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Thermogalvanic measurement of low partial pressures of oxygen with oxygen ion conductors: a disregarded possibility?

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The thermogalvanic e.m.f. of O^{2-} conducting solid oxide cells can be used to detect small electronic contributions to the oxide conductivity, as a function of the ambient O_2 partial pressure. When this contribution is negligible, the thermocell can serve as an 'oxygen gauge'. Gas-tightness of the oxide specimen is not required, in contrast to more conventional (concentration cell) techniques.

List of symbols

E	potential (V)
p	partial pressure (atm)
S	entropy (J K^{-1} $mole^{-1}$)
S^0	standard entropy (at 1 atm)
$\mathbf{S}$	transported entropy
$\bar{S}$	partial (ionic) entropy
Q^*	ionic heat of transport (J $mole^{-1}$)
ϵ	Seebeck coefficient or thermo (galvanic) power (V K^{-1})
R, T, F	usual significance

In a current investigation on O^{2-} conducting δ-Bi_2O_3 [1, 2] and a number of its δ-stabilized mixed oxide compounds including Y_2O_3 [3–6] and oxides of rare earth metals (Tb–Lu), thermogalvanic Seebeck coefficients were measured with cells of the type:

$$\underset{(T+\Delta T)}{O_2 + N_2}, \mathrm{Pt}|\delta\text{-}(Bi_2O_3)_{1-x}(M_2O_3)_x|\mathrm{Pt}, \underset{(T)}{O_2 + N_2}. \qquad (1)$$

The experimental set-up has been described earlier [7] and a more detailed account will be published elsewhere [8]. Some typical results are shown in Figs. 1 and 2, referring to pure δ-Bi_2O_3 and the $(Y_2O_3)_{0.30}$ compound, respectively. Slowly flowing O_2/N_2 mixtures of various O_2 partial pressures were led through the cells. As expected from entropy considerations and similar to various ZrO_2–CaO–Y_2O_3 systems [9, 10], all Seebeck coefficients in the O_2 partial pressure range 1–10^{-4} atm are negative (hotter electrode has more negative potential). For an assumed transport number $t(O^{2-}) = 1$, i.e., no electronic conduction and absence of Sôret effects in the mixed oxide, the Seebeck coefficient for the reversible electrode reaction:

$$1/2\ O_2(g) + 2e(\mathrm{Pt}) \rightarrow O^{2-}(s)$$

is given by [9]:

$$\lim_{\Delta T \to 0} \Delta E/\Delta T = \epsilon(O_2/O^{2-}) = (1/F)\,[-\tfrac{1}{4}S^0(O_2) + \tfrac{1}{4}R\ln p(O_2) - \mathbf{S}(e, \mathrm{Pt}) + \tfrac{1}{2}\bar{S}(O^{2-}) + Q^*(O^{2-})/2T] \qquad (2)$$

This can be written as:

$$\epsilon(O_2/O^{2-}) = \epsilon^0(T) + 2.303\,R/4F \log p(O_2) \qquad (3)$$

where $\epsilon^0(T)$ includes all temperature-dependent terms in Equation 2. Briefly summarized, except for the heat of transport term, the other terms are either known from tabulations [$S^0(O_2)$, $\mathbf{S}$(e, Pt)] [11, 12] or can be estimated [$\bar{S}(O^{2-})$] using entropy data for the oxides in question and accounting for cationic and anionic mass ratios, compare Pitzer's approach [13]. Thus the kinetically important heat of transport $Q^*(O^{2-})$ can, in principle, be found from the observed $\epsilon^0(T)$, e.g.

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by plotting $\epsilon^0(T)$ versus $1/T$. However, for strongly oxygen deficient lattices such as the stabilized zirconias and thorias, and correspondingly for some cationic (Ag^+) 'superconductors', Q^*(ion) is very small. Accordingly, in these cases $\epsilon^0(T)$ has been found to be almost constant in the relevant (ionic) T range [9, 10, 14, 15]. The present data confirm this fact. In view of experimental errors, uncertainties in estimated partial ionic entropies $\bar{S}$ and the occasional neglect of terms such as S(e, Pt) in various calculations, it seems risky to correlate the small Q^*(ion) data thus found with corresponding activation energies for electrolytic ('superionic') conduction. For the stabilized zirconias, the latter are typically in the order 0.8–1.5 eV [16], in disagreement with the slight temperature dependency of ϵ^0. For δ-Bi_2O_3 (Fig. 1), $Q^*(O^{2-})$ cannot be found with any precision whereas ΔH (ionic conduction) is reasonably well known: 0.30 eV [2].

From a practical viewpoint Equation 3 suggests the use of (oxidic) thermo-galvanic cells as a check on the absence of significant electronic conduction and, if so, their use as a '$p(O_2)$ meter' (oxygen gauge).† The analogy with the conventionally used $p(O_2)$ isothermal concentration cell technique is obvious, but a major advantage of the former method is that gas tightness requirements play no role (except for cell enclosure) and that mechanical properties of the electrolyte are not very critical. Since $\epsilon^0(T) \approx$ constant, accurate ΔT control is the main demand over a wide T range. Dead space of the cell should be small. Limitations for δ-Bi_2O_3 based oxides become clear from Figs. 1 and 2. The pure δ-Bi_2O_3 phase has a rather narrow T range (thermodynamically stable from m.p. 824° C down to δ–α transition at 729° C, with meta-stable extension mostly down to about 650° C), but more disadvantageous is the onset of electronic conduction at $p(O_2) < 2 \times 10^{-3}$ atm.

The yttria-stabilized specimen operates purely 'ionicly' over a much wider T and $p(O_2)$ range. No Sôret effects were observed and response of the e.m.f. to $p(O_2)$ variations was rapid: typically < 15 s. The low temperature limit is most probably caused by failures in reversibility of the Pt electrodes (no efforts were made to optimize their porosity). It is noteworthy that the measured ϵ^0 values ($-285 \pm 5\,\mu V\,K^{-1}$) for both specimens are the same. Based upon a vacant site concentration of 25% (2 O^{2-} unoccupied per 8 sites in the disordered fluorite unit cell), ϵ^0 appears to fall quite reasonably on the extrapolated graph of Pizzini *et al.* [10, Fig. 3], where ϵ^0 for various stabilized zirconias has been plotted as a function of oxygen vacancy concentration. The location of the 'plateaux' in Figs. 1 and 2 is in fair accordance (± 5%) with the $49.6 \log p(O_2)\,\mu V\,K^{-1}$ prediction of Equation 3. It must be noted that in an absolute sense, the lower $p(O_2)$ limit for the δ-Bi_2O_3 based

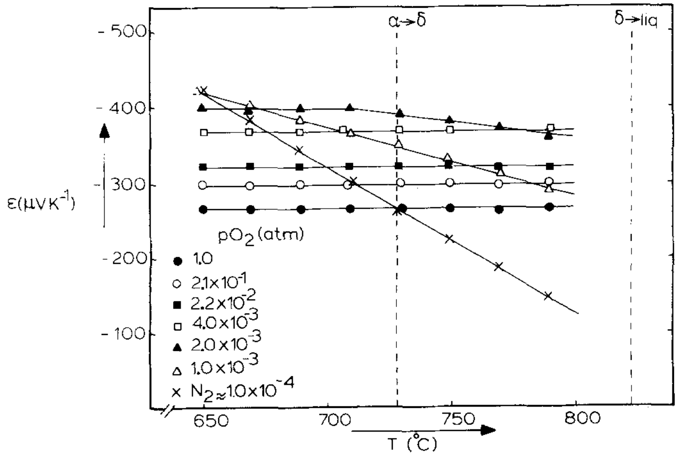

Fig. 1. Corrected Seebeck coefficients $\epsilon(p, T)$ of pure δ-Bi_2O_3 in various $O_2 + N_2$ atmospheres. Thermodynamic transition temperatures are indicated but there is a metastable extension of the δ-phase in cooling direction down to ≈ 650° C. Electronic contributions are observable for $p(O_2) < 2 \times 10^{-3}$ atm. The ϵ values have been corrected for the contribution of $S(e, Pt)/F = 18\,\mu V\,K^{-1}$ (see Equation 2), i.e. measured values are $18\,\mu V\,K^{-1}$ more negative.

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† This suggestion, pertaining to the use of calcia-stabilized zirconias, was made by Pizzini and Bianchi in 1973 [17] but no further developments have been reported.

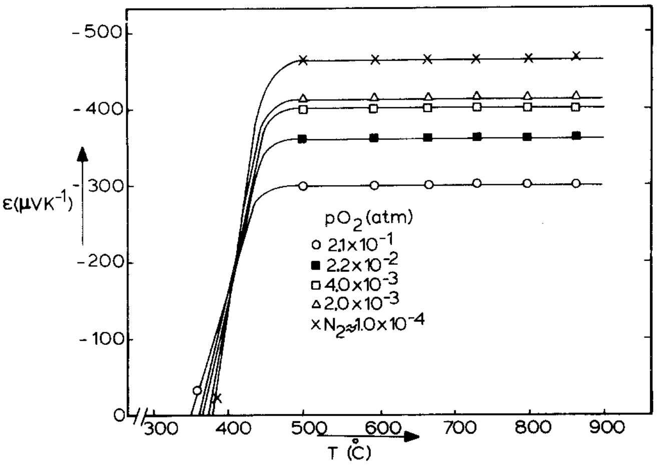

Fig. 2. $\epsilon(p, T)$ of δ-stabilized $(Bi_2O_3)_{0.70}$ $(Y_2O_3)_{0.30}$ in various $O_2 + N_2$ atmospheres. Breakdown of ϵ below 490–450° C is most probably caused by increasing irreversibility of the Pt/O_2 electrodes at decreasing p and T. Here, the possible use as an oxygen guage is obvious. The ϵ values have been corrected for the contribution of $S(e, Pt)/F = 18$ $\mu V\ K^{-1}$ (see Equation 2), i.e. measured values are $18\,\mu V\ K^{-1}$ more negative.

oxides is set by thermodynamic stability of the Bi^{3+} ions with regard to metal formation. From Takahashi's data [6] on the stability of $(Bi_2O_3)_{0.73}$ $(Y_2O_3)_{0.27}$ this is calculated as:

$$\log p(O_2)(\text{atm}) = -20.12 \times 10^3/T + 9.80\ (-13.3 \text{ at } 600^\circ\ C).$$

Above this limit however, either electronic conduction or irreversibility of the electrodes may cause unreliable measurements in flowing gases which, on the other hand, will seldom contain less than 0.1–1 ppm O_2.

Zirconia and thoria-based oxides are stable in reducing atmospheres, too, and the same thermogalvanic technique can be applied for $p(H_2)$ or $p(CO)$ measurement in H_2O or CO_2 buffered mixtures. Finally molten carbonates in a paste form [18] allow thermogalvanic detection and measurement of both $p(O_2)$ and $p(CO_2)$, the relevant expression being:

$$\epsilon(O_2, CO_2) = \epsilon^0 + R/4F \ln p(O_2) + R/2F \ln p(CO_2)$$

where ϵ^0 has an almost constant value of -1.12 mV K^{-1} for various Li–Na–K mixtures in the temperature range 550–800° C, and negligible Sôret effects.

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