

USE OF OXYGEN PROBES IN THE STUDY OF THERMODYNAMIC PROPERTIES OF THE SYSTEM $\text{Na}_2\text{O} - \text{SiO}_2$ AND THE EFFECT OF ELECTRON CONDUCTIVITY OF SOLID ELECTROLYTE ON EMF OF THE CONCENTRATION CELL

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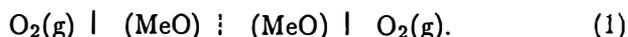
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A study of the thermodynamic properties of the $\text{Na}_2\text{O} - \text{SiO}_2$ binary melt by means of a concentration cell with conversion made use of the oxygen probe with solid ZrO_2 electrolyte stabilized with Y_2O_3 as the reversible electrode. The partial molar values $\Delta G(\text{Na}_2\text{O})$, $\Delta H(\text{Na}_2\text{O})$ and $\Delta S(\text{Na}_2\text{O})$ were determined from the temperature dependence of emf with respect to the reference melt 0.40 (Na_2O) - 0.60 (SiO_2). The values of partial molar enthalpy and entropy show a distinct minimum in the region of 50 molar % of SiO_2 , which is indicative of stability of the Na_2SiO_3 compound. On the basis of measuring the partial pressure of oxygen in the $\text{Na}_2\text{O} - \text{SiO}_2$ melt, a contribution of electron conductivity of the solid electrolyte was established only with the basic system at a high Na_2O content. The error due to electron conductivity of the solid electrolyte was proved to have no effect on the emf value of the concentration cell in view of the experimental error involved in the application of oxygen probes.

INTRODUCTION

Direct high-temperature potentiometry is frequently employed in the study of thermodynamic properties of melts of oxides. However, a number of problems associated with high temperatures, aggressive behaviour of the electrolyte melts, their high viscosity, the occurrence of reduction-oxidation potentials, and other factors are encountered in practical application of the method. The most significant among those problems are related to the selection of high-temperature materials suitable for the construction of electrodes.

Platinum in flowing oxygen, classified as a gas electrode, is the most favourable inert material used in the study of concentration cells with conversion, (1)



However, utilization of the Pt, O_2 electrodes brings about a number of disadvantages. The oxygen at the platinum-melt interface may oxidize some components of the polycrystalline system, and this represents a serious limitation of the suitable measurable systems. The time of establishing equilibrium potential on platinum is of the order of tens of minutes.

From this point of view, oxygen electrodes using a solid electrolyte with ionic conductivity are highly promising. The solid electrolyte in the form of a semi-closed tube containing the reference mixture, the so-called oxygen probe, represents an enclosed system

with a precisely defined partial pressure of oxygen, which does not affect the outer environment and exhibits rapid attainment of equilibrium potential. The advantages of solid electrolytes in the study of type (1) concentration cells were already discussed in [1].

The present paper had the purpose to demonstrate the possibility of using oxygen probes in the study of the thermodynamic properties of oxide melts by means of concentration cells with conversion. A discussion is also presented of the effect of electron conductivity of the solid electrolyte on the value of the electromotive force of the cell.

EXPERIMENTAL

The specimens were prepared from Na_2CO_3 and SiO_2 of A.R. purity. The binary mixtures with various molar ratios of the components were first melted in a Pt crucible at 1573 K in an SF 2 muffle furnace. The Pt crucibles with the materials were then placed in a Tamman furnace in argon atmosphere, and there heated for 3 hours at 1473 K. To remove completely the CO_2 released by decomposition of Na_2CO_3 , argon was blown into the melt through a corundum tube for 1 hour. A perfectly homogeneous binary mixture of the desired composition was then obtained by casting and grinding the glass obtained.

The experiments were carried out in a Tamman resistance furnace with an inner protective tube of Al_2O_3 in inert argon atmosphere. The value of partial pressure of oxygen in the furnace atmosphere amounted to 10^{-9} Pa. The temperature was measured with a PtRh30-PtRh6 thermocouple.

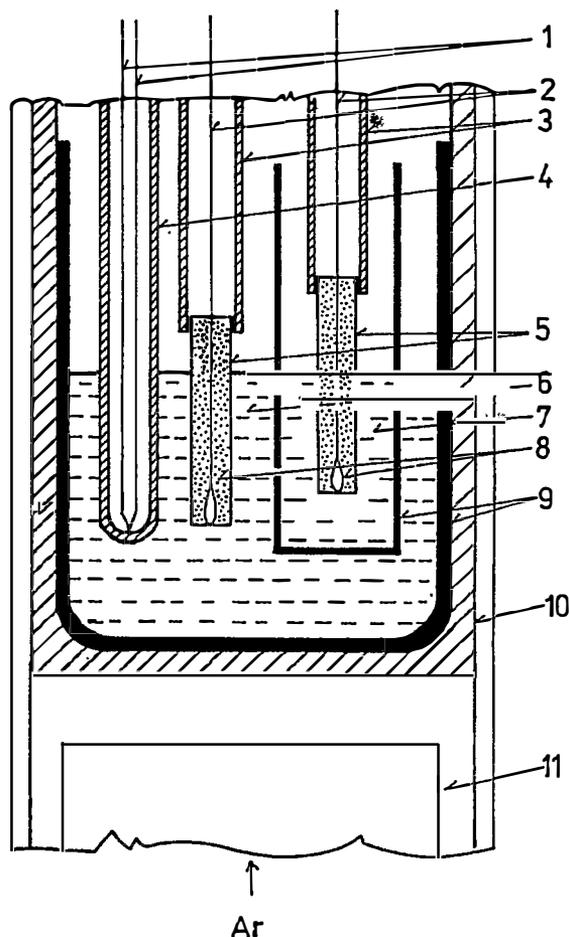
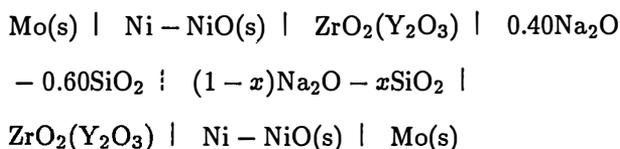
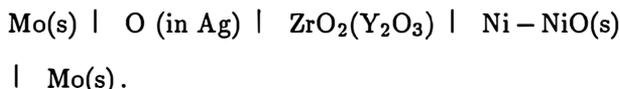


Fig. 1. Experimental arrangement: 1 - thermocouple PtRh6-PtRh30, 2 - Mo wire, 3 - SiO₂ tube, 4 - protective corundum tube, 5 - solid electrolyte ZrO₂(Y₂O₃), 6 - melt being measured, 7 - reference melt, 8 - reference mixture Ni + NiO, 9 - PtRh crucible, 10 - corundum tube, 11 - corundum pad.

The following galvanic cells were investigated:
cell (I)



and cell (II)



The measuring element of cell (I) in Fig. 1 was composed of two platinum-rhodium crucibles. The inner crucible always contained the reference melt having the composition 0.4Na₂O - 0.60SiO₂, and the outer one a melt whose molar content $x(\text{SiO}_2)$ was varied

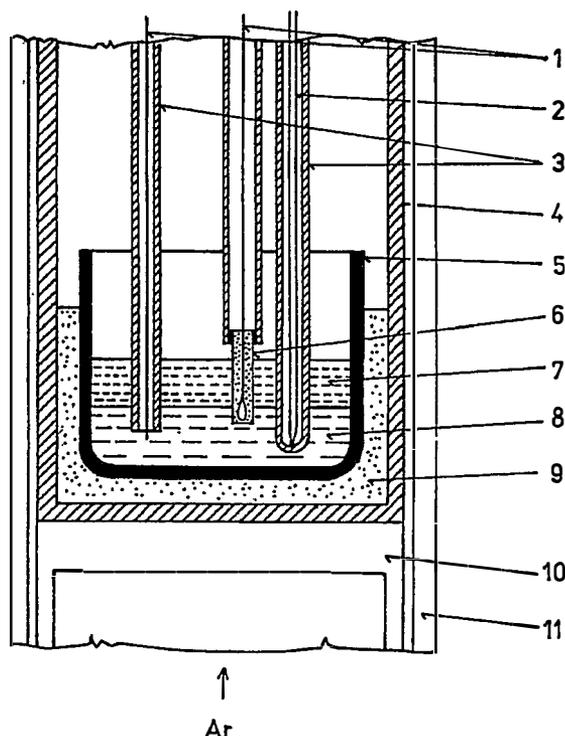


Fig. 2. Experimental arrangement: 1 - Mo wire, 2 - thermocouple PtRh6-PtRh30, 3 - protective corundum tube, 4 - corundum tube, 5 - corundum crucible, 6 - solid electrolyte ZrO₂(Y₂O₃), 7 - oxide melt, 8 - liquid Ag, 9 - Al₂O₃ fill, 10 - corundum pad, 11 - heating graphite tube.

over the range of 0.45 to 0.75. The contact between the two electrolytes was provided by an opening 1mm in diameter in the inner crucible wall. The experiments were carried out over the temperature interval of 1373 to 1573 K.

The arrangement of cell (II) is shown in Fig. 2. A corundum crucible contains 10 g of pure Ag (99.9%) and 10 g of the melt being measured, $(1-x)\text{Na}_2\text{O} - x\text{SiO}_2$, where $x = 0.75, 0.70, 0.60, 0.50$ and 0.45 respectively. To attain perfect attainment of equilibrium of the distribution of oxygen between liquid Ag and the oxide melt, the system was heated for 3 hours at 1473 K.

In the role of oxygen electrodes, use was made of oxygen probes with solid ZrO₂ electrolyte, stabilized with Y₂O₃ (ZrO₂ + 9 mol% Y₂O₃) exhibiting anionic conductivity of O²⁻ ions. The probe consists of a solid electrolyte in the form of a semiclosed tube and containing the Ni - NiO reference mixture, a molybdenum wire acting as the electron conductor. The oxygen probes were immersed in the melt and the equilibrium values of *emf* took on the average 30 seconds to establish. The *emf* and temperature were recorded by the Goerz SE 461 recorder having a high input resistance. Reversibility of the electrode reac-

Table I

Experimental values of EMF of a conversion concentration cell (I) for $[(1-x)\text{Na}_2\text{O} - (x)\text{SiO}_2]$ melts related to reference melt $0.40 \text{ Na}_2\text{O} - 0.60 \text{ SiO}_2$

$x(\text{SiO}_2)$	T/K	EMF/mV	T/K	EMF/mV	T/K	EMF/mV
0.45	1581	-305	1573	-285	1523	-278
	1473	-280	1425	-278	1423	-280
	1378	-280	1363	-265		
0.50	1523	-210	1516	-190	1473	-180
	1423	-175	1418	-170		
0.55	1578	-70	1581	-72	1518	-80
	1529	-82	1478	-80	1473	-80
	1432	-79	1383	-74		
0.65	1563	85	1573	90	1531	100
	1480	90	1463	88	1413	105
	1598	75				
0.70	1573	110	1528	125	1491	140
	1483	120	1433	135	1478	128
0.75	1571	153	1526	160	1478	170
	1573	150	1471	180	1423	187

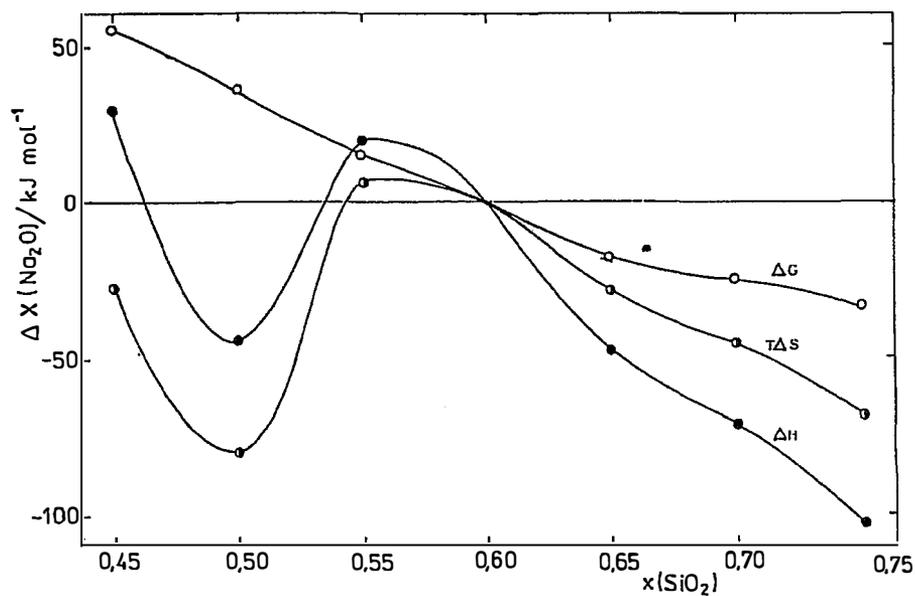


Fig. 3. Relative partial molar quantities of Na_2O related to reference melt ($0.40\text{Na}_2\text{O} - 0.60\text{SiO}_2$) at 1473 K; $\Delta X(\text{Na}_2\text{O})/\circ - \Delta G(\text{Na}_2\text{O})$; $\bullet - \Delta H(\text{Na}_2\text{O})$; $\bullet - T\Delta S(\text{Na}_2\text{O})$.

tion was checked by shorting the electrodes and their reconnecting, where the original *emf* value was re-established within several seconds. The reproducibility of *emf* values in several subsequent measurements at constant temperature amounted to ± 10 mV.

RESULTS AND DISCUSSION

Thermodynamic properties of the system $\text{Na}_2\text{O} - \text{SiO}_2$

In concentration cell (I), the electrode process is given by the oxidation-reduction reaction



which takes place at both electrodes in opposite directions. The effect of the transition of O^{2-} ions through the $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ solid electrolyte on the potential of the oxygen electrode will be discussed in detail below. The electrode reaction is accompanied by charge transfer through the liquid connection. In the sodium silicate melt, the charge is carried by Na^+ ions. The electromotive force of cell (I), which is thus a resultant of oxygen transfer at the electrodes and transport of sodium ions, can then be expressed by the equation

$$E = -\frac{RT}{2F} \ln \frac{a(\text{Na}_2\text{O})}{a^0(\text{Na}_2\text{O})}, \quad (3)$$

where $a(\text{Na}_2\text{O})$ and $a^0(\text{Na}_2\text{O})$ are the activities of sodium oxide in the melt being measured and the reference melt (0.40 $\text{Na}_2\text{O} - 0.60 \text{SiO}_2$) respectively.

The experimentally established values of *emf* listed in Table I were for each set of results processed as a function of temperature by the least squares method. The temperature dependence were then used to calculate, for 1473 K, the partial Gibbs energies of Na_2O related to the reference melt, and the other thermodynamic functions, $\Delta S(\text{Na}_2\text{O})$ and $\Delta H(\text{Na}_2\text{O})$. The partial molar quantities calculated are listed in Table II and plotted in Fig. 3. The values of the confidence interval at the significance level of $\alpha = 0.05$ (Table II) indicate a poor accuracy of $\Delta H(\text{Na}_2\text{O})$ and $\Delta S(\text{Na}_2\text{O})$, due to the dispersion of values around the approximation line in the temperature dependence of *emf*. This dispersion may be due to the fact that a fresh couple of oxygen probes was always used for each point, and the probes have a poor reproducibility.

Fig. 3 shows a sharp increase in the value of $\Delta G(\text{Na}_2\text{O})$ within the composition interval measured; this increase corresponds to the order of 10^3 of the Na_2O activity ratios. This is in agreement with the acidobasic behaviour of the system [2]. On the curves of thermodynamic functions $\Delta H(\text{Na}_2\text{O})$ and $\Delta S(\text{Na}_2\text{O})$ one can see a sharp minimum at $x\text{SiO}_2 = 0.5$, which is indicative of stability of the Na_2SiO_3 compound according to the phase diagram.

Table II

Partial molar quantities of Na_2O in $[(1-x)\text{Na}_2\text{O} - x\text{SiO}_2]$ melts for the temperature of 1473 K

$x(\text{SiO}_2)$	$\frac{\Delta G(\text{Na}_2\text{O})}{\text{kJmol}^{-1}}$	$\frac{\Delta S(\text{Na}_2\text{O})}{\text{JK}^{-1}\text{mol}^{-1}}$	$\frac{\Delta H(\text{Na}_2\text{O})}{\text{kJmol}^{-1}}$
0.45	54.4 ± 3.8^a	-19 ± 17	26.4 ± 28.7
0.50	35.8 ± 5.1	-55 ± 52	-44.7 ± 81.3
0.55	15.0 ± 2.1	4 ± 12	20.8 ± 19.5
0.60	0	0	0
0.65	-18.3 ± 3.7	-20 ± 22	-47.2 ± 37.3
0.70	-25.2 ± 4.4	-31 ± 41	-71.5 ± 65.0
0.75	-33.8 ± 1.7	-47 ± 13	-103.0 ± 21.0

^aThe numbers behind \pm are the values of the confidence interval at the 95% level of significance.

To allow the experimental results obtained in the present study to be compared with those by other authors investigating the $\text{Na}_2\text{O} - \text{SiO}_2$ system by means of galvanic cells [2, 3, 4], the activity of Na_2O was calculated from equation (3). The value of $a^0(\text{Na}_2\text{O})$ was taken over from [4] where beta alumina had been used as solid electrolyte. The results obtained by other authors have likewise been related to this standard state, and for the temperature of 1473 K plotted in Fig. 4. The courses of the curves indicate a very satisfactory agreement of our results with those from the literature. In studies [2, 3, 4], the classical gas electrode, i.e. platinum saturated with oxygen, was used as the oxygen electrode.

Knowing the activity of Na_2O , one can calculate $a(\text{SiO}_2)$ by integrating Gibbs-Duhem's equation

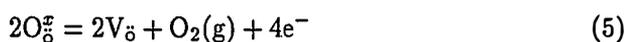
$$\log a(\text{SiO}_2) = -[x(\text{Na}_2\text{O})/x(\text{SiO}_2)] \times \quad (4)$$

$$\times d \log a(\text{Na}_2\text{O}).$$

The course of activity of SiO_2 in terms of composition and for 1473 K is likewise plotted in Fig. 4.

N-type of electron conductivity of stabilized ZrO_2 as solid electrolyte

The potential of the oxygen electrode and thus also the electromotive force of cell (I) may involve an error due to electron conductivity of the solid electrolyte. The formation of free electrons can be expressed by means of defective equilibrium [5,6]:



where $\text{O}_\text{O}^\ominus$ is the oxide ion in the standard oxide position, $\text{V}_\text{O}^\ominus$ is the double-ionized oxide vacancy, and e^- is

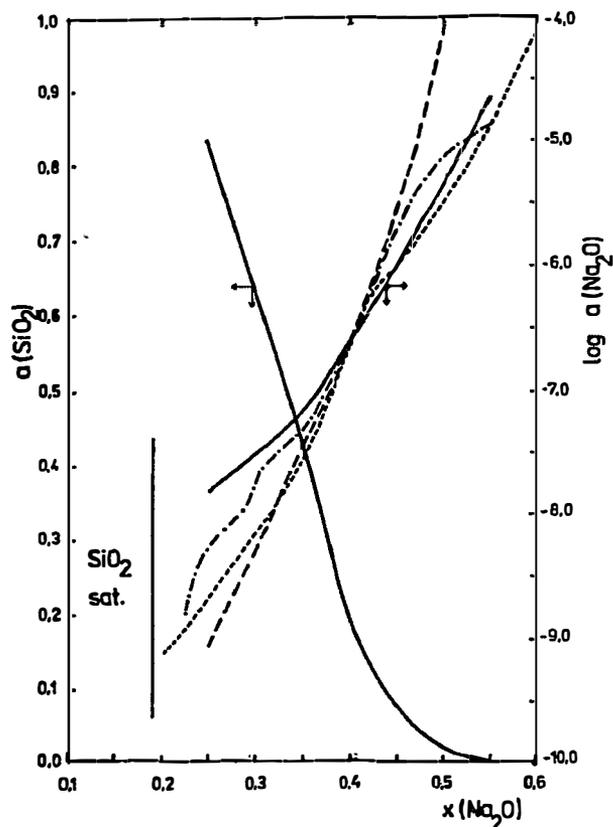


Fig. 4. Activities of Na_2O and SiO_2 vs. composition at 1473 K, and comparison of $a(\text{Na}_2\text{O})$ values with those reported by other authors:

— the present study;
 — Froberg et al. [2];
 ··· Kohsaka et al. [3];
 - - - Yamaguchi et al. [4].

the excess electron. On the assumption that the concentrations of oxide anionic vacancies and oxide anions are approximately constant, it follows from equation (5) that the electron conductivity will change with partial pressure of oxygen according to the relation $p\text{O}_2^{-1/4}$. The conversion number of ions in the stabilized ZrO_2 solid electrolyte for mixed ionic and electron conductivity is then given by the equation

$$t_{\text{ion}} = \frac{p_{\ominus}^{-1/4}}{p\text{O}_2^{-1/4} + p_{\ominus}^{-1/4}} \quad (6)$$

where p_{\ominus} is the partial pressure of oxygen at which the electron conductivity is equal to the ionic one.

In calculating p_{\ominus} for the solid electrolyte $\text{ZrO}_2 + 9 \text{ mol\% Y}_2\text{O}_3$, use was made of the equation [7]

$$\log \frac{p_{\ominus}}{p^0} = -\frac{67400}{T} + 21.55. \quad (7)$$

The partial pressure of oxygen in the $\text{Na}_2\text{O} - \text{SiO}_2$ melt was determined by means of concentration

cell (II). The following reaction takes place in this cell:



$\text{Ag}(l)$ thus represents the oxygen electrode at which the potential corresponding to the partial pressure of oxygen in the oxide melt is established. This can be calculated from the equation

$$E = \frac{RT}{F} \ln \frac{p_{\ominus}^{1/4} + p(\text{O}_2)_{\text{ref}}^{1/4}}{p_{\ominus}^{1/4} + p(\text{O}_2)_{\text{exp}}^{1/4}} \quad (9)$$

where $p(\text{O}_2)_{\text{ref}}$ is the partial pressure in the oxygen probe and for the reference mixture Ni - NiO is given by the equation [8]

$$RT \ln \frac{p(\text{O}_2)_{\text{ref}}}{p^0} = -468316 + 169.78T. \quad (10)$$

Table III

Experimental values of EMF of concentration cell (II) for 1473 K, calculated partial pressure of oxygen and conversion number t_{ion} of the solid electrolyte for $[(1-x)\text{Na}_2\text{O} - x\text{SiO}_2]$ melts

$x(\text{SiO}_2)$	EMF/mV	$p\text{O}_2/\text{Pa}$	t_{ion}
0.75	350	2.99×10^{-8}	0.999
0.70	375	1.36×10^{-8}	0.999
0.60	460	9.29×10^{-10}	0.997
0.50	580	2.08×10^{-11}	0.993
0.45	730	1.72×10^{-13}	0.976

The *emf* values measured and those of $p\text{O}_2$ calculated for the $\text{Na}_2\text{O} - \text{SiO}_2$ system are listed in Table III. The values indicate that the $\text{Na}_2\text{O} - \text{SiO}_2$ melt shows a low partial pressure of oxygen. In the acidic region, the $p\text{O}_2$ does not change by an order of magnitude, but decreases sharply with increasing Na_2O content.

By substituting the known $p\text{O}_2$ in the melt and the contribution of electron conductivity (equation (7)) into equation (6), the conversion numbers of the O^{2-} ion of the solid electrolyte were calculated. The values of t_{ion} , which are also listed in Table III, can be regarded as being equal to unity. According to the criterion given in [9], a solid electrolyte exhibits purely ionic conductivity when $t_{\text{ion}} > 0.99$. This criterion is met for all the compositions of the system being studied, except for the melt 0.55 $\text{Na}_2\text{O} - 0.45 \text{SiO}_2$. Knowing the value of t_{ion} and using equation (9), one can determine the error involved in the electromotive force of concentration cell (II) and thus also the

cell (I), which is due to electron conductivity of the solid electrolyte. For the $0.55 \text{ Na}_2\text{O} - 0.45 \text{ SiO}_2$ compound the error represents one tenth of millivolt of the *emf* value, being thus negligible from the standpoint of the experimental error. It may be pointed out that the error due to reproducibility of oxygen probes is greater by a factor of 100 than that caused by electron conductivity of the solid electrolyte.

The results obtained indicate that even in melts with a low partial pressure of oxygen it is possible to use an oxygen probe as a reversible electrode in studying concentration cells with conversion. This represents a substantial expansion of the possible field of utilization of this experimental technique. A highly promising range of study in this respect are the thermodynamic properties of systems including reduction-oxidation components, where classical gas electrodes cannot be employed.

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VYUŽITÍ KYSLÍKOVÝCH SOND PŘI STUDIU TERMODYNAMICKÝCH VLASTNOSTÍ SOUSTAVY $\text{Na}_2\text{O} - \text{SiO}_2$ A VLIV ELEKTRONOVÉ VODIVOSTI TUHÉHO ELEKTROLYTU NA EMN KONCENTRAČNÍHO ČLÁNKU

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Práce se zabývá využitím kyslíkových sond realizovaných tuhým elektrolytem ZrO_2 stabilizovaným Y_2O_3 jako reverzibilních elektrod při studiu termodynamických vlastností oxidových tavenin pomocí galvanických článků.

Bylo měřeno EMN koncentračního článku s převodem (I) pro binární taveninu $(1-x)\text{Na}_2\text{O} - x\text{SiO}_2$, kde molární obsah $x(\text{SiO}_2)$ se měnil v rozmezí 0.45 - 0.75. Z teplotní závislosti EMN (tabulka I) byly vzhledem k referenční tavenině 0.40 $\text{Na}_2\text{O} - 0.60 \text{SiO}_2$ vypočteny pro teplotu 1473 K parciální molární veličiny $\Delta G(\text{Na}_2\text{O})$, $\Delta H(\text{Na}_2\text{O})$ a $\Delta S(\text{Na}_2\text{O})$, které jsou zakresleny na obr. 3. Hodnoty parciální molární entalpie a entropie vyzakují v oblasti 50 molárních % výrazné minimum, což potvrzuje stabilitu sloučeniny Na_2SiO_3 .

Ve druhé části práce byla studována chyba, kterou může být zatíženo EMN článku (I) vlivem elektronové vodivosti tuhého elektrolytu. Pro určení iontového převodového čísla tuhého elektrolytu pro směšovanou iontovou a elektronovou vodivost je potřeba znát parciální tlak kyslíku ve studované tavenině $\text{Na}_2\text{O} - \text{SiO}_2$, který byl řešen pomocí koncentračního článku (II). Ukázalo se, že i přes velmi nízký parciální tlak kyslíku tohoto systému se elektronová vodivost uplatňuje pouze u složení 0.55 $\text{Na}_2\text{O} - 0.45 \text{SiO}_2$ (tabulka III). Chyba způsobená elektronovou vodivostí tuhého elektrolytu pak představuje desetinu hodnoty EMN koncentračního článku, což je zanedbatelné z hlediska reprodukovatelnosti kyslíkových sond.

Obr. 1. Experimentální uspořádání; 1 - termočlánek PtRh6-PtRh30, 2 - Mo drát, 3 - SiO_2 trubice, 4 - ochranná trubice Al_2O_3 , 5 - tuhý elektrolyt $\text{ZrO}_2(\text{Y}_2\text{O}_3)$, 6 - měřená tavenina, 7 - referenční tavenina, 8 - referenční směs Ni, NiO, 9 - PtRh kelímek, 10 - Al_2O_3 trubka, 11 - Al_2O_3 podstavec

Obr. 2. Experimentální uspořádání; 1 - Mo drát, 2 - termočlánek PtRH6-PtRH30, 3 - ochranná trubice Al_2O_3 , 4 - Al_2O_3 trubka, 5 - Al_2O_3 kelímek, 6 - tuhý elektrolyt $\text{ZrO}_2(\text{Y}_2\text{O}_3)$, 7 - oxidová tavenina, 8 - Ag liquid, 9 - Al_2O_3 zásyp, 10 - podstavec Al_2O_3 , 11 - topná grafická trubka.

Obr. 3. Relativní parciální molární veličiny Na_2O vztažené k referenční tavenině (0.40 $\text{Na}_2\text{O} - 0.60 \text{SiO}_2$) při teplotě 1473 K; $\Delta X(\text{Na}_2\text{O}) / \text{O}^\circ - \Delta G(\text{Na}_2\text{O})$; ● - $\Delta H(\text{Na}_2\text{O})$; ○ - $T\Delta S(\text{Na}_2\text{O})$.

Obr. 4. Závislost aktivit Na_2O a SiO_2 na složení při 1473 K, a srovnání $a(\text{Na}_2\text{O})$ s dalšími autory:

- the present study;
- — — — — Froberg et al. [2];
- · — · — · — Kohsaka et al. [3];
- — — — — Yamaguchi et al. [4].