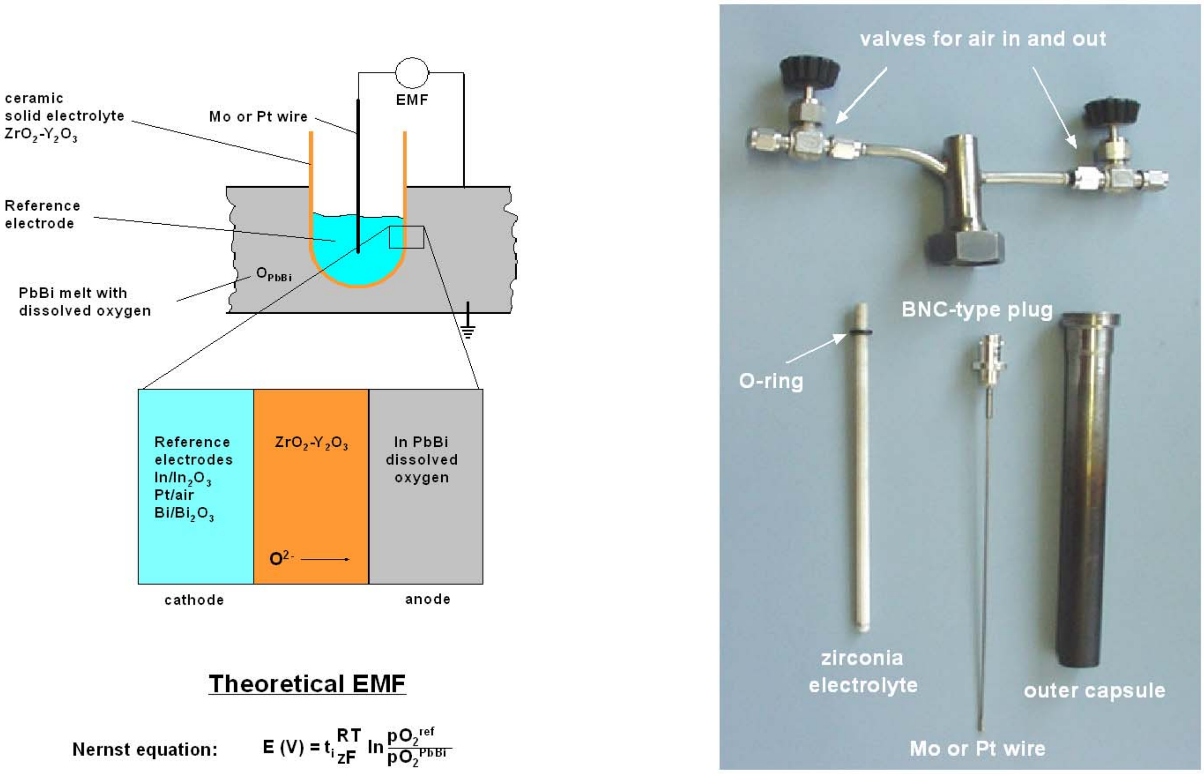

Figure 5: Photograph and schematic view of the electrochemical oxygen probe

The meter was connected to the test capsules with a leak tight Conoseal™ flange. Regardless of the type of reference electrode, only O^{2-} ions are moving through the ceramic solid electrolyte lattice towards the PbBi-side where the oxygen ions are subsequently discharged. Afterwards, the electrons are transported through the connecting wires back to the reference side where oxygen atoms are ionized into the O^{2-} state. The cationic flux and the electronic flux through the ceramics are negligible in that temperature range. The solid electrolyte made of YSZ was supplied by Friatec. The EMF was measured by means of a Keithley high impedance voltmeter; the acquired data were stored on a PC. In case of liquid indium/indium sesquioxide, a 4/1 molar mixture of the powder was used to produce the Nernst mass of the coexistence reference electrode. All oxygen meters were built and prepared for testing in an inert gas argon glove box. Tests were performed in the KOSIMA facility (Fig. 6). This abbreviation stands for: **K**arlsruhe **O**xygen **S**ensors **i**n **M**olten **A**lloys. This easy to handle facility was built and set up in operation with the purpose of simultaneous testing and calibrating of oxygen probes (6 independent test stands) immersed in the melt parallel to gas phase p_{O2} measurements– all this under stagnant conditions.

Figure 6: KOSIMA facility

For comparison and calibration of oxygen sensors, the KOSIMA-AT (advanced technology) facility was designed and constructed (Fig. 7).

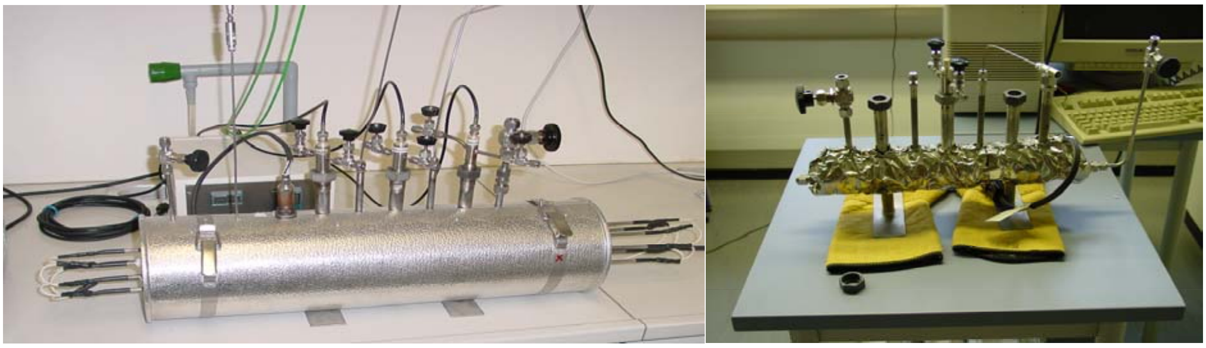

Figure 7: KOSIMA-AT facility with and without the thermal insulation

In Fig. 7 one can see the positions of the oxygen sensors, the thermocouples, the gas inlet and outflow and the metallic heating elements. The temperature was controlled by an inside thermocouple at ± 2°C. For the gas change experiments, dry air for oxidizing and Ar-5%H_2 for reducing conditions could be bubbled through the melt. The software periphery is the same as of the THESYS loop of KALLA lab (KOCOS oxygen control system).

The meter-to-meter performance, EMF selectivity and accuracy of several probes, their specific ranges of EMF reproducibility, long time endurances (defined as the time without change of meter characteristics: EMF– mean values, internal impedances due to absence of plugging or precipitation of non-conducting phases on surface in contact with the LM), further times without change of the root mean squared values of the intrinsic electrochemical EMF-noise, voltage noise sources), resistivities against thermal and mechanical shocks of the probes, failures of the YSZ ceramics of unprotected oxygen probes, shielding (external noise pick–up), probe mounting, sealants are some of the main topics which can be convenient multi-tested here. The loops CORRIDA, THEADES and THESYS will all benefit – immediately – from the information feedback obtained with the help of that new experimental device. The arrangement of many sensors in the same liquid alloy bath, may also help to further development in the oxygen control (KOCOS at KALLA) since the meter EMF responses on local oxygen activity changes (perturbations) either in the gas phase or in the liquid alloy solution can be examined in a simple way at laboratory scale. Although the experimental conditions of a stagnant and a flowing (especially non-isothermal) setup are not the same, EMF drifts appear and "engineering" –correction factors are required, stagnant meter quality tests allow however to point out possible risks of meter employment which are not easily provable (not easy to found) in a large scale loop technology at KALLA.

4 Results and discussion

A large number of different oxygen-meters with platinum/air and In/In_2O_3 reference electrodes were tested in liquid PbBi with varying amounts of dissolved oxygen. The results of the EMF-measurements are compared with the expected dependencies of the EMF on temperature and concentration of oxygen dissolved in PbBi, according to theoretical calculations (Figs. 8, 9).

In both figures the dashed lines represent the theoretical temperature dependency of the EMF for unsaturated solutions of oxygen in the liquid PbBi eutectic corresponding to the indicated oxygen concentrations, given in wppm, whereas the full lines give the EMF–temperature dependency for oxygen saturated PbBi.

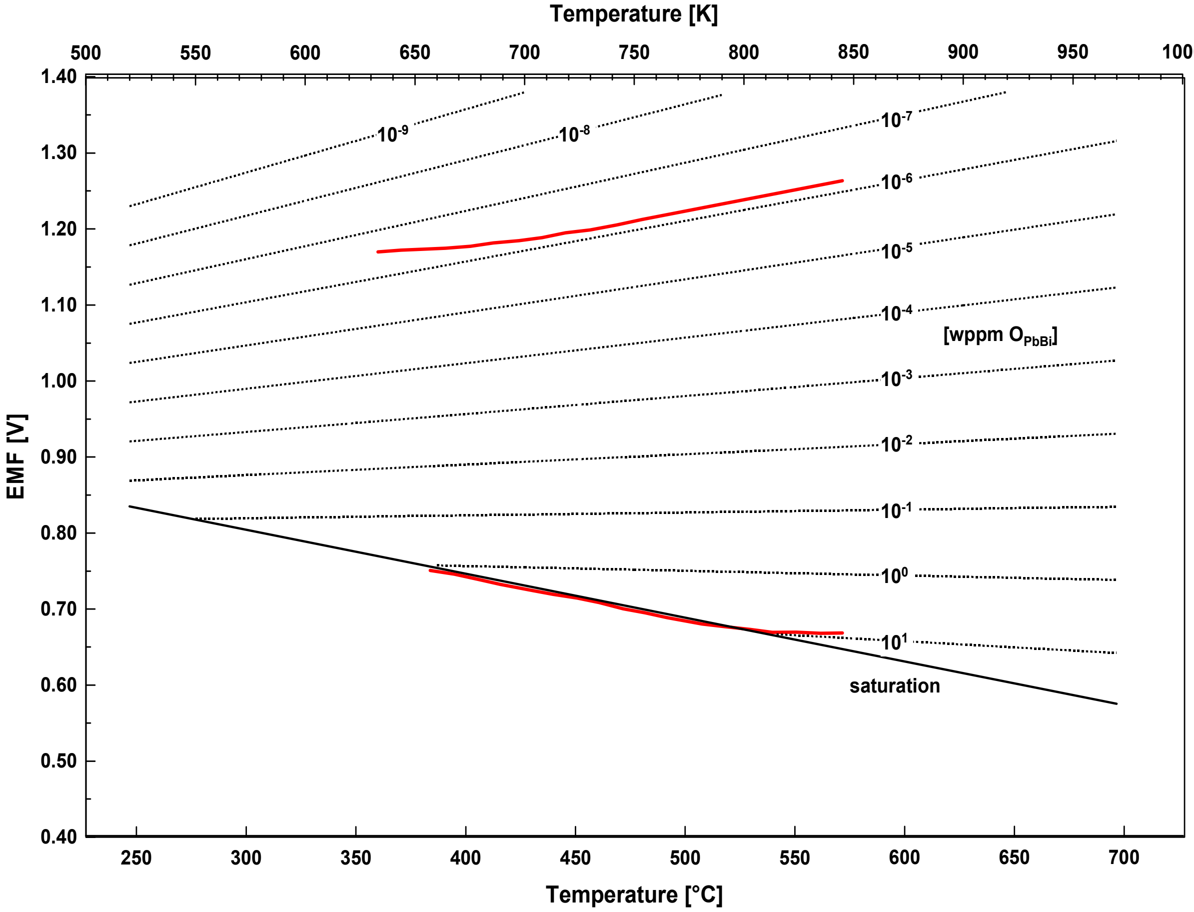

Figure 8: Comparison of calculated and measured EMF's for oxygen sensors with Pt/air reference electrodes

For the Pt/air system (Fig. 8) coming from the unsaturated state (high temperature), the point of coincidence of the cooling curve with the theoretical expected EMF(T) line for the oxygen-saturated state is reached at about 530°C. At lower temperatures both lines are in excellent agreement for the whole temperature range of about 150 degrees down to ca. 370°C. Regarding EMF measurements in strong unsaturated oxygen solutions, the slope and magnitude of the EMF(T) cooling curve coming from 570°C down to 370°C are identical with the expected values for a solution with dissolved oxygen content slightly below 10^{-6} wppm. A very flat ascending deviation to higher EMF–values was observed here only at temperatures below 400°C, according to the knowledge about the ionic transference number (values smaller than one) for YSZ.

In that figure the EMF lies at about 0.7V for the loop-relevant temperatures between 500°C and 550°C. In oxygen saturated PbBi nearly theoretical behavior of the EMF(T) dependency with the same negative slope down to 400°C and a small constant shift in the EMF level is observed. Another test in nearly oxygen-free PbBi solution revealed also the expected EMF dependency – in this case a positive slope of the straight line was detected – as predicted from the theory. However such low real values for the oxygen concentration could not be evaluated analytically up to now. Special analytical methods and equipment have to be developed. In comparison to Pt/air with its very good EMF-response, the dependency on temperature of the EMF readings obtained with meters based on In/In_2O_3 reference system, exhibit a much different behavior (Fig. 9). New experimental data are obtained as an addition to the work done before. These data are compared with new theoretical calculations regarding the sign of cells with such a reference electrode. The measurements showed a sufficient coincidence with the theoretical straight lines even for the oxygen saturated solution: Coming from the unsaturated state (high temperatures) the tangential point of the cooling curve with the theoretical expected EMF(T) line for the oxygen-saturated state is reached by ca. 480°C. An agreement of both lines was only found in a temperature band of about 60 degrees down to 410°C. Measurements in a strong unsaturated oxygen solution exhibited the slope of the EMF(T) cooling curve (straight line) – to be lower as expected from the theory and will not be reported here. The reason for the slope deviation is maybe of kinetic nature (coexistence electrode, transport phenomena between liquid indium and the solid indium sesquioxide).

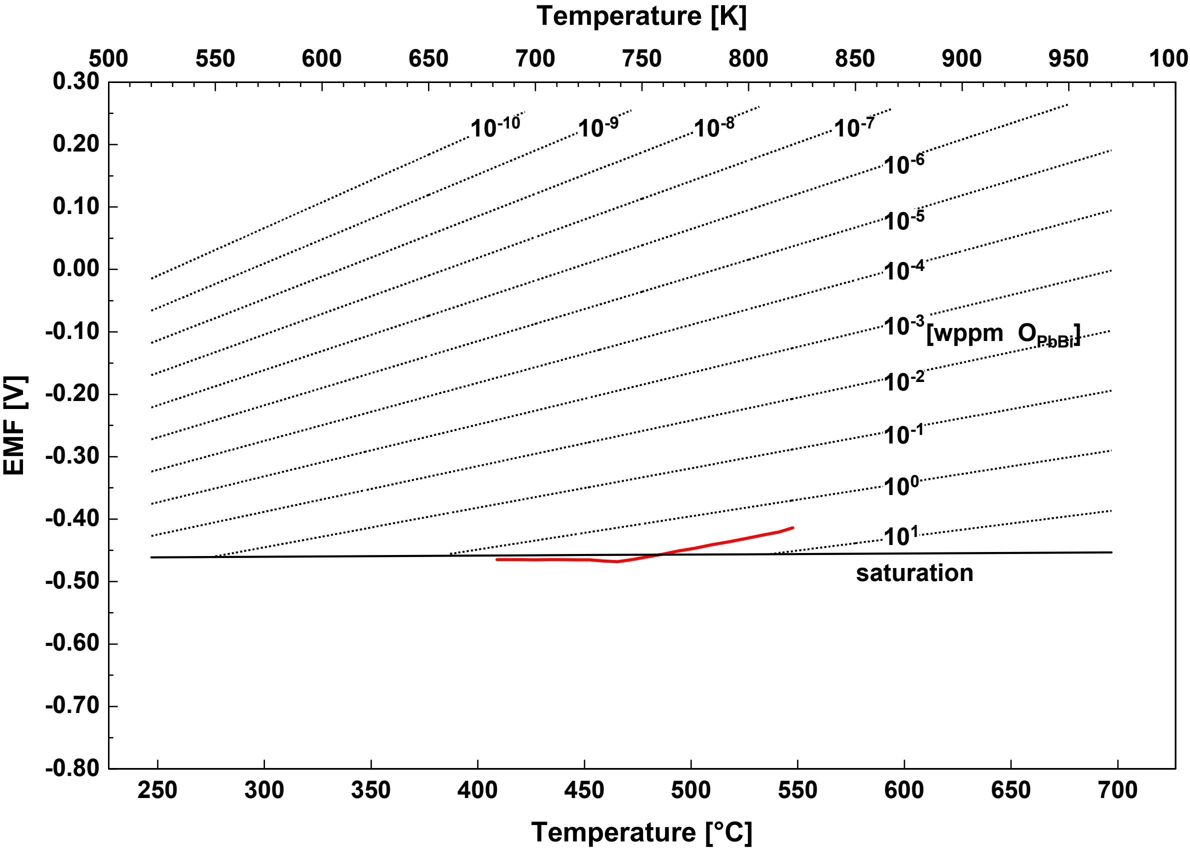

Figure 9: Comparison of calculated and measured EMF's for an oxygen sensor with In/In_2O_3 reference electrode

The general conclusion is, that for the oxygen-saturated probes, the In/In_2O_3 cell gives the best performance at temperatures of about 410-470 °C. The non-linearity at higher temperatures could be a limiting factor for the general use of that electrode in PbBi, but because this non-linearity's are deterministic (reliable data obtained), the observed performance of In/In_2O_3 on temperature seems not to be a serious disadvantage [Kata99]. This non-linearity may also be due to partial electronic conduction of YSZ [Mai94] [Nas74] in connection with liquid indium. Cells, which exhibit even partial irreversible behavior, cannot be linearly calibrated. Fig.10 describes the response of an oxygen meter with Pt/air reference system during bubbling of reducing and oxidizing gases through the PbBi melt. First $Ar+5\%H_2$, then air (p=0.21bar) with subsequent $Ar+5\%H_2$ bubbling was performed. The rate of meter response to oxygen activity changes in the PbBi has been found to be very rapid. Transient response to step changes of the oxygen activity in PbBi exhibit no unusual behavior. The excellent time response of the EMF values after replacing of the $Ar+5\%H_2$ with air bubbling (no time delay) is temperature fluctuations at the beginning of the curve (Fig. 10 lower part) are due to the reaction enthalpies of oxide scales degradation (oxygen removed by $Ar+5\%H_2$) and growth of oxides (air bubbling) respectively, whereas at the end of the curve only the noise level of the control unit was measured.

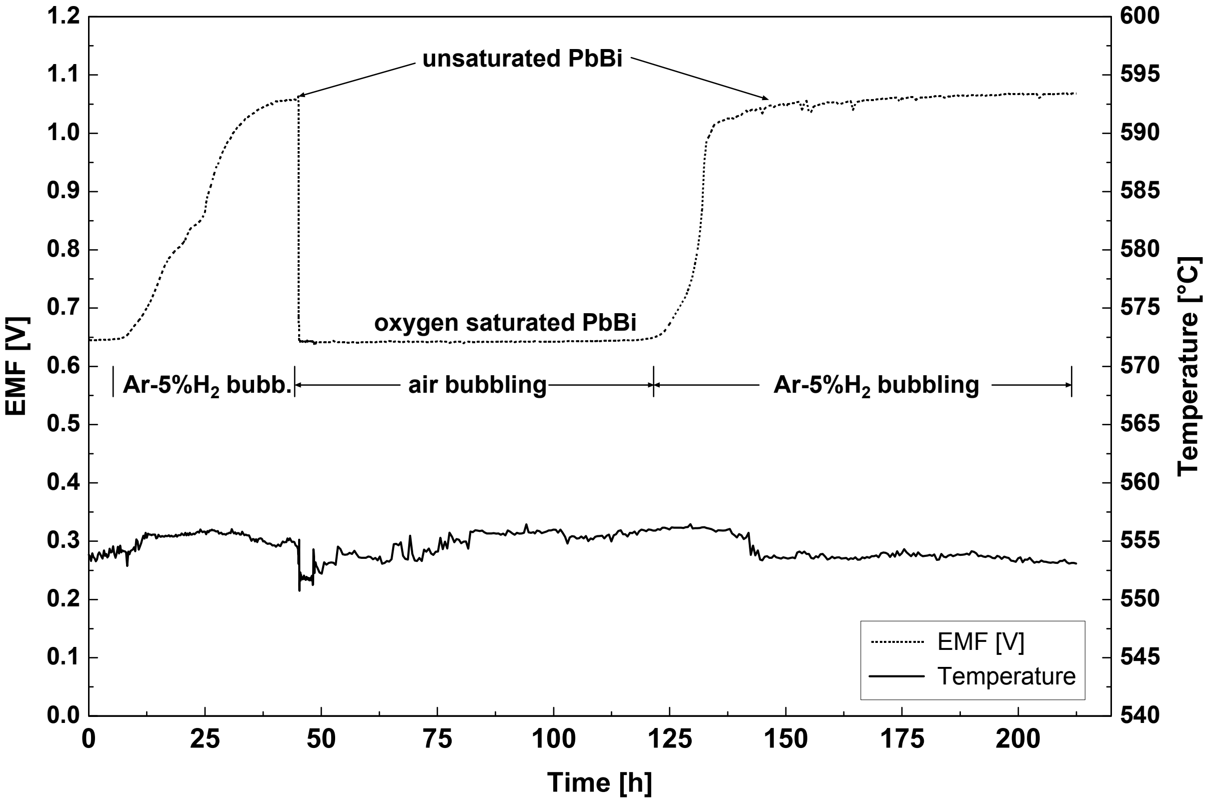

Figure10: Changes of EMF for an oxygen sensor with Pt/air reference electrode due to bubbling of reducing and oxidizing gases through the liquid PbBi

A very similar behavior was seen for the In/In_2O_3 cell at ca 550°C (Fig. 11). Shortly after starting of Ar+5%H_2 bubbling from an intermediate oxygen level, a strong increase of the EMF, corresponding to a decrease in oxygen activity in the PbBi, was measured. After about 10-12 hours, an EMF level of ca. -0.05V was reached, which stayed nearly constant for the rest of the bubbling period.

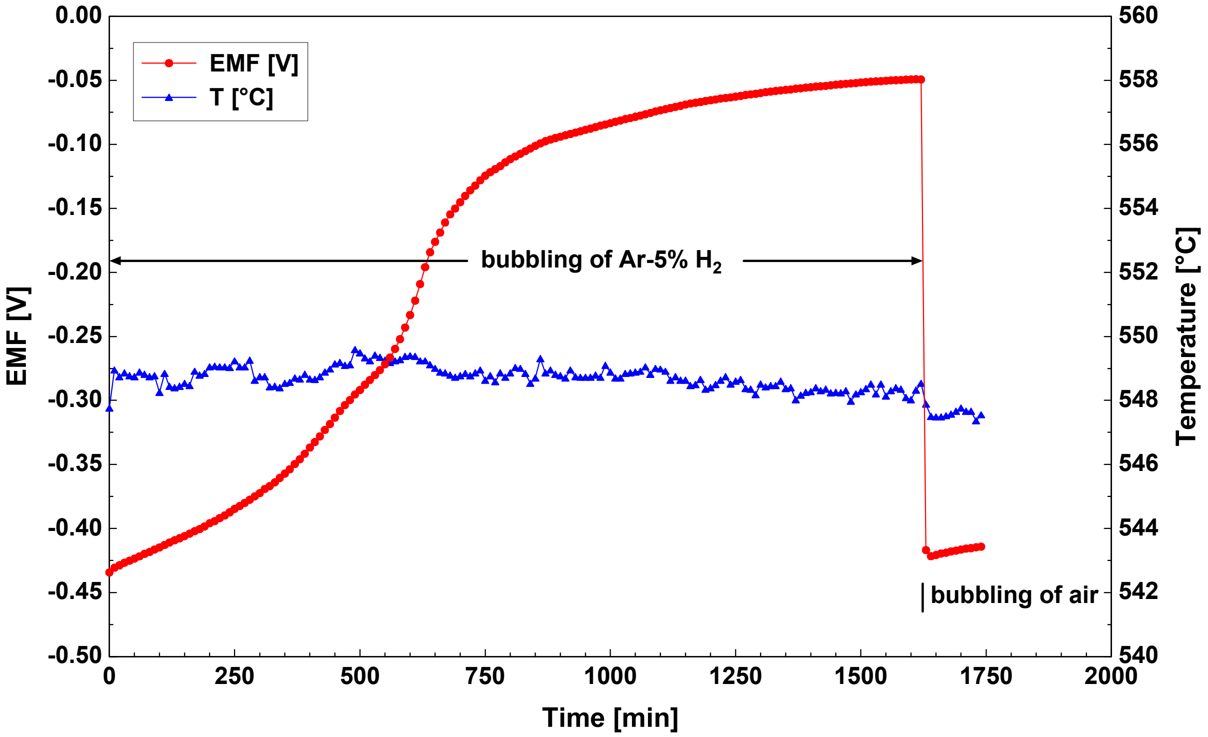

Figure 11: Changes of EMF for a typical cell with In/In_2O_3 reference system due to bubbling of reducing and oxidizing gases through the liquid PbBi

Figure 12 shows the long-term stability of the EMF of a cell with Pt/air reference electrode at 555°C over 1 year of continuous collecting of data during the exposure of the oxygen-meter in the PbBi melt. Regardless of the high level of the EMF during and after the equilibration, the long-time stability within a small range of 75 mV over 12 months without any intermittencies buried in noise seems to be very good. The ascending of the EMF at the beginning of the experiment was due to the chemical reaction of the dissolved oxygen with the steel of the container wall with increasing exposure time to the melt. Figure 8 demonstrates the long-term stability of the EMF of a cell with Pt/air reference electrode at 555°C over a year of continuous collecting data during the immersion of the oxygen meter in the PbBi melt. Regardless of the high level of the EMF during and after the equilibration, the long-time-stability within a small range of some mV over 12 months without any intermittencies or noise seems to be very good.

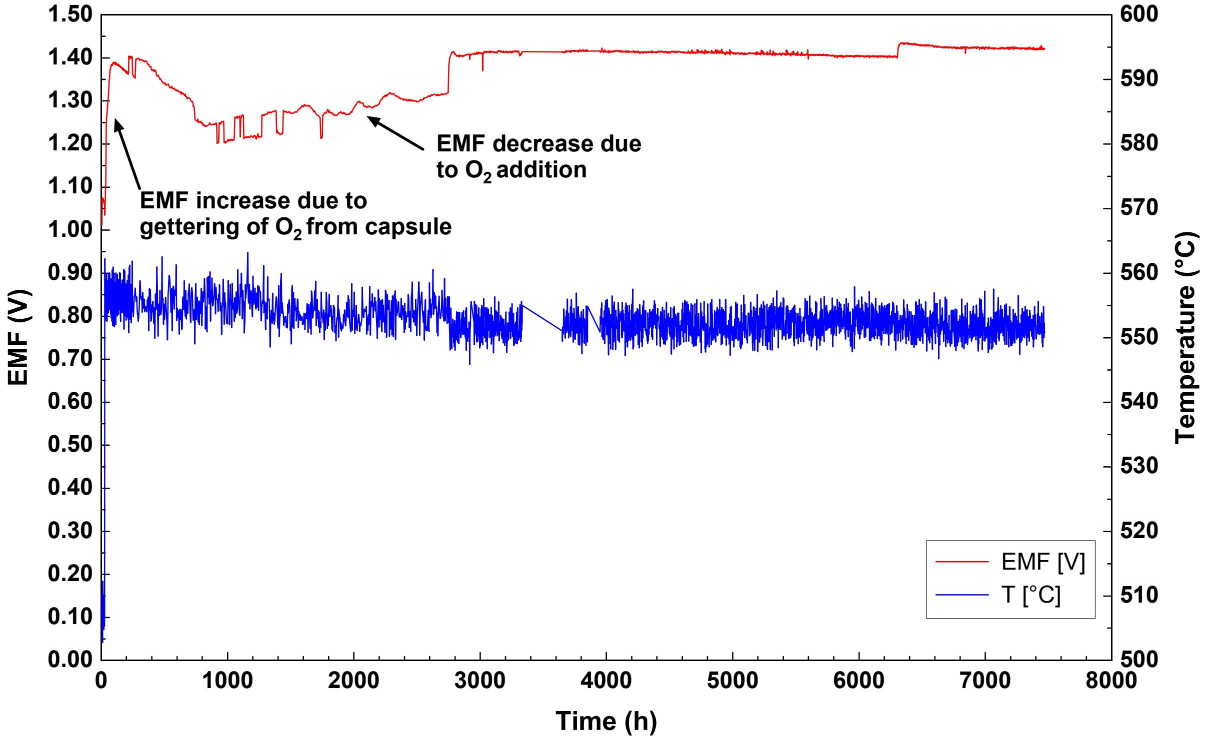

Figure 12: Long-term behavior of EMF at 555°C for a cell with Pt/air reference system

The ascending of the EMF at the beginning of the experiment was due to the chemical reaction of the dissolved oxygen with the steel of the container wall (EMF increase due to gettering of oxygen). The non-linear behavior of the collected EMF–data during the first 2800h of immersion is due to short–time oxygen loss and uptake experiments at the beginning. Soon after the long–time performance of the oxygen probe were the main point of interest. The probe was not subject to any changes for more than 5000h – it is enough to recognize the excellent long time stability of acquired voltage data.

General remarks

To secure correct EMF measurements many precautions must have been taken into account: the cell reaction studied must be reversible, any thermoelectric potentials must be excluded or avoided, at every temperature the cell itself must be allowed to attain equilibrium, and one must be sure that these equilibrium could be reached from both higher and lower temperatures (in some cases it could require many hours). Further precautions of importance are: the solid electrolyte must exhibit (nearly) pure ionic conduction in the whole temperature range examined, secondary electrode reactions are not allowed to take place, id est the EMF is allowed to be generated only by the considered (virtual) overall cell reaction. What depends the metrology to be applied, the requirements are among others: the measurement device (electrometer or voltmeter) must be an instrument of high input impedance (Giga- or

Teraohm), the electrical leads (metallic wires) must be of the same nature at the both ends (right and left) of the cell or temperature dependent correction terms must be subtracted or added as thermoelectric incremental data etc. There is no doubt about this, that Pt/air [Ond95] and In/ In_2O_3 are well known coexistence reference electrodes. We applied them successfully in our laboratory for years by measuring the oxygen activities in liquid sodium so that our measurement equipment, the design and the performance of experiments cannot be a real source of error. The facilities were set up in operation correctly: Many electrochemical probes with the In/In_2O_3 oxide internal reference have been tested at the same time (some of them were carefully sealed, the others – for the sake of comparison – were allowed to remain open to the air). The meter –to - meter performance in both classes was not so good as originally expected.

Measurement of the oxygen activity in flowing PbBi (THESYS loop of KALLA)

Our main objective was to test Pt/air oxygen sensors, developed in the stagnant KOSIMA facility, under dynamic loop conditions. Two of our oxygen sensors were adapted to the THESYS loop of the KALLA lab to measure the oxygen activities in the flowing PbBi before and after the oxygen control chamber (Figs. 13, 14). The oxygen sensors are a part of the oxygen control system KOCOS, which allows the control of the oxygen content in the flowing PbBi by establishing an oxygen partial pressure in the gas phase above the melt via a definite H_2/H_2O ratio. Both sensors should reveal the equilibrium constant of oxygen between the gas and the liquid phase [Wala85].

The EMF values were measured and stored periodically together with data for the H_2/H_2O molar ratio, the dew points of the in- and out coming gas, the oxygen partial pressures in the gas phase and the temperatures of the sensors. The time needed to reach a desired oxygen activity in a PbBi system of a given Reynolds number is an important issue for the operation of large-scale loops. This kinetics was investigated with respect to oxygen uptake or loss in the flowing PbBi melt. A gas with a definite p_{O2} determines the activity of oxygen dissolved in PbBi. To set the desired pO_2 in the gas phase, a mixture of argon carrier gas and Ar+5%H_2 adjusted the H_2 concentration and the needed steam was added by passing the gas through water in a thermostat. The H_2/H_2O ratio (and so the p_{O2} value in the gas phase) was fixed by changing the gas flow of Ar+5% H_2. The gases were flowing through a moisture sensor and then over the PbBi surface of the test stand at a constant (low) loop temperature of ca. 400°C. Further details are given in [Lefh01]. The pO_2 in the outlet gas was measured by two different oxygen probes: an industrial lambda gas phase sensor and the XIROX™ sensor (pre-heated to

750°C). The total gas flow rate (Ar + Ar+5% H_2) was kept constant. Changes in the H_2/H_2O ratio were made stepwise. EMF-measurements were performed until equilibration in each step was reached. Our Pt/air oxygen sensors have been installed in the melt to obtain data about the oxygen activity in the liquid metal and to correlate them with known values of the oxygen partial pressure in the gas phase. The oxygen control was reversible in time and the setting of pO_2 was accurate (exhibited only a small error) but one could only detect relatively high oxygen exchange rates between the phases corresponding to a stepwise change in the H_2/H_2O ratio of about one order of magnitude (Fig. 13). The time response (i.e. the kinetics) of the immersed Pt/air probes was slower than the fast response of both types of gas phase sensors.

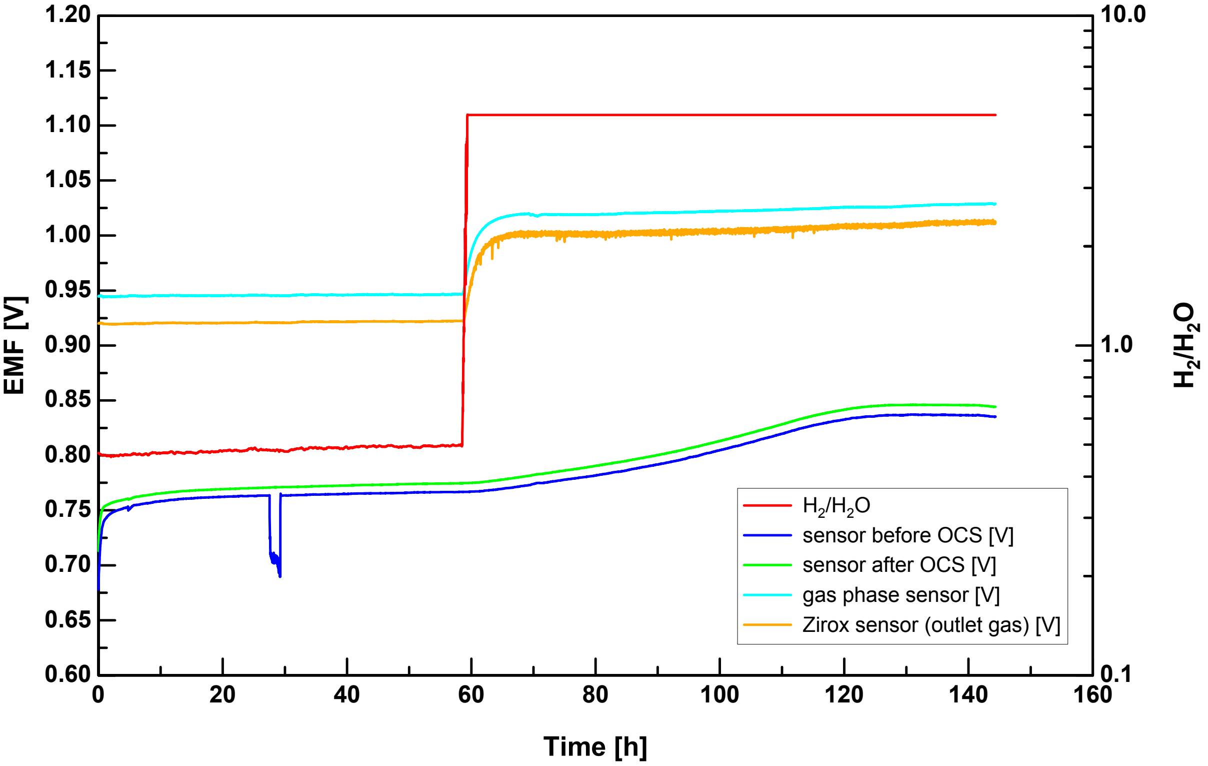

Figure 13: The dynamic behavior of an online Pt/air oxygen probe under loop conditions in the THESYS loop of KALLA (oxygen loss)

A comparison of some experimental results obtained under the PbBi-loop conditions after a stepwise change of the H_2/H_2O ratio in the opposite direction i.e. from dry to wet steam-hydrogen mixture, shows that the amplitude resolution (precision, accuracy) of the time responses obtained in case of the Pt/air oxygen probes compared to the data acquired at the same time from the gas phase sensors, was low probably due to the low operating temperature in the THESYS loop (Fig. 14). Despite of this, the time constants for the EMF response as well as the absolute value of the steady state EMF, before and after the p_{O2} step, were in both cases the same. The KOCOS oxygen control system installed at KALLA is fast enough to allow the investigation of processes, which determine the kinetics of oxygen transport from the gas phase towards the melt for flowing PbBi in dynamic loops.

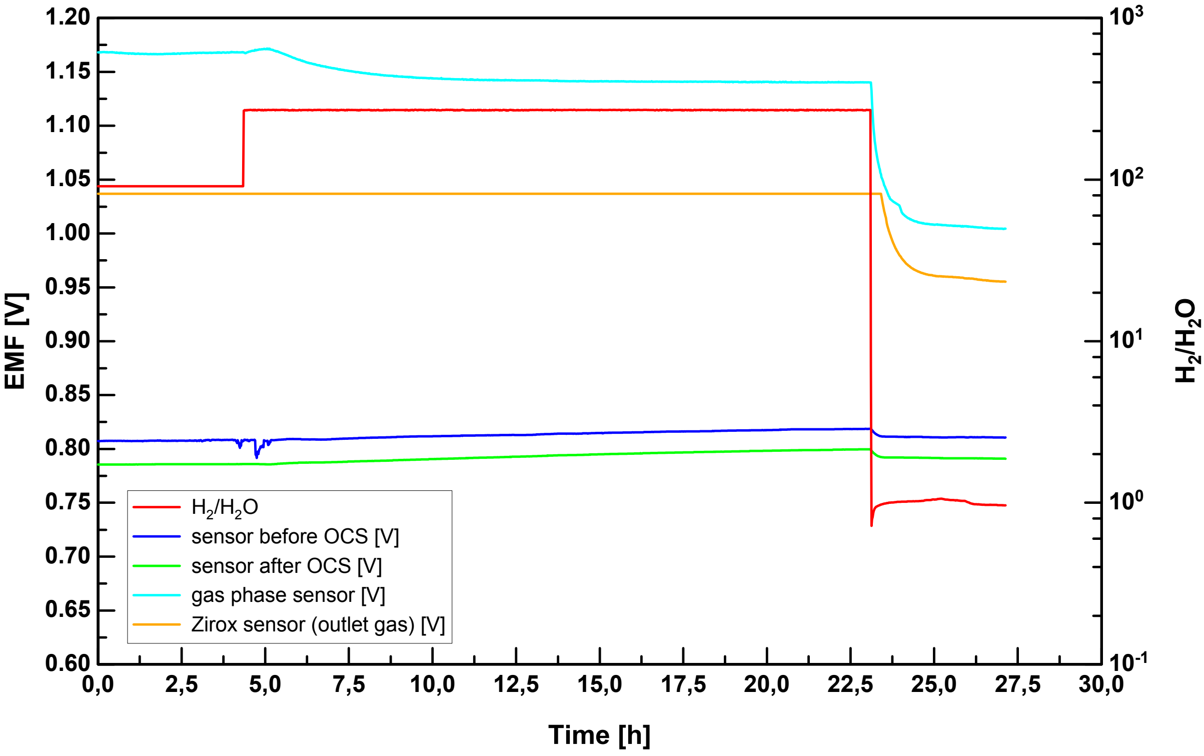

Figure 14: The dynamic behavior of an online Pt/air oxygen probe under loop conditions in the THESYS loop of KALLA (oxygen uptake)

5 Conclusions

Development of on-line electrochemical oxygen sensors is needed for controlling and fixing acceptable trigger levels of the oxygen activity in PbBi under loop conditions. This general issue - including impurity control - is correlated with other main topics, linked strongly to corrosion and stable protection of structural materials in flowing PbBi via dissolved oxygen. For measuring the oxygen activity the relevant thermodynamic data of oxide formation as well as the solubility data have to be considered. We have established a thermodynamic database for 3 types of oxygen probes: i.e. systems with Pt/air, In/In_2O_3 and Bi/Bi_2O_3 reference electrodes. The resulting predictions concerning the theoretical EMF-temperature dependencies, both for oxygen saturated and unsaturated PbBi solutions, were verified and proved by experimental meter calibration. We have compared the performance of these different electrode systems taking into consideration actual thermodynamical data and new formalism in the calculations. The EMF-measurements agreed very well with the expected dependencies of the EMF on temperature and activity of oxygen dissolved in PbBi, according to the theory. One should especially point out, that the experiments with the Pt/air sensors exhibited a lowest operational temperature of about 380°C. Excellent long-term stability of oxygen sensors based on Pt/air reference have been experimentally proved in stagnant tests continued over 1 year of data acquisition. No thermal or mechanic shocks occurred. The bubbling of oxidizing and reducing gases through the lead-bismuth melt did not show any problem during the cell operation. Important development can be reported also in connection with the reliability of the EMF data obtained with our oxygen probes based on the In/In_2O_3 coexistence electrode reference system. Our experimental data indicate that the design of our sensors with In/In_2O_3-reference system would allow us to integrate them in a large scale PbBi-loops, although the lower operational temperature limit is in the range of 420°C. Results with the Bi/Bi_2O_3 system have shown, that they are able to give reliable data, too, as we have expected from oxygen measuring systems utilized successfully over a long time at IPPE Obninsk, Russia.

The first experimental results of oxygen sensors with Pt/air reference system under flowing conditions (THESYS loop) have proven, that they are able to work properly, giving reliable oxygen activity values. Further experimental work must be been done in the field of meter-to-meter performance, calibration (several meters in the same PbBi oxygen solution) as well as in the correlation between the results of EMF measurements under stagnant and flowing PbBi conditions. The future efforts will be focused mainly on the long-term-behavior of oxygen meters under dynamic PbBi flow. The accuracy and sensitivity of the meter response of different types of oxygen probes on changes of oxygen activity in the melt have to be proven and further developed, too.

Acknowledgements

This work has been performed in the framework of the Nuclear Safety Project of the Forschungszentrum Karlsruhe and is supported by the HGF Hermann von Helmholtz Gesellschaft Deutscher Forschungszentren as the Strategy Fund Project 99/16. The support of the HGF for this work is gratefully acknowledged.

6 References

[Add84] C.C. Addison: The chemistry of the liquid alkali metals, John Wiley & Sons, NY (1984), ISBN 0 471 90508 9.

[Agar00] R.C. Agarwala, A.K. Jena: EMF cell set-up and thermodynamic investigation of liquid PbBi alloys at 550°C and 575°C, Z. Metallk., 91 (2000) 5, 366.

[Alc64] C.B. Alcock, T.N. Belford: Propertes thermodynamiques et solubilité de O_2 dans les metaux liquides á partir de mesure de fem avec des electrolytes solides, Trans. Faraday Soc., 60 (1964) 497, 822, in French.

[Alc65] C.B. Alcock, T.N. Belford: Thermodynamics and solubility of oxygen in liquid metals from EMF measurements involving solid electrolytes, tin, Trans. Faraday Soc., 61 (1965) 443.

[Alc68] C.B. Alcock (ed.): Measurements in high temperature systems, Proceedings of a symposium held by the Nuffield Research Group, Imperial College, London (13-14 4.1967), printed: The Institution of Mining and Metallurgy, 44 Portland place, London W1 (1968) (papers of Steele, Alcock, Richardson, Rickert and others).

[Alp70] A.M. Alper: Phase diagrams of refractory materials, Academic Press NY (1970).

[And77] T.J. Anderson, L.F. Donaghey: J. Chem. Thermodynamics, 9 (1977) 617.

[Ani87] S. Anik, M.G. Frohberg: Thermodynamics and solubility of oxygen in liquid BiPb and BiSb alloys, Ber. Bunsen Ges. Phys. Chem., 91 (1987) 8 pp. 790-794.

[Ash77] R.C. Asher, D. Davies, S.A. Beetham: Corr. Sci., 17 (1977) p. 545.

[Bae00] H. Baehr: Thermodynamik, Springer, Berlin (2000) in German.

[Bag93] V.S. Bagotsky: Fundamentals of electrochemistry, Plenum Press NY (1993) in English.

[Bann84] M.J. Bannister: The standard molar Gibbs free energy of formation of PbO. Oxygen concentration cell measurements at low temperatures, J. Chem. Thermodynamics, 16 (1984) (8) pp. 787-792.

[Bar73] I. Barin, O. Knacke: Thermochemical data of pure substances, Springer, Berlin, (1973).

[Bar88] M.G. Barker, J.A. Lees, T. Sample: Proc. of the 4th Int. Conf. on Liquid Metal Engineering and Technology (1988) Avignon, France, 17 – 21 Oct. 1988, Vol. 1, p. 206.

[Barr71] G. Barrow: Physikalische Chemie, Uni-Texte Bd. 1,3, Vieweg (1971) in German.

[Bau99] G. Bauer, M. Salvatores, G. Heusener: The MEGAPIE Initiative– Executive Outline and Status as per November 1999, Paul Scherrer Institut, Würenlingen, Switzerland.

[Bena00] G. Benamati, C. Latge, J.U. Knebel: (2000) Technologies for Lead Alloys, TECLA Project within the 5th Europ. Framework Program, Ref. No. FIS5-(1999)-00308.

[Ber71] W.E. Berry in Corrosion in Nuclear Applications, John Wiley and Sons: The corrosion monograph series, H. H. Uhlig (ed.), New York (1971) p. 308.

[Beth55] A. de Bethune: J.W. Gibbs and the Stockholm convention, J. Electrochem. Soc., (Dec. 1955), pp. 288C-292C.

[Bhat81] H.U. Borgstedt, N.P. Bhat: Calibration of oxygen meters for sodium in a static test and under loop conditions, Nuclear Technology, 52 (1981) pp. 153-161.

[Bhat87] N.P. Bhat, C.K. Mathews: Solubility of oxygen in liquid potassium, J. of less-common Metals, 135 (1987) pp. 285-292.

[Bhat88] N.P. Bhat: unpublished report, Forschungszentrum Karlsruhe (1988).

[Bhat94] N.P. Bhat, H.U. Borgstedt: The application of solid electrolyte oxygen meters in liquid metals used in fission and fusion reactor concepts, Nat. Symp. on Electrochemistry in Nucl. Techn., Kalpakkam, India (1994).

[Bie81] R.M. Biefeld, S.S. White: Phase Diagram Bi_2O_3 – PbO, J. Am. Ceram. Soc. 64 (1981) [3] pp. 182-184.

[Bock59] J.O.M. Bockris, N. Reddy: Electrochemical measurements by the EMF–method, in Modern aspects of electrochemistry, Butterworth, London (1959).

[Boiv69] J.C. Boivin, G.Tridot: L'étude du système oxide de Bi_2O_3–PbO, C.R. Acad. Sci. Paris t. 268 (1969), Serie C, p.1149, in French.

[Boiv74] J.C. Boivin, G.Tridot: Les phases solides du système Bi_2O_3 – PbO, C.R. Acad. Sci. Paris t. 278 (1974), Serie C, p.865, in French.

[Bor71] H.U. Borgstedt: Bestimmung der Sauerstoff-Konzentration in Natrium Kreisläufen, Tagungsbericht, Report in German (1971).

[Bor72] H.U. Borgstedt, Z. Peric: Zur Messung der Sättigungskonzentration des Sauerstoffs im Natrium mit der EMK Methode, Atomwirtschaft-Atomtechnik, (1972) pp. 361-362, in German.

[Bor74a] H.U. Borgstedt, G. Frees: Sauerstoffsonden in Natrium-Kreisläufen im Hinblick auf einen Reaktoreinsatz, Reaktortagung des deutschen Atomforums, Berlin, (2.-5. April 1974), in German.

[Bor84] H.U. Borgstedt: Sauerstoff in flüssigen Alkalimetallen, Fachtagung Gase in Metallen, DGM, Oberursel (1984) pp.117-130, in German.

[Bor90] H.U. Borgstedt, Ch. Adelhelm: Measurement of oxygen solubility in liquid Pb17Li, in Nichtmetalle in Metallen, ed. D. Hirschfeld, DGM Gesellschaft Verlag (1990).

[Bord87] G.A. Bordovskii, A.B. Zarkoi: Polymorphic phase transition in the 5PbO $4Bi_2O_3$ system, Phys. Stat. Solidi A 87 K7 (1987).

[Borg82] H.U. Borgstedt (ed.): Material behavior and physical chemistry in liquid metal systems, Plenum Press, NY (1982) Vol.1 (papers of Gromov, Krasin, Bhat, Periaswami).

[Borg87] H.U. Borgstedt, V. Ganesan: Measurement of oxygen solubility in liquid alkali metals, in: Nichtmetalle in Metallen, D. Hirschfeld (ed.), DGM Gesellschaft (1987).

[Borg87a] H.U. Borgstedt, C.K. Mathews: Applied chemistry of the alkali metals, Plenum Press, NY (1987)

[Chan81] A. Chang: Proc. on techniques for measurement of thermodynamic properties, N.A. Gokcen, L.B. Pankratz (eds.), Bur. Mines Inf. Circular, 8853 (1981) p. 385.

[Chan93] M. Zhang, A. Chang: Stability of an alloy/oxide interface with O^{2-} ions, Acta Metall. Mater., 3 (1993) 41, pp. 739-746.

[Chat73] D. Chaterji, J.V. Smith: Free energy of formation of Bi_2O_3 from EMF measurements, J. Electrochem. Soc., 120 (1973) p. 889.

[Cod72] B. Codron, P. Perrot, G. Tridot: Détermination par mesure de forces électromotrices des propriétés thermodynamiques dans le systéme Pb-Bi-O á l’état liquide, C.R. (=Comptes Rendues) Hebd. Sciences Acad.Sci., No.274 (1972) p. 398, in French.

[Con84] D.S. Conochie. C. Ebiogwu: Oxygen solubility in molten lead, Trans. Inst. Min. Metall, SECT. C 93 (March 1984) pp. 45-48.

[Dar53] L.S. Darken, R.W. Gurry: Physical chemistry of metals, Mc Graw Hill NY, (1953), p.132.

[DECH92] DECHEMA Monographien: Elektrochemische Sensorik, Tutzing (1992) Vol.126 (papers of Göpel, Sandstede, Baucke, Möbius, Gerblinger, Kiesele/Clark, Leonhardt, Wiemhöfer, Jahnke, Rickert, Kaden).

[Dell78] R.M. Dell, A. Hooper, AERE Harwell: Oxygen ion conductors in Solid electrolytes, P. Hagenmuller (ed.), Academic Press NY (1978) pp. 291-312.

[Den71] K. Denbigh: The principles of chemical equilibrium, Cambridge (1971).

[Dond36] Th. de Donder, P. van Rysselberghe: Thermodynamic theory of affinity, Stanford Univ. Press (1936).

[Du95] Y.H. Du, N.M. Sammes, G.A. Tompsett et al.: $4Bi_2O_3$ 5PbO at high temperatures Solid state communications, Vol. 8 (1995) pp. 545-548.

[Du96] Y.H. Du, N.M. Sammes, G.A. Tompsett et al.: Stability of $4Bi_2O_3$ 5PbO Solid state ionics 86-88 (1996) pp. 125-130.

[Du97] Y.H. Du, N.M. Sammes, G.A. Tompsett et al.: The $4Bi_2O_3$ 5PbO fast ion conductor, Solid state ionics, 95 (1997) pp. 183-189.

[Du99] Y.H. Du, N.M. Sammes, G.A. Tompsett et al.: Phase stability of $xBi_2O_3\ yPbO_z\ Sb_2O_3$, Solid state ionics, 117 (1999) pp. 291-299.

[Ell65] R.P. Elliot Constitution of binary alloys, Mc Graw Hill (1965).

[Fir60] L.P. Firsova, A.N. Nesmeyanov: Degree of dissociation and partial vapor pressure of the oxides of Pb Zh. Fiz. Khim., (1960) 34 pp. 2615-2616, in Russian.

[Fis75] W.A. Fischer, D. Janke: Metallurgische Elektrochemie (1975), Springer Verlag; Verlag Stahleisen, Düsseldorf, in German.

[Fitz88] A. Chang, K. Fitzner, M.X. Zhang: Solubility of gases in liquid metals and alloys in Progress in materials science, P. Haasen, T.B. Massalski (editors), Vol. 32 (1988) pp. 97-259.

[Fou76] J. Fouletier: J. Electrochem. Soc., 127 (1976) p. 204.

[Froh76] M.G. Frohberg et al: Standard free energy of formation of Bi_2O_3, Z. phys. Chem. NF ,(1976) Vol. 99 pp. 304-307.

[Froh79] M.G. Frohberg: Activity determination of the oxide system lead (II) oxide bismuth (III), Neue Huette, 24 (1979) pp. 225-227.

[Froh80] M.G. Frohberg: Thermodynamik für Metallurgen und Werkstofftechniker, Verlag f. Grundstoffindustrie, Leipzig (1980), in German.

[Gan85] V. Ganesan, H.U. Borgstedt, J. less-common Metals, 114 (1985) pp. 343-354.

[Geb54] E. Gebhardt, I. Obrowski: The system Pb-PbO, Z. Metallk., Vol. 45 (1954), p.333.

[Gibb31] J.W. Gibbs: Collected works, Vol.1, pp. 55-372, Longmans, NY (1931).

[Good87] J. Goodisman: Electrochemistry - theoretical foundations, Wiley (1987).

[Göp89] W. Göpel, J. Hesse: Sensors, a comprehensive survey, VCH, Vol. 1-9 Basic equations, terminology, (1989-1994) p. 356, Chapter 8.

[Goto72] K.S. Goto, W. Pluschkell in ed. J. Hladik: Physics of electrolytes Vol. 2, Thermodynamics of electrode processes in solid state electrolytes, Academic Press London, NY (1972).

[Gro95] B. F. Gromov, Yu. I. Orlov, P. N. Martynov, K. D. Ivanov, V. A. Gulevski: Physical-chemical principles of lead-bismuth coolant technology, in liquid metal systems, edited by H.U. Borgstedt and G. Frees, Plenum Press (1995) p. 339.

[Gugg49] E.A. Guggenheim: Thermodynamics, North Holland, Amsterdam (1949).

[Haas56] R. Haase: Thermodynamik der Mischphasen, Springer (1956) in German.

[Ham75] C.H. Hamann, W.Vielstich: Electrochemie, Verlag Chemie, Weinheim, Vol. 1 (1975) in German.

[Hans77] R. Hans, K. Dumm: Atomic Energy Review, 15 4 (1977).

[Hau56] K. Hauffe: Oxidation von Metallen und Metallegierungen, Springer, Frankfurt (1956) in German.

[Hau66] K. Hauffe: Reaktionen in und an festen Stoffen, 2nd edition (1966) (with C. Seyfarth), pp. 56-73,123-133, 182 and the literature cited there.

[Heu98] G. Heusener, M. Salvatores: Use of heavy liquid metals: a perspective for critical/ subcritical fast neutron concepts, Heavy Liquid Metals Conference, Obninsk, Russia (1998).

[Hill98] M. Hillert, R. Schmid-Fetzer: Phase equilibria: thermodynamic modeling of CdTe, defect chemistry, J. Electron. Mater. (USA), Vol. 27 (1998) No. 8 pp. 961-971.

[Hla72] J. Hladik (ed.): Physics of electrolytes Vol.2, Thermodynamics of electrode processes in solid state electrolytes, Academic Press, London (1972).

[Hob82] M.R. Hobdell, C.A. Smith: Monitoring dissolved gases in liquid metals, J. Nucl. Mater., 110 (1982) pp. 125-139.

[Hor61] W. Horsley: UKAEA Report AERE-R-3037 (1961).

[IPPE98] Conference on heavy metal coolants in nuclear technology, Obninsk (1998), R. Tsirlin, p. 23, A. Rusanov pp. 49, 50.

[Ise76] B. Isecke, J. Osterwald: On the solubility of oxygen in liquid lead, Erzmetall, (1976) 29 (1) pp. 11-12.

[Ise77] B. Isecke: Dr.-Ing. Thesis, TU Berlin (1977).

[Ise79] B. Isecke, J. Osterwald: Z. phys. Chem. N.F., Vol.115 pp.17-24 (1979).

[JANAF] JANAF Thermochemical Tables, J. Phys. Chem. Ref Data, 14 (1985).

[Kata99] I. Katayama: Japan Patents on In/ dispersed In_2O_3 particles as a perowskite type reference electrode working at 350-550°C in a ZrO_2 oxygen probe (1999).

[Kaz83] I.V. Kazakova, B.M Lepinskich, S.A.Lyamkin: Effect of alloying elements on solubility of oxygen in lead – bismuth melts, UDK 669.4`76-154:541.8
Inst. Metall., Sverdlovsk, USSR.
Deposited Doc. (1983), VINITI pp. 6931-83, 11, , avail. VINITI, in Russian.

[Keith] Keithley 2100 electrometer, Users guide.

[Khar1] Y.A. Kharif et al: Fusibility diagram and pO_2-T diagram of PbO UDC 546.817-31, Inorg. Mater., (1982) p.1213 in English.

[Khar2] Y.A. Kharif et al: Polymorphism of PbO UDC 546.817-31, Inorg. Mater., (1982) p.67 in English

[Khar3] Y.A. Kharif et al: Solubility of Pb in PbO UDC 546.815-31-165, (1982) p.138 in English.

[Khar4] Y.A. Kharif et al: Thermodynamic properties of excess Pb, O in PbO, UDC 546.815-31-165: 541.11, Inorg. Mater., (1982) p.70 in English.

[Kir88] R. Kirchheim in: Progress in materials science (editors P. Haasen, T.B. Massalski),Vol. 32 (1988) pp. 261-325

[Kiu57] K. Kiukolla, C. Wagner: J. Electrochem. Soc., Vol. 104 (1957) pp. 308-316, 379-387.

[Kley97] H. Kleykamp, H. Glasbrenner: Z. Metallkd., 88 (1997) p. 230.

[Kof66] P. Kofstad: High temperature oxidation, J. Wiley & Sons, NY (1966).

[Kom62] K.L. Komarek: in Thermodynamics of nuclear materials , Vienna IAEA (1962) Vol. 1 p. 749.

[Kom73] K.L. Komarek: Z. Metallk., 64 (1973) p. 325.

[Kon99] J. Konys (ed.): Forschungszentrum Karlaruhe - Wissenschaftliche Berichte, FZKA 6389, Minutes of the Workshop on Heavy Liquid Metal Technology (16.-17.9.1999) and the papers presented there

[Kon01] J. Konys, H. Muscher, Z. Voß, O. Wedemeyer: Development of oxygen meters for the use in lead-bismuth, J. Nucl. Mater., 296 (2001) pp. 289-294.

[Kort57] G. Kortüm: Lehrbuch der Elektrochemie, Verlag Chemie, Weinheim (1957) in German.

[Kort66] G. Kortüm: Einführung in die chemische Thermodynamik, Verlag Chemie, Weinheim (1966) in German.

[Kov79] P.W. Kovtunienko: Solubility of oxygen in PbO, Z. fiz. khim., Vol. 53 Nr. 8 pp. 2000-2002 (1979) in Russian.

[Kov81] P.W. Kovtunienko et al: The pO_2 -T- x PbO – diagram, MChTI, Moscow: UDK 541.121:536.7, Inorg. Mat., (1981) pp. 163-164 in Russian.

[Krö56] F.A. Kröger, H.J. Vink: Relations between the concentration of imperfections; in: crystalline solids in solid state physics, Vol.3 Academic Press NY (1956), D. Turnbull (ed.) pp. 307-435.

[Kry74] W.W. Krysko: Solubility of oxygen in liquid lead, Erzmetall, (1974) pp.342-347.

[Kub62] O. Kubaschewski, B.E. Hopkins: Oxidation of metalls and alloys, Butterworth's (1962).

[Kuba58] O. Kubaschewski, E. Evans: Metallurgical thermochemistry, Pergamon Press, London (1958).

[Kudo90] T. Kudo, K. Fueki: Solid State Ionics, VCH (1990).

[Kün94] K. Künstler et al: EMF measurements based on zirconia at lower temperatures, Solid state Phenomena, Volumes 39-40 (1994) pp.255-262.

[Lang62] E. Lange, H. Göhr: Thermodynamische Elektrochemie, Hüthig Verlag (1962) in German.

[Lefh01] C.H. Lefhalm, J. U. Knebel, K. J. Mack: Kinetics of gas phase OCS for stagnant and flowing PbBi systems, J. Nucl. Mater., 296 (2001) pp. 301-304.

[Lev64] E.M. Levin, R.S. Roth: Effect of oxide additions on the polymorphism of Bi_2O_3, J. Research National Bur. Standards, 68A, 2 (1964) pp.189-199 till 206, Part I, II.

[Lew23] G.N. Lewis, M. Randall: Thermodynamics and the free energy of chemical substances (1923), McGraw-Hill, NY.

[Lew61] G.N. Lewis, M. Randall: Thermodynamics (1961), McGraw Hill, K. Pitzer (ed.).

[Lupi72] C.H.P. Lupis: On the thermodynamic formalism of metallic solutions in Sylvan Beer´s Liquid metals chemistry and physics, Marcel Dekker Inc. (1972).

[Mai94] J. Maier: Electrochemical investigation methods of ionic transport properties in solids, Solid State Phenomena, Vol. 39-40 (1994) pp. 35-60.

[Mar97] V. Markov: Corrosion of structural materials in PbBi and Pb, Seminar on the concept of lead-cooled fast reactor, Cadarache (September 22-23, 1997).

[Mas90] T.B. Massalski (ed.): Binary Phase Diagrams, ASM Int. (1990).

[McK74] J.M. McKee: Calibration stability of oxygen meters in liquid sodium, Nuclear technology, Vol. 21 (March 1974).

[Mont95] C. Monty et al: Ionic transport properties of YSZ, Solid State Phenomena, Vol. 41 (1995) pp.103-112.

[Moor73] W.J. Moore, W. Hummel: Physikalische Chemie, de Gruyter, Berlin (1973) in German.

[Mos73] Z. Moser: Thermodynamic properties of liquid lead-bismuth solutions, Z. Metallk., 64 (1973) (1) pp. 40-46.

[Mül00] G. Müller, G. Schumacher, F. Zimmermann: J. Nucl. Mater., 278 (2000) 85.

[Nas74] M.M. Nasrallah, D.L. Douglas: Ionic and electronic Conductivity in YSZ, J. Electrochem. Soc., (Feb. 1974) pp. 255-262.

[Ond95] B. Onderka: EMF measurements of Sb-Te using zirconia sold electrolyte and Pt/air reference Z. Metallk., (1995) pp. 313-318.

[Ond96] B. Onderka: Gibbs free energy of formation for phases related to Eu_2O_3-CuO–BaO, J. of solid state chemistry, 126 (1996) pp. 38-43.

[Ond99] B. Onderka: Gibbs free energy of formation for solid Sm_2CuBaO_5 determined by the EMF method, J. Chem. Thermodyn., 31 (Apr. 1999) pp. 521-536.

[Orl98] Y. I. Orlov: Personal communication (1998).

[Ost65] J. Osterwald: Habil.-Schrift, TU Berlin (1965) in German.

[Ots75] S. Otsuka Z. Kozuka: Diffusivity of oxygen in liquid lead, Metall. Trans., 6B (1975) pp. 389-394.

[Ots79] S. Otsuka Z. Kozuka: Activities of oxygen in liquid Pb by electrochemical measurements, Metall. Trans. B, Vol. 10B (Dec. 1979).

[Ots80] S. Otsuka: EMF measurements in liquid Te, oxygen activity scales; Metall. Trans. 11B; (1980) pp. 119-124.

[Ots81] S. Otsuka, Z. Kozuka: Further study on the activities of oxygen in liquid Pb and Sb by a modified coulometric titration method, Metall. Trans., 12B (3) (1981) pp. 616-620.

[Otto65] E.M. Otto: Pressions de O_2 sur les oxydes de Pb a diverses température, J. Electrochem. Soc., 112, 8 (1965) p. 174C, Resum. Communic., in French

[Otto66] E.M. Otto: Equilibrium pressures of oxygen over oxides of lead, J. Electrochem. Soc., 113 No. 6 (1966) p. 525.

[Patt67] J.W. Patterson, R.A. Rapp: J. Electrochem. Soc., 114 No7 (1967) p. 752.

[Patt71] J.W. Patterson: Conduction domains for solid electrolytes, J. Electrochem. Soc., Vol. 118 (Jul. 1971) p. 1033.

[Per87] G. Periaswami, S.R. Babu, C.K. Mathews: Oxygen-meter in sodium coolants, Kalpakkam Report Nr. IGC-92 (1987).

[Per88] G. Periaswami: Ph.D. Thesis Univ. Madras (1988).

[Pred67] B. Predel: Thermodynamics of the PbBi system, Werkstoffe und Korrosion, (engl. Materials and Corrosion) Bd.58 (1967).

[Pred82] B. Predel (ed.): Heterogene Gleichgewichte, Grundlagen und Anwendungen, Steinkopff Darmstadt (1982) in German.

[Prig54] I. Prigogine, R. Defay: Chemische Thermodynamik, Leipzig (1962), German translation from: Chemical thermodynamics, Longmans, NY (1954).

[Prin66] A. Prince et al.: Phase diagrams and alloy phase equilibria, Elsevier (1966).

[Rama80] A. Ramanarayanan: Limiting factors in measurements using the EMF method; in: solid electrolytes and their applications, C. Subbarao (ed.), Plenum Press, NY (1980) p. 81.

[Rapp63] R.A. Rapp, K.E. Oberg, R. Szwarc: Metall. Trans., 4 (1963) p. 61
R.A. Rapp, K.E. Oberg, R. Szwarc: J. Iron Steel Inst., 210 (1972) p. 359.

[Rapp68] R.A. Rapp: Mixed conduction in solid oxide electrolytes; in: Thermodynamics of nuclear materials, IAEA, Vienna (1968) p. 559.

[Rapp70] R.A. Rapp, D.A. Shores: Solid electrolyte galvanic cells in Rapp (ed.), Techniques of metal research (MR): Physicochemical measurements in metals research, Interscience Publishers, NY (1970).

[Ray71] G. Bandyopadhyay Ray: Kinetics of oxygen dissolution in molten lead, Metallurgical Transactions Vol. 2 (Nov. 1971).

[Ray72] H. Shanker Ray et al: Trans. of the Indian Inst. of Metals (Sept. 1972): Diffusivity of oxygen in molten Pb, Ni/ NiO reference.

[Ric66] H. Rickert, H. Wagner: Chem. Ing. Tech., 38 (1966) p. 6.

[Ric66a] H. Rickert, H. Wagner: Electrochim. Acta, (1966) Vol. 11 p. 83-91.

[Ric69] H. Rickert: Ber. Bunsen Phys. Chem., 67 (1963) p. 621.
H. Rickert: Z. phys Chem N.F., 49 (1966) p. 127.
H. Rickert: Z. phys Chem N.F., 98 (1975) p. 339.
H. Rickert: C. J. Keller J. Inorg. and Nuclear Chem.,31 (1969) pp. 342-360
H. Rickert: Solid State Ionics, 11 (1983-1984) p. 257.
H. Rickert: G. Pajonk Electrochim. Acta, 42 (1997) p. 3167.

[Ric73] H. Rickert: Einführung in die Elektrochemie fester Stoffe, Springer (1973)
in German.

[Ric77] H. Rickert, H. Holzäpfel: Die Naturwissenschaften, 64 Nr. 2 (Feb. 1977).

[Ric78] H. Rickert: Feste Ionenleiter - Grundlagen, Angew. Chem. 90 (1978) pp. 38-48
in German.

[Rich68] C.M. Diaz, F.D. Richardson in: EMF measurements in high temperature systems ed. C.B. Alcock, p. 29, The Inst. Min. Met. London (1968).

[Rich74] F.D. Richardson: Physical chemistry of melts in metallurgy, Vol.1, p. 143, Academic Press Inc. London (1974).

[Rich80] 2nd int. conf. on liquid metal technology in energy production, Richmond, Washington (1980), papers of P.F. Tortorelli, Oak Ridge; M.G. Down, Westinghouse; J.W. Privalov, Dimitrovgrad; R. Thompson, Harwell and others.

[Rie94] I. Riess: Mixed ionic/electronic conductors, Solid State Phenomena, Vol. 39-40 (1994) pp. 89-98.

[Ris98] D. Risold, J.I. Nagata, R.O. Suzuki: Thermodynamic description of the Pb-O-system, J. Phase Equil., 19, 3 (1998) pp. 213-233.

[Roma63] A.J. Romano et al: Thermal convection loops - container materials for Bi and Pb alloys, Upton Lab. BNL-811 (Jul. 1963).

[Rub95] C. Rubbia, J.A. Rubio, S. Buono, F. Carminati: Conceptual design of a fast neutron operated high power energy amplifier, CERN/AT/95-44(ET).

[Rud67] P. S. Rudman et al.: Phase Stability in Metals and Alloys, Mc Graw Hill (1967) Proc. 1st Batelle Colloquium, dedicated to William Hume Rothery.

[Rum80] N.A. Rumbaut: Solvation of some nonmetals in liquid lithium and sodium, Report Centre Etude Energ. Nucl., Mol, Belgium (1980).

[Rum82] N.A. Rumbaut et al: Thermodynamic potential of N, C, O and H in liquid lithium and sodium; in: Material Behavior and Phys. Chem. in Liquid Metal Systems, H.U. Borgstedt (ed.) Plenum Press NY (1982).

[Rum83] N.A. Rumbaut: Ph.D. Thesis, Univ. Leuven, Belgium (1983).

[Rus00] Coordinator: A. Rusanov, Corrosion investigations of 1.4970, 1.4948, Optifer andEM10 steels in liquid Pb, IPPE Obninsk, final report (2000).

[Rus98] A. Rusanov: Stages of Development of Lead-Bismuth as a Coolant for Nuclear Reactors in Russia, Presentation at Forschungszentrum Karlsruhe, IATF (July 7, 1998) Wissenschaftlich-Technische Zusammenarbeit, Abkommen „Korrosionsverhalten von Strukturmaterialien“, Projekt-Nummer RUS-372-98 BMBF (1998).

[Sch73] W. Schottky (with C. Wagner): Thermodynamik, Springer (1973), reprint, in German.

[Schm63] H. Schmalzried: Z. phys. Chem. N.F., 38 (1963) pp. 8-102.

[Schm66] H. Schmalzried in Thermodynamics of nuclear materials, Vienna IAEA (1966) Vol.1 p. 97.

[Schm72] H. Schmalzried: Z. phys. Chem. N.F., 82 (1972) pp. 206-208.

[Schm75] H. Schmalzried: Festkörperreaktionen, Chemie des festen Zustandes, Verlag Chemie, Weinheim (1975) in German.

[Schm85] R. Schmid–Fetzer, A. Chang: CALPHAD, 9 (1985) p. 363.

[Schw65] K. Schwerdtfeger: Acta metall., 13 (1965) pp. 509-515.

[Schw70] K. Schwerdtfeger, E.T. Turkdogan: Equilibria and transport involving gas mixtures; in: R.A. Rapp´s "Physicochemical measurements in metal research" Part one ed. R.F. Bunshah, Intersci. Publishers, NY (1970).

[Skor79] V.V. Skorchelletti: Theoretical electrochemistry, Moscow (1952) in Russian.
V.V. Skorchelletti: Theory of metal corrosion, Jerusalem (1976) in English.

[Ste76] B.C.H. Steele: Solid solution electrodes in critical material problems, C. Stein (ed.), Academic Press, NY (1976) pp.711-728.

[Ste82] H. Steen, O. Grinder: Solubility of oxygen in liquid lead and two lead alloys Scand . J. Metall., 11 (1982) 3 pp. 155-157.

[Stee65] B.C.H. Steele: Thermodynamic studies using cells with solid electrolytes, Ph.D. Thesis, London (1965).

[Stre52] H. Strehlow: Z. Elektrochemie, 56 (1952) p. 827.

[Stub77] V.S. Stubican, R.C.Hink, S.P. Ray: Phase equilibria, ordering ZrO_2-Y_2O_3 J. Am. Ceram. Soc., Vol. 61 No.1-2 (1977).

[Szw72] R. Szwarc, K.E. Oberg, R.A. Rapp: Diffusivity and solubility of oxygen in liquid lead by the EMF method, High Temp. Sci., 4 (1972) pp. 347-356.

[Task79] A. Taskinen: Thermodynamics and solubility of oxygen in liquid Pb Scand. J. Metall., 8 (1979) 4 pp. 185-190.

[Task82] A. Taskinen: Activity coefficient of oxygen in PbBi and PbSb melts Z. Metallk., (1982) 73 (3) pp. 163-168.

[Tay83] R.G. Taylor, R. Thompson: Testing and performance of oxygen meters for use in liquid sodium, J. Nucl. Mater., 115 (1983) pp. 25-38.

[Tol66] G. M. Tolson, A. Taboada: A study of lead and lead-salt corrosion in thermal-convection loops, ORNL-Report TM-1437 (1966).

[Tosh96] G.I. Toshinsky (IPPE Obninsk): Review article: PbBi coolant, 1st int. "white land" chapter conference, St. Petersburg, Russia (4.-7. Feb. 1996).

[Ull73] H. Ullmann, K. Teske, T. Reetz: Kernenergie, 16 (1973) p. 291.

[Vett61] K. Vetter: Elektrochemische Kinetik, Springer, (1961) in German.

[Wag30] C. Wagner: Z. phys. Chem., Abt. B 21 (1930) p. 25.

[Wag52] C. Wagner: Thermodynamics of alloys, Addison-Wesley (1952), English translation of Thermodynamik metallischer Mehrstoffsysteme, in German.

[Wag56] C. Wagner: Oxidation of alloys involving noble metals, J. Electrochem. Soc., (1956) p. 571.

[Wag70] C. Wagner: Introduction to Rapp's Physicochemical measurements in metal research, ed. R.F. Bunshah, Intersci. Publishers, NY (1970).

[Wala85] S.M. Walas: Phase equilibria in chemical engineering, Butterworth, Boston (1985), ISBN 0-409-95162-5.

[Week70] ed. J. Draley, J.R. Weeks: Corrosion by liquid metals, Plenum Press (1970).

[Week71] J.R. Weeks: Brookhaven National Lab, Upton, NY: Nuclear Eng. and Design, 15 (1971) pp. 363-372.

[Week96] J.R. Weeks: Brookhaven National Lab, Upton, NY: Materials compatibility with liquid Bi, Pb, PbBi in solubility driven systems, 1st int. "white land" chapter conference, St. Petersburg, Russia (4.-7. Feb. 1996).

[Weis70] Ch. Weissmantel, W. Forker: Kleine Enzyklopädie Atom, galvanische Zellen (1970) p. 590, VEB BI Leipzig, in German.

[West84] A.R. West: Solid state chemistry and its applications, Wiley (1984).

[Worr66] W.L. Worrell: in: Thermodynamics of nuclear materials, Vienna, IAEA (1966) Vol. 1 pp.131-143.

[Worr73] W.L. Worrell: in: Fast ion transport in solids, Van Gool (ed.), IUPAC, North Holland (1973).

[Worr77] W.L. Worrell: Oxide solid electrolytes in Topics in applied physics, Solid electrolytes, ed. S. Geller, Springer (1977) Vol. 21 pp. 143-167.

[Wri88] H. A. Wriedt: Bull. of Alloy Phase Diagrams, Vol. 9 No. 2 (1988).