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THERMODYNAMIC PROPERTIES AND CATION DISTRIBUTION OF THE $ZnFe_2O_4$–Fe_3O_4 SPINEL SOLID SOLUTIONS AT 900 °C

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ABSTRACT

The thermodynamic properties of the Fe_3O_4–$ZnFe_2O_4$ spinel solid solution were determined at 900 °C by the use of the solid electrolyte galvanic cell

$$Fe_2O_3 + Fe_3O_4|O^{2-}|Fe_2O_3 + Zn_xFe_{3-x}O_4$$

The activity values obtained exhibit slight negative deviation from the ideal solution model. An analysis of the free energy of mixing of the spinel solid solution provided information on the distribution of cations between the tetrahedral and octahedral sites of the spinel lattice. This is the basis for the estimation of the free energy of formation of pure zinc ferrite from oxides.

$$\Delta G^0_{ZnFe_2O_4} = -2740 - 1.6\,T \text{ cal mole}^{-1}$$

INTRODUCTION

The thermodynamic properties of the system Fe_3O_4–$ZnFe_2O_4$ have attracted much interest. Zinc ferrite and magnetite are both classified as spinel-type crystal structures and their solid solutions are considered to be products of mixing inverse and normal spinels. It is well known that thermodynamic properties of the spinel solid solutions are connected with cation distribution[1–4]. On the other hand, cation distribution is closely related to their magnetic properties. Thus, the choice of a proper composition of solid solutions can control the magnetic properties of these materials, which are of interest to the electronic industry. From the metallurgical point of view, the formation of zinc ferrite during roasting is one of the major obstacles, creating zinc losses during electrolytic zinc refining. Therefore, a knowledge of the thermodynamic properties of zinc ferrite and its solid solutions is desirable. The aim of this study is to examine the thermodynamics of the binary spinel solutions through experimental investigations and to find out the relationship between experimental results and structural information through theoretical calculations.

The first study conducted on the $ZnFe_2O_4$–Fe_3O_4 solid solution was made by Benner and Kenworthy[5] who calculated the activities of both components, which show large positive deviations from Raoult's law. Using the method of e.m.f. measurements, Tretyakov[6] determined the equilibrium oxygen pressures for solid solutions coexisting with Fe_2O_3 and found activities showing negative deviations from Raoult's law.

Recently, Katayama et al.[7] measured the activity of Fe_3O_4 directly in the spinel solid solution by means of the solid oxide galvanic cell and found the properties of the solution to be nearly ideal.

EXPERIMENTAL

Materials

The ZnO powder used in this study was obtained from "CIECH" Poland, the Fe_3O_4 powder from Baker Chemical Co., and the Fe_2O_3 powder from Merck. Zinc ferrite ($ZnFe_2O_4$) was synthesized by heating pressed pallets containing an equimolar mixture of ZnO and Fe_2O_3 for up to one week in air at 900 °C. The formation of the compound was confirmed by X-ray diffraction analysis. The spinel solid solutions were prepared by heating a fine mixture of $ZnFe_2O_4$ and Fe_3O_4 in the required ratio in small evacuated silica capsules for 7 days at 900 °C. Since the volume of a capsule was very small, the extent of decomposition of the ferrite solid solution to establish an oxygen pressure in the capsule should be negligible. After the heat treatment, the capsules were quenched in water. The formation of solid solutions was confirmed by X-ray diffraction analysis. The Fe_2O_3/Fe_3O_4 reference electrode was prepared by heating pressed pallets containing an equimolar mixture of powders in evacuated silica capsules for 24 h at 1000 °C.

Oxygen potential measurements

An e.m.f. cell of the type

$$Fe_2O_3 + Fe_3O_4/ZrO_2 + CaO/Fe_2O_3 + Zn_xFe_{3-x}O_4 \tag{I}$$

was used for oxygen potential measurements. Under the condition that the mutual solubility of the solid solution and Fe_2O_3 is very small, the overall cell reaction is

$$Fe_3O_4 \rightarrow Fe_3O_{4\,\mathrm{s.s.}} \tag{1}$$

and the e.m.f. of the cell (I) is directly related to the activity of Fe_3O_4 in the spinel solid solution by

$$\ln a_{Fe_3O_4} = -\frac{FE}{RT} \tag{2}$$

where $F = 23063$ cal V^{-1} mole^{-1}, E is the e.m.f. in volts, R is the gas constant and T is the absolute temperature.

A schematic diagram of the cell assembly is shown in Fig. 1. A solid electrolyte tube was inserted into an alumina crucible filled with $Fe_2O_3 + Fe_3O_4$ sintered powder. The spinel solid solution powder mixed with Fe_2O_3 and sintered in an evacuated

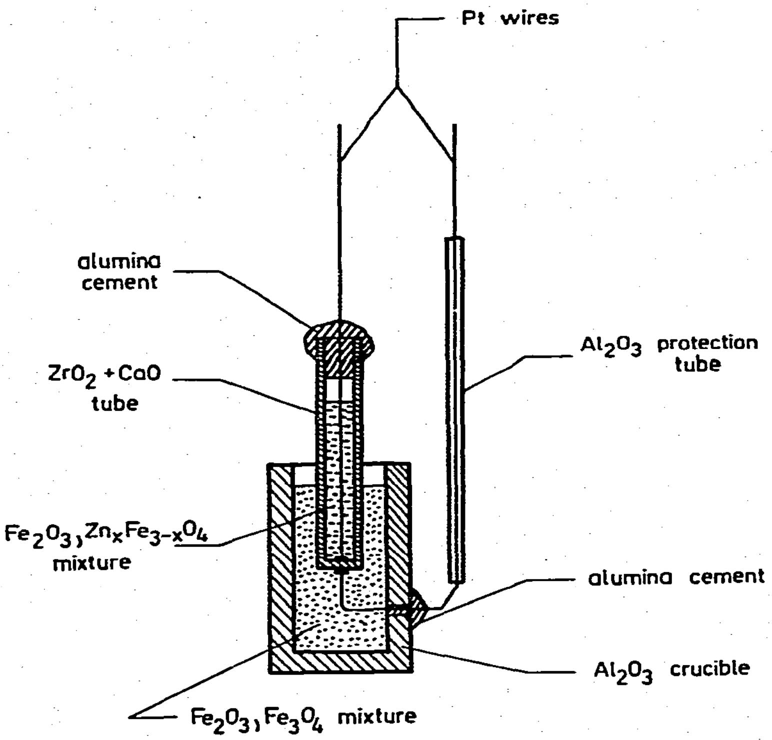

Fig. 1. Schematic diagram of the cell assembly.

silica capsule for 24 h at 950 °C, was ground and sealed inside the CSZ tube by use of an alumina cement. The cell was kept in the constant temperature zone of a resistance furnace under a stream of pure argon. A copper foil was used as the internal getter inside the furnace tube to maintain the desired oxygen pressure in the gas phase. After constant temperature had been reached, the flow of argon was cut off and the cell was left for 6–10 h to attain equilibrium. Then, the e.m.f. was recorded by means of a digital voltmeter V 534 (Elwro, Poland). The procedure was repeated for every sample.

RESULTS

The function of the cell assembly was checked by e.m.f. measurements of the free energy change of the reaction

$$4\,Fe_3O_4 + O_2 = 6\,Fe_2O_3 \qquad (3)$$

while the mixture of $Cu + Cu_2O$ powders was used as a reference electrode in the cell. The determined electromotive force values are shown in Fig. 2 in the range 1100–1250 K and the free energy change of reaction (3) is given by

$$\Delta G^0_{(3)} = -\,120037 + 70.5\,T \pm 500\ \text{cal} \qquad (4)$$

The value of the standard free energy of formation of cuprous oxide used in this calculation was taken from investigations of Charette and Flengas[8]. The above result

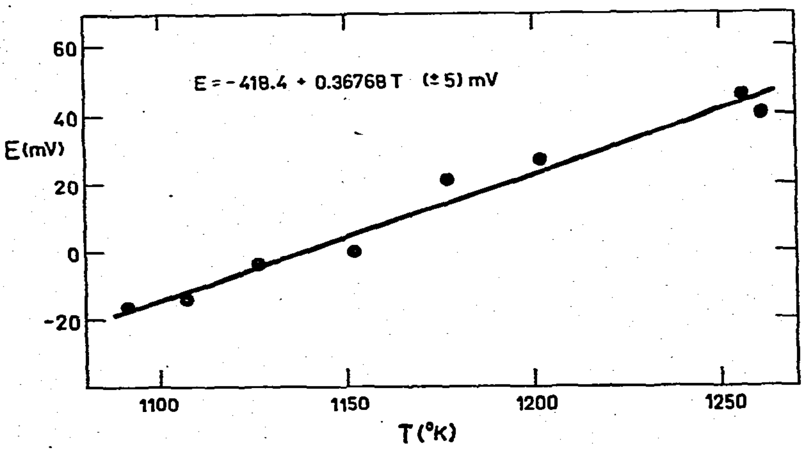

Fig. 2. Cell potential for the reaction 6 Fe_2O_3 + 4 Cu → 4 Fe_3O_4 + 2 Cu_2O.

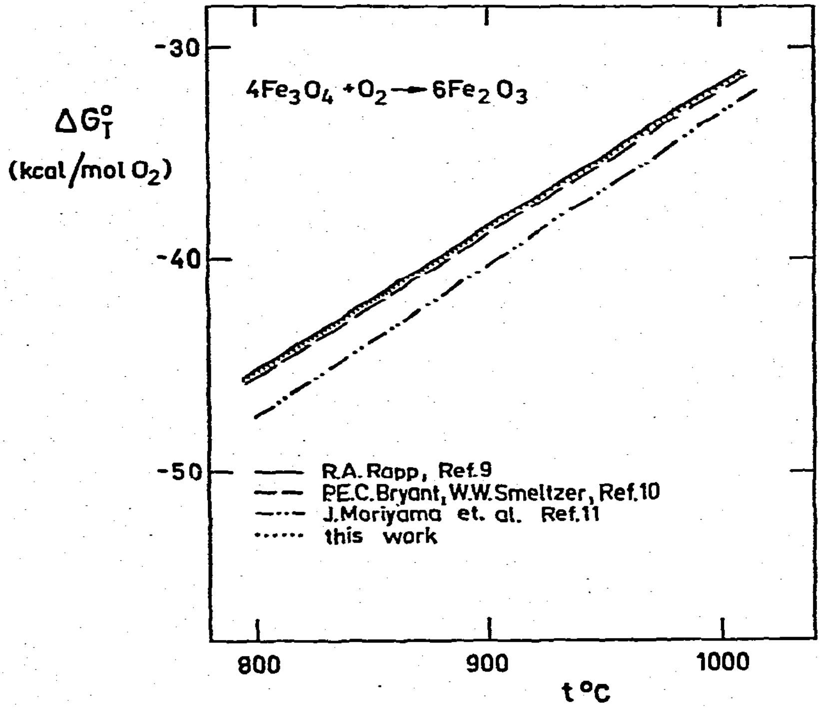

Fig. 3. The standard free energy of formation of hematite.

and those reported in the literature$^{9-11}$ are found to be in good agreement and are shown in Fig. 3.

The results of e.m.f. measurements produced by the cell (I) at 900 °C are shown in Table 1. Activity coefficients of $ZnFe_2O_4$ were calculated by integration of Gibbs–Duhem equation

$$\ln \gamma_{ZnFe_2O_4} = -\int_{1.0}^{X_{ZnFe_2O_4}} \frac{X_{Fe_3O_4}}{X_{ZnFe_2O_4}}\, d\ln \gamma_{Fe_3O_4} \qquad (5)$$

TABLE 1

ACTIVITIES AND FREE ENERGY OF MIXING OF SPINEL SOLID SOLUTION AT 900°C

$X_{Fe_3O_4}$	E ($\pm$ 1 mV)	$a_{Fe_3O_4}$	$a_{ZnFe_2O_4}$	$\Delta G_{s.s.}^M$ (cal mole^{-1})
0.1	278	0.06	0.9	− 877
0.3	163	0.20	0.68	−1755
0.5	97	0.38	0.44	−2084
0.7	42	0.66	0.19	−1839
0.9	8	0.92	0.05	− 873

The activities and corresponding partial free energies of mixing of Fe_3O_4 + $ZnFe_2O_4$ solid solutions were calculated at 900°C. Numerical results are summarized in Table 1, while activities of both components and integral free energy of mixing are shown and compared with those obtained by Tretyakov[6] and Katayama et al.[7] in Figs. 4 and 5.

Distribution of cations between the tetrahedral and octahedral sites of the spinel lattice

It has been shown previously[2, 12] that distribution of cations between the tetrahedral and octahedral sites of pure spinels can be estimated from Dunitz and Orgel's[13] crystal field octahedral site preference energies, assuming ideal Temkin mixing of cations on each cation sublattice. In the light of that theory, the competition of cations Zn^{2+}, Fe^{2+}, Fe^{3+} for the occupancy of the tetrahedral and octahedral sites in the $Zn_xFe_{3-x}O_4$ spinel lattice is governed by the site preference energies of the cations. From values tabulated earlier[2, 13] and the measured cation distribution

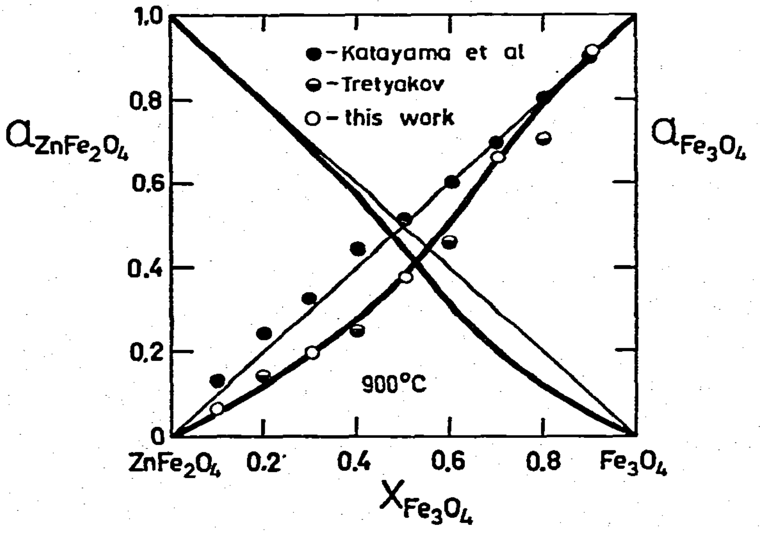

Fig. 4. Activities of magnetite and zinc ferrite in Fe_3O_4–$ZnFe_2O_4$ spinel solid solutions.

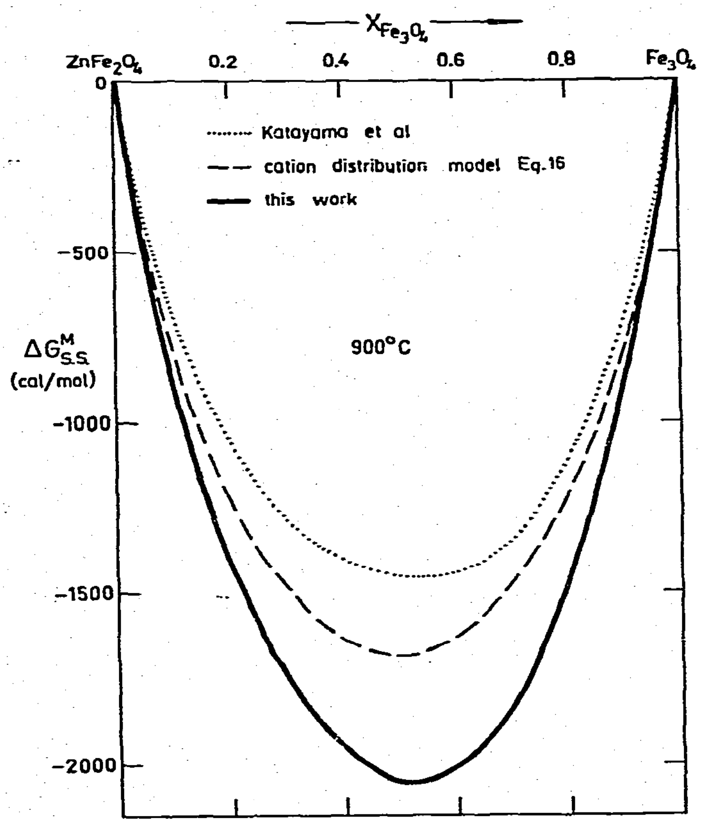

Fig. 5. Integral free energies of formation of Fe_3O_4–$ZnFe_2O_4$ spinel solid solutions.

in $ZnAl_2O_4$, which enabled the site preference energy of Zn^{2+} ion to be assessed (−1.2 kcal), the following equations at 900 °C are obtained.

$$(Zn^{2+}) + [Fe^{3+}] \rightarrow [Zn^{2+}] + (Fe^{3+})$$

$$\Delta H_{\text{exchange}} = 1200 \text{ cal}$$

$$K = \frac{N_{[Zn^{2+}]}\, N_{(Fe^{3+})}}{N_{(Zn^{2+})}\, N_{[Fe^{3+}]}} = 0.60 \tag{6}$$

$$(Fe^{2+}) + [Fe^{3+}] \rightarrow [Fe^{2+}] + (Fe^{3+})$$

$$\Delta H_{\text{exchange}} = -4000 \text{ cal}$$

$$K = \frac{N_{[Fe^{2+}]}\, N_{(Fe^{3+})}}{N_{(Fe^{2+})}\, N_{[Fe^{3+}]}} = 5.56 \tag{7}$$

Where () and [] denote the tetrahedral and octahedral sites, respectively, and N_i is the ionic fraction of cation "i" on each site. By definition

$$\sum N_{(i)} = 1 \tag{8}$$

$$\sum N_{[j]} = 1 \tag{9}$$

TABLE 2

CALCULATED CATION DISTRIBUTION, ENTROPY, ENTHALPY AND FREE ENERGY OF MIXING OF SPINEL SOLID SOLUTION AT 900 °C

Composition of spinel phase	*Ionic fractions, octahedral sites*			*Ionic fractions, tetrahedral sites*			$\Delta S_{s.s.}^{M}$ *(cal deg⁻¹ mole⁻¹)*	$\Delta H_{s.s.}^{M}$ *(cal mole⁻¹)*	$\Delta G_{s.s.}^{M}$ *(cal mole⁻¹)*
$X_{ZnFe_2O_4}$	$N_{[Zn2+]}$	$N_{[Fe2+]}$	$N_{[Fe3+]}$	$N_{(Zn2+)}$	$N_{(Fe2+)}$	$N_{(Fe3+)}$			
0	0	0.4386	0.5614	0	0.1228	0.8772	0	0	0
0.2	0.0465	0.3560	0.5975	0.1070	0.0880	0.8050	0.98	− 70	−1220
0.4	0.1005	0.2715	0.6280	0.1990	0.0570	0.7440	1.31	−108	−1645
0.6	0.1605	0.1830	0.6565	0.2790	0.0340	0.6870	1.32	−100	−1648
0.8	0.2240	0.0922	0.6839	0.3520	0.0157	0.6323	0.98	− 64	−1214
1.0	0.2945	0	0.7055	0.4110	0	0.5889	0	0	0

while from mass balance requirements

$$2\,N_{[Zn^{2+}]} + N_{(Zn^{2+})} = X_{ZnFe_2O_4} \qquad (10)$$

and

$$2\,N_{[Fe^{2+}]} + N_{(Fe^{2+})} = X_{Fe_3O_4} \qquad (11)$$

Cation distributions at 900 °C were calculated while solving the above equations for different compositions of the spinel solid solution. Obtained results are summarized in Table 2.

The entropy of mixing of the spinel solid solution is obtained by subtracting the mole fraction weighted sum of the cation mixing entropy of two pure component spinels from the cation mixing entropy of the solid solution.

$$\Delta S^{M}_{s.s.} = \Delta S^{CM}_{s.s.} - (X_{Fe_3O_4}\,\Delta S^{CM}_{Fe_3O_4} + X_{ZnFe_2O_4}\,\Delta S^{CM}_{ZnFe_2O_4}) \qquad (12)$$

where the Temkin ideal cation mixing contribution $\Delta S^{CM}_{s.s.}$ to the total entropy of the spinel solid solution is given by

$$\Delta S^{CM}_{s.s.} = -R\,\{\sum N_{(i)}\ln N_{(i)} + 2\sum N_{[i]}\ln N_{[i]}\} \qquad (13)$$

Similarly, the heat of mixing of the spinel solid solution due to cation rearrangement can be calculated from octahedral site preference energies.

$$\Delta H^{M}_{s.s.} = \Delta H^{M}_{total} - (X_{ZnFe_2O_4}\,\Delta H^{M}_{ZnFe_2O_4} + X_{Fe_3O_4}\,\Delta H^{M}_{Fe_3O_4}) \qquad (14)$$

where the total heat of mixing is

$$\Delta H^{M}_{total} = 2\,\{N_{[Zn^{2+}]}(1200) + N_{[Fe^{2+}]}(-4000)\}\ \text{cal} \qquad (15)$$

The free energy of mixing is given by

$$\Delta G^{M}_{s.s.} = \Delta H^{M}_{s.s.} - T\Delta S^{M}_{s.s.} \qquad (16)$$

Calculated values of $\Delta G^{M}_{s.s.}$ are shown and compared with the experimental results obtained at 900 °C in Fig. 4.

Estimation of the free energy of formation of zinc ferrite

The heat of formation of zinc ferrite was measured by Navrotsky and Kleppa[1] who obtained a mean value of -2740 cal mole^{-1} at 970 K. The knowledge of cation distribution in pure zinc ferrite enabled the entropy change during zinc ferrite formation from respective oxides to be estimated.

$$ZnO_{(wurtzite)} + Fe_2O_{3(corundum)} \rightarrow ZnFe_2O_{4(spinel)} \qquad (17)$$

The entropy change of reaction (17) is given by

$$\Delta S_{(17)} = \Delta S^{M} + \Delta S' \qquad (18)$$

where ΔS^{M} is the entropy change of cation mixing in pure spinel which can be calculated from crystal field site preference energies. In the range 1173–1373 K, it varies slowly with temperature and it can be considered equal to 3.75 cal mole^{-1} deg^{-1}, which is a value calculated at 1173 K. The entropy change of the reaction of formation from respective oxides, $\Delta S'$, can be estimated from the known entropy change of the reaction of spinel structure formation.

(r.salt structure) + (corundum-like structure) → (spinel structure) (19)

and from the reaction

(wurtzite structure) → (r.salt structure) (20)

It has been shown recently[14, 15] that $\Delta S_{(19)} = -1.75$ cal mole^{-1} deg$^{-}{}_{1}$ and $\Delta S_{(20)} = -0.4$ cal mole^{-1} deg^{-1}. Thus, the entropy change of the reaction (17) is equal to

$$\Delta S_{(17)} = 3.75 - 1.75 - 0.4 = 1.6 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

(The Jahn–Teller effect is not expected in this case.) Consequently, the free energy of formation of zinc ferrite is given by

$$\Delta G^0_{\mathrm{ZnFe_2O_4}} = -\,2740 - 1.6\,T \text{ cal mole}^{-1} \qquad (21)$$

The value calculated from eqn. (21) at 1153 K (−4585 cal) is found to be in good agreement with results obtained by Tretyakov and co-workers[6, 16] (−4630 cal and −4840 cal). The result obtained by Gilbert[17] at 1400 K (−6500 cal) is more negative than that calculated from eqn. (21) (−4980 cal).

CONCLUSIONS

The results obtained are found to be in fair agreement with those obtained previously[6, 7]. The measured activity of Fe_3O_4 shows slight negative deviation from Raoult's law.

An analysis of the free energy of mixing of the Fe_3O_4–$ZnFe_2O_4$ spinel solid solution showed fair agreement between calculated and measured integral free energies of mixing on the basis of a cation mixing model. Unfortunately, cation distribution has not been measured in this spinel solid solution so far. However, it has been demonstrated previously[12] that the treatment presented above led to reasonable agreement between measured and calculated cation distributions. Thus, one can draw the conclusion that calculated values should correspond well to true cation distribution.

The most difficult point of the experimental work is to keep the reaction

$$3\,\mathrm{ZnFe_2O_{4_{s.s.}}} \rightarrow 2\,\mathrm{Fe_3O_{4_{s.s.}}} + 3\,\mathrm{Zn_{(g)}} + 2\,\mathrm{O_{2_{(g)}}} \qquad (23)$$

under control.

The consequences of this reaction are not compatible with proper cell operation. Low P_{O_2} is required for proper $Fe_2O_3 + Fe_3O_4$ reference electrode operation, but it brings about the increase of P_{Zn}($P_{Zn} + P_{O_2}$ = const. at T = const.), which is connected with $ZnFe_2O_4$ decomposition. Thus, alumina cement was used to seal the spinel solid solution electrode inside the CSZ tube in order to keep P_{Zn} low and to limit the possibility of zinc evaporation.

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