THERMOGALVANIC POWER AND FAST ION CONDUCTION IN δ - Bi_2O_3 AND δ -(Bi_2O_3) $_{1-x}$ (R_2O_3) $_x$ WITH $\text{R} = \text{Y}, \text{Tb-Lu}$

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The thermogalvanic power ϵ (Seebeck coefficient) of O^{2-} conducting δ - Bi_2O_3 and δ -(Bi_2O_3) $_{1-x}$ (Y_2O_3) $_x$ has been measured directly as a function of temperature and partial oxygen pressure in N_2 - O_2 mixtures. The ϵ of δ -(Bi_2O_3) $_{0.75}$ (R_2O_3) $_{0.25}$ with $\text{R} = \text{Tb-Lu}$ was indirectly determined using an isothermal concentration cell technique. Except for pure δ - Bi_2O_3 , the heat of transport is much smaller than the activation energy for O^{2-} conduction for all materials. The vibrational freedom of O^{2-} ions in all δ -stabilized materials is reflected in their IR spectra at room temperature. Two prototypes of a thermogalvanic P_{O_2} meter were tested.

1. Introduction

Solid Bi_2O_3 was found to be an ionically conducting material ($t_{\text{O}^{2-}} = 1.0$) in the temperature range 730–824°C (mp) [1]. The specific electrical conductivity σ of this δ phase is $\approx 1 \Omega^{-1} \text{cm}^{-1}$ [1–4]; its structure is (defect) fluorite with two vacant oxygen ion sites per unit cell [5–8]. In heating direction, from room temperature up till the α - δ transition at 730°C, conduction is (mainly) electronic [1]; the σ value of this α phase is about three decades lower than σ of the δ phase [1–4]. The structure of the low-temperature phase is monoclinic [5,7–10]. In cooling direction starting from a temperature above 730°C, the δ phase may (metastably) persist down to 640°C [2–4,11,12] and the sudden, strongly exothermic transition to the α phase is accompanied with a volume decrease of 7% [11,13]. Besides, two other metastable phases may come into existence: the tetragonal β phase [5,7,8,14,15] somewhere between 650 and 330°C [2,4,11,12], and the bcc γ phase [5,7,8,11] somewhere between 640 and 500°C [4,11,12]. Partial replacement of Bi^{3+} ions by other R^{3+} ions ($\text{R} = \text{Y}$ [16–18], Tb-Lu [16,19]) can stabilize the δ phase towards room temperature.

Thermogalvanic measurements yield information about the transport properties of the oxygen ions in the (R_2O_3 -stabilized) δ phase of bismuthsesquioxide. Seebeck

measurements on α -Bi₂O₃ were performed by Mansfield [20] who found that the sign of the thermogalvanic power was positive (+ defined as: hotter electrode has the more positive electric potential), which suggests n-type conductivity. Rao et al. [2] reported a change of sign of the Seebeck coefficient at the $\alpha \rightarrow \delta$ transition of Bi₂O₃. Zolyan and Regel [21] found a (temperature-dependent) negative Seebeck coefficient of pure Bi₂O₃ in the α as well as (what he calls) the β phase and the liquid phase. However, in view of their sample pretreatment (melting of the specimen in a cordundum crucible) we doubt whether he did measurements on pure Bi₂O₃.

In this work results are presented of Seebeck-coefficient measurements on pure δ -Bi₂O₃ and on (Bi₂O₃)_{1-x}(Y₂O₃)_x as a function of temperature and partial oxygen pressure. Partially, these results have been published before [22–24]. The thermoelectric power of δ -(Bi₂O₃)_{0.75}(R₂O₃)_{0.25} with R = Tb–Lu was determined indirectly using an isothermal concentration cell technique. Because these thermogalvanic cells may be used as an oxygen gauge, two prototypes were tested. As was reported before [24] the infrared absorption spectrum of sintered δ -(Bi₂O₃)_{0.70}(Y₂O₃)_{0.30} shows disappearance of discrete absorption peaks as compared with the unreacted mixture in the range 600–200 cm⁻¹. Here we present results of IR spectroscopy on δ -(Bi₂O₃)_{0.75}(R₂O₃)_{0.25} (R = Tb–Lu) and on its (unreacted) components.

2. Theory *

2.1. Thermogalvanic cells

Consider the thermogalvanic cell [25]:

We assume $t_{O^{2-}} = 1$, i.e. no electronical conduction in the electrolyte, and furthermore no chemical diffusion, i.e. absence of Soret effects. The temperature gradient ΔT then will cause a potential difference $\Delta\varphi$; the Seebeck coefficient $\epsilon(T)$ is given by:

$$\epsilon(T) = \lim_{\Delta T \rightarrow 0} (\Delta\varphi/\Delta T) = (1/F) \left(\frac{1}{2} \tilde{S}_{O^{2-}} - \tilde{S}_{e,Pt} - \frac{1}{4} \bar{S}_{O_2} \right), \quad (1)$$

where F is the Faraday constant; $\tilde{S}_{O^{2-}}$ the transported entropy of O²⁻ ions; $\tilde{S}_{e,Pt}$ the transported entropy of electrons in the platinum electrodes and leads; and $\bar{S}_{O_2}$ the partial entropy of oxygen molecules.

From crude entropy considerations (colder electrode tends to become hotter, which is established by “condensation” of O₂ gas to O²⁻ ions) it follows that the colder electrode will have positive sign, i.e. $\epsilon < 0$. $\bar{S}_{O_2}$ may be written as:

$$\bar{S}_{O_2} = S_{O_2}^0 - R \ln P_{O_2}, \quad (2)$$

* See also list of symbols in appendix I.

where $S_{O_2}^0$ is the standard entropy of O₂(g) and P_{O_2} the (partial) pressure of O₂(g). Furthermore, $\tilde{S}_{O^{2-}}$ may be written as:

$$\tilde{S}_{O^{2-}} = Q_{O^{2-}}^*/T + \bar{S}_{O^{2-}}, \quad (3)$$

where $Q_{O^{2-}}^*$ is the heat of transport, and $\bar{S}_{O^{2-}}$ the partial entropy of oxygen ions, which is composed of the partial entropies of vibration and configuration of the O²⁻ ions in the lattice.

By combining expressions (2) and (3) into (1) we find:

$$\epsilon(T) = (1/F)(-\frac{1}{4}S_{O_2}^0 + \frac{1}{4}R \ln P_{O_2} - \tilde{S}_{e,Pt} + \frac{1}{2}\bar{S}_{O^{2-}} + \frac{1}{2}Q^*/T), \quad (4)$$

which may be written as:

$$\epsilon(T) = [\epsilon^0(T) + 49.60 \log P_{O_2}(\text{atm})] \mu\text{V K}^{-1}. \quad (5)$$

$\bar{S}_{O^{2-}}$ cannot be found directly, but an estimated value can be found from the (tabulated) entropy of the oxide itself, taking into account the ratio of cationic and anionic mass (cf. Pitzer's approach [26]):

$$\bar{S}_{O^{2-}} = \frac{1}{2}S^0(\delta\text{-Bi}_2\text{O}_3) - \frac{3}{5}R \ln(M_{\text{Bi}}/M_{\text{O}}), \quad (6)$$

where M is the atomic mass.

In a mixed oxide (e.g. $\delta\text{-(Bi}_2\text{O}_3)_{1-x}(\text{R}_2\text{O}_3)_x$), $\bar{S}_{O^{2-}}$ may be estimated by using the method described by Fischer [27]:

$$\bar{S}_{O^{2-}} = (1-x)\bar{S}_{O^{2-}}(1) + x\bar{S}_{O^{2-}}(2), \quad (7)$$

where $\bar{S}_{O^{2-}}(1)$ and $\bar{S}_{O^{2-}}(2)$ refer to eq. (6), applied to $\delta\text{-Bi}_2\text{O}_3$ and $\delta\text{-R}_2\text{O}_3$ (which is R_2O_3 , with a hypothetical structure of $\delta\text{-Bi}_2\text{O}_3$, i.e. (defect) fluorite), respectively. Numerical values of $S^0(\text{R}_2\text{O}_3)$ and $S_{O_2}^0$ as a function of temperature can be found in tabulations [28]; the α - to $\delta\text{-Bi}_2\text{O}_3$ transition entropy at 1002 K is $S_{\text{trans}} = 7.06$ eu [4] and the same value was adopted for the (virtual) transition to a $\delta\text{-R}_2\text{O}_3$ phase from the C-type rare-earth structure. Numerical values of $\tilde{S}_{e,Pt}$ were found in the work of Cusack and Kendall [29].

2.2. Concentration cells

Since direct thermogalvanic measurements are rather time-consuming, the indirect type of isothermal concentration cell measurements can be performed in order to estimate the Seebeck coefficient of $(\text{Bi}_2\text{O}_3)_{0.75}(\text{R}_2\text{O}_3)_{0.25}$ with $\text{R} = \text{Tb-Lu}$. Consider the thermoelectric cell in its initial state:

$$\text{air, Pt} | \delta\text{-(Bi}_2\text{O}_3)_{1-x}(\text{R}_2\text{O}_3)_x | \delta\text{-(Bi}_2\text{O}_3)_{1-x}(\text{R}_2\text{O}_3)_x | \text{Pt, air}, \quad (8)$$

(T) (T+ΔT)

with an initial thermoelectric power $\epsilon_{t=0}(T)$. In the final state these compositions may be different as a result of thermal diffusion (Soret steady state):

$$\text{air, Pt} | \delta\text{-(Bi}_2\text{O}_3)_{1-x'}(\text{R}_2\text{O}_3)_{x'} | \delta\text{-(Bi}_2\text{O}_3)_{1-x''}(\text{R}_2\text{O}_3)_{x''} | \text{Pt, air}, \quad (9)$$

(T) (T + \Delta T)

with a final thermoelectric power $\epsilon_{t \rightarrow \infty}(T)$. Furthermore, consider the isothermal concentration cell with the same concentration, as is the case in (9):

$$\text{air, Pt} | \delta\text{-(Bi}_2\text{O}_3)_{1-x'}(\text{R}_2\text{O}_3)_{x'} | \delta\text{-(Bi}_2\text{O}_3)_{1-x''}(\text{R}_2\text{O}_3)_{x''} | \text{Pt, air}, \quad (10)$$

(T) (T)

with a potential difference $\Delta\epsilon$.

Haase [30] has shown that the potential difference between the cell in its final state (9) and the same cell in its initial state (8) equals the potential of the corresponding isothermal concentration cell when this cell has the same compositions at the electrodes as are present in the final-state thermoelectric cell (10), i.e. $\Delta\epsilon = \epsilon_{t \rightarrow \infty}(T) - \epsilon_{t=0}(T)$. If we only observe very small potential differences for the isothermal concentration cells mentioned above (i.e. $\Delta\epsilon \approx 0$) we may conclude that when applying a temperature difference ΔT across this cell, resulting in the situation described in (9), the thermoelectric power $\epsilon_{t \rightarrow \infty}(T)$ of this cell will have the same value as that of cell (8), i.e. $\epsilon_{t=0}(T)$. Ergo, the Seebeck coefficient of $\delta\text{-(Bi}_2\text{O}_3)_{1-x''}(\text{R}_2\text{O}_3)_{x''}$ will have the same value, as that of $\delta\text{-(Bi}_2\text{O}_3)_{1-x}(\text{R}_2\text{O}_3)_x$. Therefore, if one knows the Seebeck coefficient of $\delta\text{-(Bi}_2\text{O}_3)_{1-x}(\text{R}_2\text{O}_3)_x$ from direct thermogalvanic measurements and finds no (or very small) potential differences when performing measurements on isothermal concentration cells of type (10) the Seebeck coefficient of the material in the left and the right side of this cell should have the same value.

In practice, isothermal concentration cells were used of type:

$$\text{air, Pt} | \delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30} | \delta\text{-(Bi}_2\text{O}_3)_{0.75}(\text{R}_2\text{O}_3)_{0.25} | \text{Pt, air}. \quad (11)$$

(T) (T)

The Seebeck coefficient of $\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ at $P_{\text{O}_2} = 1$ atm is known from direct thermogalvanic measurements (i.e. $\epsilon^0(T) = (270 \pm 15) \mu\text{V K}^{-1}$), in the range 750–1170 K. Our isothermal concentration cell measurements revealed no significant $\Delta\epsilon$ value in all cases. All Seebeck coefficients must therefore have approximately the same value, as that of $\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ i.e. $(270 \pm 15) \mu\text{V K}^{-1}$ and that of pure $\delta\text{-Bi}_2\text{O}_3$, too.

2.3. Models concerning heat of transport

There are two main models to describe the movement of ions in a solid conductor caused by a thermal gradient.

In the “free ion model” described by Rice and Roth [34] the existence of an energy gap, $\epsilon_g(T)$ is postulated in the ion density of states. Conduction occurs via the excitation of ions from localized states at zero energy into a “continuum” state above the gap. This ϵ_g value can be obtained from measurements of the temperature

dependence of the ionic conductivity,

$$E_a = - \frac{\partial(\ln \sigma T)}{\partial(1/kT)} = \epsilon_g(T).$$

From this theory it follows that $\epsilon_g = E_a = ZeTe(T) = Q^*$. This relation, however, only holds for $\epsilon_g \gg kT$. In the (extended) lattice gas model described by Girvin [35] and Pardee and Mahan [36] the potential energy aspects of the problem are emphasized. The ion-ion Coulomb interaction is replaced by nearest-neighbour interaction on the lattice and ionic motion is allowed through a phenomenological hopping term. The kinetic energy and the static part of the background potential are otherwise ignored. This model takes into consideration ion-phonon interaction. In the case of no phonon coupling and conductivity dominated by only one type of defect one has $Q^* = |E_a|$. However, at high temperatures the lattice gas disorders and the conductivity becomes dominated by the phonon coupling. The "homogeneous part" of the thermopower, reflected in Q^*/T , is then no longer correlated with the activation energy for conduction. One now finds $Q^* = E_a - E_b/2$; E_b (the polaron binding energy) $\approx 2kT$. So the basic result of this model yields $Q^* = E_a - kT$. In the case of pure δ -Bi₂O₃ we find Q^* (1000 K) = 0.19 ± 0.03 eV (see section 3), the activation energy for conduction is ≈ 0.30 eV (calculated from results published in ref. [3]), and kT equals 0.09 eV. The free ion model is not applicable, since the condition $\epsilon_g(T) \gg kT$ does not hold here. However, taking into account phonon coupling we do find $Q^* \approx E_a - kT$ here. In the case of (Bi₂O₃)_{0.75}(R₂O₃)_{0.25} with R = Y, Tb-Lu we found Q^* (1000 K) to be of the order of 0.18 ± 0.03 eV. From conductivity measurements we find $E_a \approx 1$ eV in all cases [18,19]. It is clear neither of the two models explain these results.

The activation energy for conduction of (ZrO₂)_{0.88}(CaO)_{0.12} and (ZrO₂)_{0.91}(Y₂O₃)_{0.09} (which are also O²⁻ conducting materials with (defect) fluorite structure) is of the order of 1.5 and 1.0 eV, respectively [34]. Fischer [27] found Q^* (1073 K) values of 0.01 and 0.06 eV, respectively, which means here also is a misfit between observed value and theory. Generally speaking, neither of the two models can account for a relation between Q^* and E_a (with the possible exception of pure δ -Bi₂O₃) in these materials with a large concentration of unoccupied oxygen ion sites. However, one may ascribe the difference between E_a and Q^* to a particularly large value of the polaron binding energy E_b of these materials [19].

3. Experimental results and discussion

3.1. Direct thermocells

Seebeck coefficient measurements on δ -Bi₂O₃ and on δ -(Bi₂O₃)_{1-x}(Y₂O₃)_x were performed directly using the cell:

Fig. 1. Thermoelectric power ϵ of pure δ -Bi₂O₃, corrected for $\epsilon(e, \text{Pt}) \approx 18 \mu\text{V K}^{-1}$, at various partial oxygen pressures.

Fig. 2. Thermoelectric power ϵ of δ -(Bi₂O₃)_{0.70}(Y₂O₃)_{0.30}, corrected for $\epsilon(e, \text{Pt}) \approx 18 \mu\text{V K}^{-1}$, at various oxygen pressures.

Results of direct thermogalvanic measurements; the deviations (σ_s , $\sigma_{\epsilon 0}$) are given in the 90% reliability interval. $\epsilon(T) = [(\epsilon^0(T) \pm \sigma_{\epsilon 0}) + (s \pm \sigma_s) \log P_{O_2} \text{ (atm)}]$ in $\mu V K^{-1}$, cf. eq. (5)

c) Measured at $\approx 650^\circ\text{C}$ (rod-type cell).

Pellets were used here (diameter ≈ 0.8 cm; thickness ≈ 0.5 cm) which were pressed in a stainless steel holder at about 10^8 Pa (before pressing, some stearic acid slurred in acetone was added to the powder to avoid sticking problems). The pellets were heated in air at $\approx 800^\circ\text{C}$ for 60 h and subsequently cooled to room temperature in ≈ 6 h. The pellets were platinum painted (Dégussit Pt-L 42) on one side, and heated in air at 400°C for ≈ 15 min. Pellets were placed in an appropriate quartz cell with a Pt/Pt, 10% Rh thermocouple on both sides of the pill-stack; the Pt leads were also used for emf measurements. The cell was placed in a furnace in a horizontal arrangement; it could be shifted so as to minimize the temperature difference across the

stack. To check accuracy of the measurements a preliminary one was performed on a pill-stack consisting of two pellets of $(\text{Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ prepared from the same batch. The temperature difference did not exceed 0.5°C ; the largest emf measured was 0.3 mV. In the case of $(\text{Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ against pure δ -Bi₂O₃ a temperature difference of 0.25°C was observed; the emf amounted 0.15 mV which confirms results of direct thermocells that both these substances have the same Seebeck coefficient (within experimental error).

Since δ -(Bi₂O₃)_{0.70}(Y₂O₃)_{0.30} has no solid-state phase transition one may extend these measurements towards lower temperatures by using this material as a standard instead of pure δ -Bi₂O₃, i.e. by performing measurements on the isothermal concentration cell:

with $\text{R} = \text{Tb-Lu}$. Actually, in all cases a stable emf was obtained within half an hour; the temperature difference typically was 0.25°C , and never exceeded 0.5°C . The emf measured was of order of 0.1–0.2 mV; in one case only ($\text{R} = \text{Tb}$) it amounted 0.38 mV. Thus, in view of the experimental errors, the potential differences are insignificant. It is important to stress the fact that the reproducibility and accuracy of the experimental data are well within the expected range for much measurements on stacks of solid compacts with relatively large dimensions. At least this isothermal method gives an efficient and quick check on the thermogalvanic power of a great number of materials. The results are gathered in table 2.

3.3. The application as an oxygen gauge

To examine the applicability of a P_{O_2} meter based on the principle of a thermogalvanic cell [see eqs. (4) and (5)] two prototypes were tested. The first model (fig. 3) essentially consisted of electrolyte $(\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30})$ backed onto the inside of an alumina tube. This was established by flowing a slurry of the electrolyte

Fig. 3. "Rigid"-type P_{O_2} meter. (1) Electrolyte: $\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$; (2) Pt paste; (3) electrolyte support (alumina); (4) autostic; (5) alumina tube; (6) araldite; (7) glass tube; (8) asymmetrical wound heating coil; (9) Pt wire; (10) Pt/10% Rh wire. Operating temperature $T = 520^\circ\text{C}$. Temperature difference $\Delta T = 35^\circ\text{C}$. Gas flow $\approx 15 \text{ cm}^3 \text{ min}^{-1}$ (STP).

Table 2
Results of isothermal concentration cell measurements. Positive ΔT signifies $T(1) > T(2)$. Positive ΔV signifies $V(1) < V(2)$

(1) air, Pt δ -Bi ₂ O ₃ δ -Y _{0.30} Pt, air (2)									
T		T		T		T		T	
$T = 750^{\circ}\text{C}$									
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$							
0.25		0.15							
(1) air, Pt δ -Y _{0.30} δ -Y _{0.30} Pt, air (2)									
T		T		T		T		T	
$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$					
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$			
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	
$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$		$\Delta V(\text{mV})$		$\Delta T(^{\circ}\text{C})$	
0.25		0.11		- 0.18		-0.5		0.3	
(1) air, Pt δ -Y _{0.30} δ -R _{0.25} Pt, air (2)									
T		T		T		T		T	
$T = 650^{\circ}\text{C}$		$T = 700^{\circ}\text{C}$		$T = 750^{\circ}\text{C}$		$T = 800^{\circ}\text{C}$		$T = 850^{\circ}\text{C}$	

in water through the alumina tube and then heating the tube for some time at 800°C. This procedure was repeated several times, until there was a uniformly distributed layer of electrolyte on the inside of the tube. The extremities of the backed electrolyte were platinum painted (Dégussit Pt-L 42). The electrolyte tube was placed in the center of a larger alumina tube, and fixed there using self-drying cement (autostick). Two Pt/Pt, 10% Rh thermocouples served for temperature and emf measurements as well.

The other model (fig. 4) consisted of a rod of (Bi₂O₃)_{0.70}(Y₂O₃)_{0.30} (density 88.5% of theoretical value) with a length of ≈ 5 cm and a diameter of ≈ 5 mm. It was placed centrally inside an alumina tube; a Pt wire around the electrolyte rod protected it from contact with the alumina wall. Two Pt/Pt, 10% Rh thermocouples, fitted in alumina tubes, were used both for temperature and emf measurements.

The cells were tested at various oxygen partial pressures (N₂ + O₂ mixtures or CO₂), the "actual" oxygen content was determined with the aid of a commercial oxygen meter (Westinghouse 209-PD C). The flow rate through the test cell typically was 15 cm³/min (at ambient T). In fig. 5 the results of these two cells are plotted as $\epsilon(\mu\text{V K}^{-1})$ versus $\log P_{\text{O}_2}$ (atm); numerical results are given in table 1. The "rigid" cell depicted in fig. 3 operated at a temperature of $\approx 520^\circ\text{C}$; the temperature difference across the electrolyte was about 35°C. Its emf was not stable, particularly at lower (partial) oxygen pressures. The "rod" cell depicted in fig. 4 operated at a temperature of about 650°C; the temperature difference was about 20°C. The emf of this cell was stable, also at lower (partial) oxygen pressures. A constant emf value was reached within a couple of minutes at lower oxygen pressures, and within one minute at higher oxygen pressures. Adding some H₂ to N₂ flowing through the cell resulted in a large, non-stable emf (local reduction of Bi₂O₃), however, when exchanging the atmosphere for nitrogen again the emf quickly reached its original value again. The use of such a cell in an accidentally reducing atmosphere for a short time therefore seems not to be fatal.

Eq. (5) predicts a slope of 49.6 $\mu\text{V K}^{-1}$ for a plot of $\epsilon(T)$ versus $\log P_{\text{O}_2}$ in all cases where $t_{\text{O}_2} = 1$, at any useful T . The results of the tentative P_{O_2} meters based

Fig. 4. "Rod"-type P_{O_2} meter. (1) Electrolyte: δ -(Bi₂O₃)_{0.70}(Y₂O₃)_{0.30}; (2) Pt coil support; (3) Pt paste; (4) outer alumina tube; (5) inner alumina tube; (6) asymmetrically wound heating coil; (7) glass tube; (8) araldite; (9) O-ring; (10) screw-cap; (11) Pt wire; (12) Pt/10% Rh wire. Operating temperature $T = 650^\circ\text{C}$. Temperature difference $\Delta T = 20^\circ\text{C}$. Gas flow $\approx 15 \text{ cm}^3 \text{ min}^{-1}$ (STP).

Fig. 5. Thermoelectric power ϵ as a function of $\log P_{\text{O}_2}$ (atm) of "rigid"-type (upper curve) and "rod"-type oxygen meter, using $\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ electrolyte. Rigid-type cell was operated at 520°C. The rod type at 650°C.

upon the $\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ system show less deviation of this value, than those of the previous measurements shown in figs. 1 and 2 (see table 1). This is probably due to a somewhat better gas tightness precaution in the former case, especially at lower partial oxygen pressures.

In the various experiments $\epsilon^0(T)$ has about the same value within experimental error, except for the results of the "rigid" cell depicted in fig. 3. This might be the result of chemical reaction of the electrolyte with the Al_2O_3 support. In the case of pure $\delta\text{-Bi}_2\text{O}_3$, $\epsilon(T)$ becomes temperature dependent at partial oxygen pressures lower than 4×10^{-3} atm (see fig. 1). With lower oxygen pressure this behaviour becomes more pronounced. This process is most likely caused by an n-type electronic contribution to the conductivity according to $\text{O}_\text{O}^\times \rightarrow \text{V}_\text{O}^\bullet + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}'$. In general, divergence of observed $\epsilon(P_{\text{X}_2})$ values from predicted values based on the assumption that $t_{\text{X}} = 1$ is a very powerful tool to detect small electronic contribution to the (ionic) conductivity mechanism. Because of the insensitivity for gas leakage across the ionic conductor, the thermogalvanic check is by far superior to the rather vulnerable concentration cell technique, in particular at low P_{X_2} values. As can be seen from figs. 2 and 5 this electronic contribution was not observed in the case of $\delta\text{-(Bi}_2\text{O}_3)_{0.70}(\text{Y}_2\text{O}_3)_{0.30}$ which suggests a stronger bonding of oxygen ions in the crystal lattice. This is also reflected in a smaller cell-axis value with higher content of Y_2O_3 [18].

The use of a thermogalvanic P_{O_2} meter offers some advantages as compared with the conventionally used (isothermal) P_{O_2} concentration cell. Since no reference gas is used electrolyte gas tightness problems play a minor role. Furthermore, the mechanical (ceramic) properties of the electrolyte are not very critical (as we experienced, mechanical breakdown of the electrolyte is the major cause of failure of commercial P_{O_2} concentration cells). Using δ -(Bi₂O₃)_{1-x}(R₂O₃)_x as an electrolyte, a P_{O_2} cell (concentration as well as thermogalvanic type) may operate at a much lower temperature (down to 500°C), as compared with cells using CSZ or YSZ which work at temperatures of 800°C. However, such a Bi₂O₃ based cell cannot continuously be used in a reducing atmosphere. As to the thermogalvanic P_{O_2} cell, an accurate ΔT control, next to a small dead space volume, is a main demand. Preferably, an electrolyte should be used with a zero, or very low (temperature-independent) $\epsilon^0(T)$ value [see eq. (5)]. For ZrO₂ based ionic conductors, Pizzini et al. [32] found a linear decrease of the absolute Seebeck coefficient $|\epsilon^0(T)|$ with increasing oxygen vacancy concentration; our results fit quite well on their extrapolated graph (taking a vacant site concentration of 25%). A material with an even lower Seebeck coefficient ϵ^0 (and therefore more appropriate for thermogalvanic cell application) might be (Bi₂O₃)_{0.55}(SrO)_{0.45} (rhombohedral) which has an oxide ion vacant site concentration of 30% [33].

3.4. Data for the heat of transport

From the results for $P_{O_2} = 1$ atm of fig. 1 the heat of transport of O²⁻ ions was calculated to be $Q_{O^{2-}}^* (1000\text{ K}) = 0.19 \pm 0.03$ eV. There are two main sources of uncertainty which cause the relatively large uncertainty value in Q^* . The first one is the inaccuracy of ϵ , as measured, due to the uncertainty of the temperature difference ΔT across the sample. The other one is the coupled uncertainty in $S^0(\text{Bi}_2\text{O}_3)$ and the related value of $\bar{S}_{O^{2-}}$, which can only be found by estimation [cf. eq. (6)]. An uncertainty of 1 eu/equivalent in the entropy values of eq. (4) would cause an uncertainty of ≈ 0.09 eV in Q^* .

In case of a mixed oxide, i.e. δ -(Bi₂O₃)_{1-x}(R₂O₃)_x, an estimation had to be made of the transition entropy of R₂O₃ to a δ -like structure, which was taken equal to the experimental α - δ transition entropy of Bi₂O₃ (i.e. 7.06 eu). In view of the similarity in structure of these ordered C-type rare-earth oxides (bixbyite structure [31]) and the disordered (defect) CaF₂ structure of hypothetical δ -R₂O₃ this estimation may be too high. Due to the “ δ -stabilization effect” of R³⁺ [18] Seebeck measurements (cf. fig. 2) could be performed in much larger temperature range as compared with pure δ -Bi₂O₃. At lower temperatures ($T < 500^\circ\text{C}$) there is a collapse of $\epsilon(T)$ as a result of growing non-reversibility of the Pt/O₂(g) electrodes. From the results of direct thermogalvanic and isothermal concentration cell measurements the heats of transport $Q_{O^{2-}}^* (1000\text{ K})$ were calculated; for all systems examined (R = Tb(65)–Lu(71)) we found $Q_{O^{2-}}^* (1000\text{ K}) = 0.19 \pm 0.03$ eV.

3.5. IR spectra

Infrared absorption spectra (Perkin–Elmer 580B infrared spectrophotometer) were obtained for pelleted samples applying the usual KBr technique. In fig. 6 IR spectra of α - Bi_2O_3 , β - Bi_2O_3 , and δ -(Bi_2O_3)_{0.70}(Y_2O_3)_{0.30} are shown. β - Bi_2O_3 was prepared by a method described by Aurivillius and Malmros [15]: a solution of $\text{Bi}_2(\text{NO}_3)_3$ was rapidly poured into a boiling solution of NaOH, followed by immediate filtration of the precipitate. The washed orange-coloured crystals were identified with the aid of X-ray diffraction (Debye–Scherrer technique, Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$); we found $a = b = 7.72$, and $c = 5.63 \text{ \AA}$, in good accord with the literature [11]. In fig. 7 IR spectra are shown of α - Bi_2O_3 , Yb_2O_3 , and δ -(Bi_2O_3)_{0.75}(Yb_2O_3)_{0.25} which clearly show the absence of discrete absorption peaks in the δ -stabilized material. Fig. 7 is representative for R_2O_3 and δ -(Bi_2O_3)_{0.75}(R_2O_3)_{0.25}

Fig. 6. Infrared adsorption spectra of α - Bi_2O_3 , β - Bi_2O_3 , and δ -(Bi_2O_3)_{0.70}(Y_2O_3)_{0.30}.

Fig. 7. Infrared absorption spectra of $\alpha\text{-Bi}_2\text{O}_3$, Yb_2O_3 , and $\delta\text{-(Bi}_2\text{O}_3)_{0.75}(\text{Yb}_2\text{O}_3)_{0.25}$.

with $R = \text{Y, Tb-Lu}$. Commercial $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ (CSZ) also showed the absence of discrete absorption peaks, as compared with pure ZrO_2 (monoclinic). To investigate whether IR spectroscopy is sensitive to the presence of a second phase of non-stabilized material, we made spectra of $\delta\text{-(Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_{0.25}$, contaminated with 5, 10, and 20 wt. % $\alpha\text{-Bi}_2\text{O}_3$, respectively. Only above 20% $\alpha\text{-Bi}_2\text{O}_3$ small absorption peaks could be observed.

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Appendix I: List of symbols

E_a	activation energy of ionic conduction	eV
E_b	polaron binding energy	eV
F	Faraday's constant	coul equiv. ⁻¹
P	partial pressure of electro-active gas	atm
Q^*	ionic heat of transport	eV
R	gas constant	J mol ⁻¹ K ⁻¹
T	temperature	K (or °C)
k	Boltzmann's constant	eV K ⁻¹
t	time	s
e_g	energy gap	eV
$e(T)$	Seebeck coefficient (T dependent)	V K ⁻¹
$e_{t=0}(T)$	Seebeck coefficient; initial value	V K ⁻¹
$e_{t \rightarrow \infty}(T)$	Seebeck coefficient; final value (Soret steady state)	V K ⁻¹
$e^0(T)$	Seebeck coefficient; standard value at $P = 1$ atm	V K ⁻¹
$\Delta\varphi$	electric potential difference	V
σ	standard deviation (table 1)	
σ	specific conductivity	$\Omega^{-1}\text{cm}^{-1}$
S	entropy (general symbol)	J mol ⁻¹ K ⁻¹
S^0	standard entropy	J mol ⁻¹ K ⁻¹
$\bar{S}$	partial entropy	J mol ⁻¹ K ⁻¹
$\tilde{S}$	transported entropy	J mol ⁻¹ K ⁻¹
Ze	charge of mobile species	

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