Ceramics International 24 (1998) 91-98
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0272-8842/97 $17.00+.00
PII: S0272-8842(96)00084-3

Composite (CaF_2+ α-Al_2O_3) Solid Electrolytes: Preparation, Properties and Application to the Solid Oxide Galvanic Cells

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(Received 19 April 1996; accepted 24 September 1996)

Abstract: Calcium fluoride based composites containing up to 25 mol.% α-Al_2O_3 disperse phase were prepared. Electrical conductivities of the samples were measured in the temperature range 400–700°C by the d.c. four-probe method. Dispersions of α-Al_2O_3 up to 5 m/o were found to enhance the conductivity of pure CaF_2. The conductivity values were increased two orders of magnitude higher than those of pure CaF_2 and they were dependent on the preparation method of the sample. The maximum conductivity values were observed for 2.5 m/o α-Al_2O_3 content. The (CaF_2+α-Al_2O_3) composites appeared to be purely ionic conductors. The materials prepared were applied as electrolytes in solid-state oxide galvanic cells. The Gibbs free energy of formation at 700°C for calcium metasilicate was determined from electromotive force (emf) measurements in this way.

1 INTRODUCTION

Calcium fluoride CaF_2 is known to be a good fluorine ion conductor. It was shown to conduct via fluorine ion interstitials alone.[1] From an electrical properties point of view, CaF_2 belongs to the best-known and widely studied materials.[2] Measurements indicated that its electrical conductivity being purely ionic amounted to 0.011 $(\Omega.cm)^{-1}$ at 900°C. A relatively high ionic conductivity as well as a high thermodynamic stability makes CaF_2 an especially reliable electrolyte in solid-state galvanic cells which are useful for many thermodynamic investigations at higher temperatures.[2,3] CaF_2 also may be applied in electrochemical devices such as sulfur gas sensors[4] and ceramic sensors for process control in the aluminium industry.[5] However, its ambient and moderate temperature conductivities are relatively low; e.g. at 700°C, they are in the region of $10^{-5}(\Omega.cm)^{-1}$.[1] This limits the use of CaF_2 as a practical electrolyte for low-temperature operations. In order to lower the operating temperature of CaF_2, a disperse heterophase can be introduced into it. Mixtures of some halide solid ionic conductors with fine particles of an insulating and insoluble second phase (e.g. Al_2O_3) were shown to increase the conductivity significantly as compared to the pure homogenous systems. The ionic conductivity first increased strongly with the concentration of the dispersed insulating phase. After passing its maximum, the conductivity decreased rapidly at larger concentrations. The discovery of this phenomenon is due to Liang,[6] who observed an enhancement by three orders of magnitude in the conductivity of LiI after addition of Al_2O_3 particles. Jow and Wagner[7] found an increase in conductivity in CuCl–Al_2O_3 system by as much as two orders of magnitude. They attempted to explain this enhancement and proposed that ultrafine Al_2O_3 particles formed well-defined space-charge regions in contact with the host CuCl electrolyte. An increase in defect concentration in the space-charge region enhanced the ionic conductivity of the electrolyte. Second-phase effects were also found for AgI–Al_2O_3,[8–10] AgCl–Al_2O_3,[11] BaF_2–Al_2O_3,[12] $SrCl_2$–Al_2O_3[13,14] and CsCl–Al_2O_3[15] systems.

To interpret the results of conductivity measurements in dispersed solid electrolytes, several theoretical models were proposed. All of them assumed that highly conducting paths were created along the interface between the host electrolyte and the dispersoid.[7,16,17] The high ionic conductivity could be quantitatively explained by a space-charge effect induced by an internal cation adsorption at the Al_2O_3 surfaces. The relevance of cation vacancies for the effect under consideration was already stressed by Wagner[18] and developed by Maier[11,19–21] and Dudney.[22] Fujitsu *et al.*[13] applied a simple matrix-particle mixing model to the simulation of the effective thickness and a high-ionic conductivity layer. However, in the theory developed by Yanagida,[23] the role of interfaces for the properties of ceramics materials was brought out. For ionic transport in dispersed ionic conductors, percolation models were also discussed.[24] Uvarov *et al.*[25] presented a model incorporating the surface conductivity and morphology of the composite solid electrolytes and used it to explain their conduction behaviour. These conductors, frequently called composite solid electrolytes, are promising materials for solid state technology (for a general review on other dispersed ionic conductors and the related theoretical models, see Ref.19).

This work was initiated to study the ceramic samples of CaF_2 containing Al_2O_3 as a disperse phase. Such an electrolyte had already been investigated. Wen *et al.*[26] measured the electrical conductivity of the CaF_2 samples containing 2 and 5 m/o in the temperature range 300–720°C. Fujitsu *et al.*[12] measured the electrical conductivity of CaF_2–Al_2O_3 at a temperature of 500°C for concentrations of Al_2O_3 up to 40 m/o. However, Khandkar *et al.*[27] prepared two series of CaF_2 electrolytes using Al_2O_3 powders in its two different forms (γ and α) and measured the electrical conductivity in the temperature range 25–900°C, for the Al_2O_3 concentration of 5, 10 and 25 m/o.

In the present work, aluminium oxide was introduced in CaF_2 in two ways: as a commercial α-Al_2O_3, and as an organic precursor, aluminium salt of 8-hydroxyquinoline. The purpose of our investigation was to examine how the presence of Al_2O_3 heterophase in CaF_2 matrix influenced electrochemical properties of the composite prepared.

2 THERMODYNAMICAL CONSIDERATIONS

Recent trends of the use of dispersed solid electrolytes in galvanic cells have increased the need for an assessment of the materials' compatibility. Then, in the design of composite electrolytes, the potential reactions between the dispersoid and the matrix must be considered. The purpose of the considerations is to focus attention on the stability constraints on materials used in advanced designs of electrochemical cells. The material used as a dispersoid for enhancing ionic conductivity should be chemically inert with respect to the matrix. In order to decide whether Al_2O_3 reacts with CaF_2, the standard Gibbs free energy changes for the chemical reactions:

$$3\,CaF_{2(s)} + Al_2O_{3(s)} = 3\,CaO_{(s)} + 2\,AlF_{3\,(s)};\ \Delta G_1^0 \quad (1)$$

and

$$CaF_{2\,(s)} + Al_2O_{3\,(s)} = CaO_{(s)} + 2\,AlOF_{(s)};\ \Delta G_2^0, \quad (2)$$

which could occur in the CaF_2–Al_2O_3 system, were calculated on the basis of the values of standard Gibbs free energy of formation given in thermochemical tables.[28] This calculation yielded ΔG_i^0 ($i = 1, 2$) as a function of absolute temperature:

$$\Delta G_1^0\,[\mathrm{kJ}] = 451.87\,(\pm 6.59) + 0.014\,(\pm 0.001)\cdot T\,[\mathrm{K}] \quad (3)$$

$$\Delta G_2^0\,[\mathrm{kJ}] = 1078.0\,(\pm 1.6) - 0.366\,(\pm 0.002)\cdot T\,[\mathrm{K}], \quad (4)$$

where T is in the range of 800–1500 K. As it results from eqn (3) and (4) the standard Gibbs free energy change assumes positive values for a whole temperature range considered. It means that calcium fluoride is more stable than calcium oxide and both the reactions cannot occur spontaneously. Since all the reagents taking part in reactions (1) and (2) are in a solid state, the reactions are not influenced by an ambient gas phase composition. Thus, the Al_2O_3 seems to be an appropriate dispersoid for CaF_2 electrolyte.

It is worth mentioning that some authors indicated on a limited mutual solubility Al_2O_3 in CaF_2.[29] Unfortunately, a lack of thermodynamic data does not allow to calculate Gibbs free energy of mixing for the solid solutions, and thus, to determine a solubility limit of Al_2O_3 in CaF_2.

An interaction of CaF_2 with moisture in the surrounding atmosphere also should be considered. The equation of the reaction of water with calcium fluoride is:

$$CaF_{2\,(s)} + H_2O_{(g)} = CaO_{(s)} + 2\,HF_{(g)};\ \Delta G_5 \quad (5)$$

As seen from eqn (5), this reaction may cause the growth of an insulating CaO layer in the grain boundaries of electrolyte material that may subsequently decrease its electrical conductivity. Moreover, the gaseous reagents of the reaction may generate pores in the specimen during sintering, and thus, they may lead also to a decrease in the mechanical strength of the material. According to chemical principles, the equilibrium of reaction with gaseous components can be influenced by controlling the surrounding atmosphere. If the HF partial pressure is high enough, the chemical equilibrium of the reaction in reaction (5) would be shifted towards the left. The stability region of CaF_2 with respect to the gaseous reagent can be estimated according to the following formula:

$$\Delta G_5 = [\Delta_f G^0\,(\mathrm{CaO}) + 2\Delta_f G^0\,(\mathrm{HF}) - \Delta_f G^0\,(\mathrm{CaF_2}) - \Delta_f G^0\,(\mathrm{H_2O})] + R\cdot T\cdot\ln\left(\frac{p^2_{\mathrm{HF}}}{p_{\mathrm{H_2O}}}\right), \qquad (6)$$

assuming solid CaF_2 and CaO to be in their standard states of unit activity; $\Delta_f G^0$ denotes here the standard Gibbs free energy of formation for a respective reagent, p_{HF} and $p_{\mathrm{H_2O}}$—the partial pressures of hydrogen fluoride and of H_2O (gas), respectively. After inserting in eqn (6) the tabularized $\Delta_f G^0$ values[28] and taking into account the condition $\Delta G_5 \geq 0$ (then the reaction (5) cannot occur spontaneously), the stability region of CaF_2 is expressed in a form of the following inequality:

$$\log(p_{\mathrm{H_2O}}) \leq -3.211 + \frac{7420}{T} + \log(p_{\mathrm{HF}}) \qquad (7)$$

From the calculations based on eqn (7), it transpires that at a temperature of 1000°C, reaction (5) will occur already by $p_{\mathrm{H_2O}}$ exceeding 0.0083 atm. if a concentration of HF amounts 20 ppm (2×10^{-5} atm.). Thus, the result of the calculations indicates that the powders containing CaF_2 should be sintered in a dry gas atmosphere.

Applying considerations similar to those presented above for the reaction of CaF_2 with oxygen:

$$\mathrm{CaF_{2\,(s)}} + 0.5\,\mathrm{O_{2\,(g)}} = \mathrm{CaO_{(s)}} + \mathrm{F_{2\,(g)}};\ \Delta G_8, \qquad (8)$$

a stability region of CaF_2 ($\Delta G_8 \geq 0$) with respect to oxygen is thus determined:

$$\log(p_{\mathrm{F_2}}) \geq -\frac{30410}{T} + 3.19 + 0.5\cdot\log(P_{\mathrm{O_2}}). \qquad (9)$$

As results from our calculations, for a typical level, i.e. 100 ppm of oxygen content in an inert gas, p_{F2} assumes a very small value of $2.0.10^{-23}$ atm. at 1000°C. Thus, a heat treatment of CaF_2 should be performed in an inert gas, well purified of oxygen.

3 EXPERIMENTAL

3.1 Preparation and characterization of the materials

Electrical conductivity enhancement in two phase composites was shown to be strongly dependent on sample preparation conditions, and higher conductivities are expected if a better contact between the solid electrolyte and dispersoid can be obtained.[10] In order to reach a good contact between the two phases, the dispersoid particles should be as small as possible. The consolidation of the composites may be difficult to be attained, especially because of possible reactions, in which the gaseous reagents take part. As discussed above, these reactions should not occur if the (CaF_2+ α-Al_2O_3) composites are prepared by a heat treatment of respective powders in dry inert gas atmosphere.

In the present work, two preparation methods were used. In the first of them, the starting substances were commercial ultrapure anhydrous CaF_2 (Merck) and α-Al_2O_3 of 99.9% purity (Vereinigte Aluminium Werke AG, Schwanndorf, Germany) powders. Appropriate amounts of CaF_2 and α-Al_2O_3 (previously dried at 250°C for 6 h) were weighed and mixed in an ultrasonic desintegrator with anhydrous acetone as a medium. Thus, obtained slurry was dried at 100°C for 2 h. Then, the mixture was pulverized, and the resulting powder was isostatically pressed at pressure 350 MPa. Cylindrical pellets thus obtained were 10 mm in diameter and 2 mm in thickness. The pellets were placed in an α-alumina support and sintered under dried argon at 1000°C for 2 h. Nine preparations containing 0, 1.0, 1.5, 2.5, 3.5, 5.0, 7.5, 10, and 25 m/o α-Al_2O_3 were obtained in this way. In the second method as a source of α-Al_2O_3, an organic precursor, aluminium salt of 8-hydroxyquinoline, was used. This was precipitated from an aluminium chloride aqueous solution by adding a solution of 8-hydroxyquinoline in acetic acid. The starting materials were weighed in a variety of mixing ratios and mixed thoroughly in an agate mortar. Then, the mixtures were pressed into pellets 2 mm thick and 12 mm in diameter. The pellets were transferred to an α-alumina support and heat-treated under a pressure of 1.7 kPa at 1000°C for 6 h, taking care to heat the pellets slowly to prevent cracking. During the heating, the aluminium salt was decomposed and the fine-coarsed α-Al_2O_3 dispersed in CaF_2 matrix was formed. Eight preparations of different α-Al_2O_3 content: 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.5 and 5.0 were prepared in this way. The starting powders were characterized by specific surface measurements, thermal analysis, granulometric analysis and by X-ray diffraction. The sintered samples were examined by X-ray diffraction and scanning electron microscopy.

3.2 Electrical conductivity

The electrical conductivity was measured using a simple d.c. four-probe method. Its application to the conductivity measurements of an ionic conductor was described in Ref.[30]. Four platinum wires were wrapped around the regular shape of 10×5×3 mm cut from the appropriate pellet. A small current was passed between the outer probes in both directions, and the potential between the inner probes was measured. The electrical conductivity was calculated directly from the measured resistance and from the dimensions of the sample. The measurements were performed in the temperature range of 400–700°C.

3.3 Emf measurements

The obtained samples have been tested as electrolytes in solid-state galvanic cells, schemes of which may be written as:

$$\mathrm{Pt|Ni,\ NiO|(CaF_2+\alpha\text{–}Al_2O_3)|Cu_2O,\ Cu|Pt} \tag{10}$$

$$\mathrm{Pt|O_2|CaO|(CaF_2+\alpha\text{–}Al_2O_3)|CaSiO_3,\ SiO_2|O_2|Pt} \tag{11}$$

The emf of the cell (10) was measured to determine the contribution of ionic conductivity in the $(CaF_2+\alpha$-$Al_2O_3)$ samples. A similar type of a galvanic cell involving pure CaF_2 was investigated by Ramanarayanan *et al.*[31] The two-phase mixtures (Ni, NiO) and (Cu_2O, Cu) having known equilibrium partial pressures at a given temperature were used as electrodes in the cell (10). For the sample separating both the electrodes having a purely ionic conduction and transporting only one type of ion, the emf of the cell (10) under thermodynamic equilibrium condition is represented by the Nernst equation:

$$E_t = \frac{R \cdot T}{4 \cdot F} \cdot \ln \left[\frac{p_{O_2}\ (\mathrm{Cu,\ Cu_2O})}{p_{O_2},\ (\mathrm{Ni,\ NiO})} \right]. \tag{12}$$

In the case of the sample, which contains two (or more) mobile electrical charge species, the emf of the cell (10) could be expressed as:

$$E = t_i E_t, \tag{13}$$

where t_i denotes an effective ionic transference number of ions deciding on electrical transport in the sample under study. The procedure of half-cells preparation, as well as the cell arrangement were the same as in Ref. 32. The emf values were monitored with a high-ohmic digital voltmeter. They were measured in purified, dried argon in the temperature range 700–900°C. Knowing the ion transference number value in the $(CaF_2+\alpha$-$Al_2O_3)$ samples, the emf of the cell (11) was measured, and the standard Gibbs free energy of calcium metasilicate ($CaSiO_3$) formation was calculated. In this way, the applicability of the materials prepared as electrolytes in the galvanic cells for thermodynamic investigations could be demonstrated. The method of preparation of the half-cell was described by two of us previously.[33] The emf was measured in a dried argon ($p_{O_2} = 100$ Pa) at 700°C.

4 RESULTS AND DISCUSSION

4.1 Characterization of the materials

The specific area of CaF_2 powder obtained from adsorption measurements (BET method) was $23.54\,m^2\,g^{-1}$. The specific area of a commercial α-Al_2O_3 was $9.78\,m^2\,g^{-1}$ and that obtained by thermal decomposition of aluminium salt of 8-hydroxyquinoline amounted to $116.8\,m^2\,g^{-1}$. Programmed with a temperature rate of $10°C\,min^{-1}$, differential thermal analysis of the organic aluminium salt identified three endothermic peaks at 110–140°C, 220–240°C and about 480°C, and two exothermic peaks at about 620°C and 940°C. The endothermic peaks could be ascribed to dehydratation and decarbonization processes in the specimen under study, and the exothermic ones to the crystallization of the γ-Al_2O_3 and α-Al_2O_3 phases, respectively. Thus, α-Al_2O_3 appeared to be a final product of decomposition of the aluminium organic salt. X-ray analysis confirmed the presence of only the α-Al_2O_3 phase in the specimen after heating. The average particle size of commercial α-Al_2O_3 powders was $0.42\,\mu m$, and that of α-Al_2O_3 prepared from organic precursor was not greater than $0.02\,\mu m$. X-ray diffraction patterns of the samples sintered from a mixture of CaF_2 and α-Al_2O_3 revealed that the material consisted of the two phases, only. Those samples prepared from CaF_2

and the organic precursor, however, indicated the presence of traces of CaO, additionally. Scanning electron microscopy of all samples showed that the CaF_2 grains had irregular shapes and that the α-Al_2O_3 particles were non-uniformly distributed along grain boundaries. The size of CaF_2 grains varied between 1 and 10 μm, whereas the α-Al_2O_3 particles were no larger than 0.5 μm in the samples sintered directly from the mixture of CaF_2 and α-Al_2O_3 and no larger than 0.02 μm in the samples prepared from CaF_2 and the organic precursor.

4.2 Electrical conductivity

The electrical conductivity, σ, was assumed to follow an Arrhenius equation of the form:

$$\sigma \cdot T = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right), \qquad (14)$$

where A is a constant, T is the absolute temperature, E_a is the activation energy for ionic motion, and R is the gas constant. Here, σ involves the grain bulk and grain boundary conductivities.

Conductivities (at temperatures of 400 and 700°C) of the samples from two series prepared are listed in Tables (1) and (2), respectively. The activation energy of the conductivity calculated in the temperature range 400–700°C is also given. As seen from the tables, the conductivity of the composite samples increased in the composition range 0–2.5 m/o α-Al_2O_3 and then fell towards smaller values. By contrast, the activation energy decreased in the same concentration range and then increased. The samples obtained by the method using an organic precursor had higher conductivities than those of the same composition obtained directly from the mixture of CaF_2 and α-Al_2O_3 powders. They exhibited a maximum conductivity for 2.5 m/o α-Al_2O_3. The respective values at a temperature of 700°C were 0.00328 $(\Omega.\mathrm{cm})^{-1}$ and 0.000942 $(\Omega.\mathrm{cm})^{-1}$. Such differences may be due to different microstructures of the samples. A similar effect was also observed by the authors of Ref. 27.

To visualize better the influence of the α-Al_2O_3 phase on conduction properties of the composite, the relative total conductivity (σ/σ_0), σ_0 being the conductivity of pure CaF_2, at 400 and 700°C is plotted against the α-Al_2O_3 content in Fig. 1 for both series of the samples. The inclusion of 2.5 m/o of α-Al_2O_3 caused an enhancement in the conductivity by a factor ranging from 40 to 230, depending on the preparation method of the sample and on the temperature at which the conductivity was measured. The relative total conductivity of the composites was higher at a temperature of 400°C than that at 700°C. These results were in a good agreement with those from Ref. 27, whereas an enhancement in the conductivity of the samples obtained by the authors of Ref. 26 was higher than that of ours.

In order to interpret the fact of changes in conductivity occurring by introduction of α-Al_2O_3 dispersoid to the CaF_2 phase, first the effect of an

Table 1. Electrical conductivity at 400°C (σ_{400}) and 700°C (σ_{700}) of the samples prepared by sintering the powders obtained by mixing of CaF_2 and α-Al_2O_3 powders

m/o α-Al_2O_3	σ_{400} $(\Omega.\mathrm{cm})^{-1}$	σ_{700} $(\Omega.\mathrm{cm})^{-1}$	E_a $(\mathrm{kJ.mol^{-1}})$
0	6.27×10^{-7}	2.37×10^{-5}	72.1
1.0	5.67×10^{-6}	1.71×10^{-4}	68.0
1.5	1.36×10^{-5}	3.56×10^{-4}	65.5
2.5	3.86×10^{-5}	9.42×10^{-4}	64.2
3.5	2.70×10^{-5}	7.86×10^{-4}	67.0
5.0	2.29×10^{-5}	7.05×10^{-4}	68.4
7.5	1.22×10^{-7}	4.25×10^{-6}	71.2
10.0	—	1.42×10^{-6}	—
25.0	—	2.69×10^{-7}	—

Table 2. Electrical conductivity at 400°C (σ_{400}) and 700°C (σ_{700}) of the samples prepared by sintering the powders obtained by mixing of CaF_2 and the aluminate salt of 8-hydroxyquinoline powders

m/o α-Al_2O_3	σ_{400} $(\Omega.\mathrm{cm})^{-1}$	σ_{700} $(\Omega.\mathrm{cm})^{-1}$	E_a $(\mathrm{kJ.mol^{-1}})$
0	6.27×10^{-7}	2.37×10^{-5}	72.1
0.1	1.20×10^{-6}	4.16×10^{-5}	70.6
0.5	2.25×10^{-6}	7.50×10^{-5}	69.2
1.0	7.52×10^{-6}	2.12×10^{-4}	66.8
1.5	3.37×10^{-5}	8.74×10^{-4}	65.3
2.0	1.14×10^{-4}	2.65×10^{-3}	63.4
2.5	1.46×10^{-4}	3.28×10^{-3}	62.7
3.5	7.27×10^{-5}	1.96×10^{-3}	65.9
5.0	2.91×10^{-5}	9.95×10^{-4}	70.3

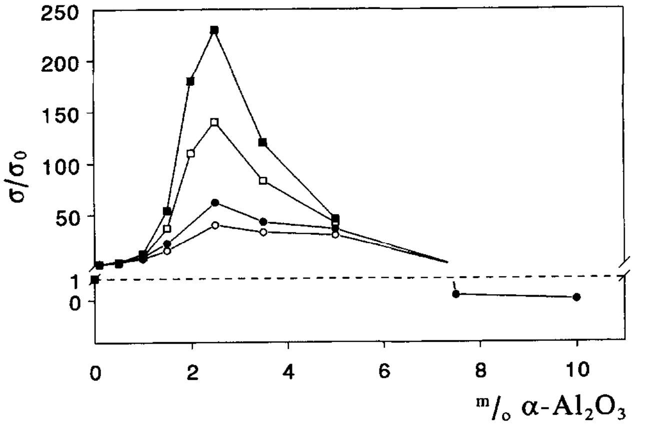

Fig. 1. The relative electrical conductivity (σ/σ_0) of the ($CaF_2+\alpha$-Al_2O_3) composites as a function of α-Al_2O_3 content. ○, ●, σ/σ_0 for the samples obtained directly from CaF_2 and α-Al_2O_3 powders at 400 and 700°C, respectively. ■, □, σ/σ_0 for the samples prepared using aluminium salt of 8-hydroxyquinoline at 400 and 700°C, respectively.

enhanced carrier concentration within the interfacial space-charge layers, caused by a presence of particles of an α-Al_2O_3 insulating phase, may be taken into account. In this way, an increase in conductivity of the samples with increasing α-Al_2O_3 content can be explained. However, at a higher concentration, the α-Al_2O_3 particles may block conductions path in the composite, and thus, they decrease its conductivity, as was observed by us for the samples containing more than 5.0 m/o α-Al_2O_3.

4.3 The contribution of the ionic conductivity

Pure CaF_2 is known as a solid electrolyte to determine fluorine activity in a high-temperature system.[2] However, the use of a CaF_2 to measure differences in oxygen activities in a galvanic cell was presented and clarified by Chou and Rapp.[34] In this type of galvanic cell, the fluorine ions are involved in both the electrode reactions and in conduction process in the electrolyte. The two half-cell reactions in the cell (10) are:

$$NiO + CaF_2 + 2e^- = CaO + Ni + 2F^- \qquad (15a)$$

$$CaO + 2Cu + 2F^- = Cu_2O + CaF_2 + 2e^- \qquad (15b)$$

and fluorine ions move from the right half-cell to the left half-cell through the calcium fluoride electrolyte. For the passage of 2 F of electricity, the virtual cell reaction is:

$$NiO + 2Cu = Ni + Cu_2O. \qquad (16)$$

Alternatively, the overall cell reaction (16) could be presented by an equation:

$$\frac{1}{2}\,O_2\,(Cu,\ Cu_2O) = \frac{1}{2}\,O_2\,(Ni,\ NiO), \qquad (17)$$

expressing the transport of oxygen from the mixture (Cu, Cu_2O), being in thermodynamic equilibrium, to the other one (Ni, NiO). Thus, CaF_2 electrolyte may be employed in combination with oxide half-cells and provides cell potential in the same way as with an oxygen ion conductor such as stabilized zirconia, which is generally used in solid-state oxide galvanic cells.[2,3] The half-cell reactions (15a) and (15b) indicate the formation of CaO at the electrolyte–electrode interfaces; the CaO phase relates the oxygen activity to the calcium activity which in turn produces a defined fluorine activity.

The results of emf measurements, E, at temperatures 700, 800 and 900°C are presented in Table 3 for pure CaF_2 and for six selected samples obtained by use of the organic precursor. They are compared with the emf, E_t, of the cell (10) involving fully calcia stabilized zirconia electrolyte, being purely an oxygen ion conductor. E_t values were calculated on the basis of data given in Ref. 35. Table 3 also shows the values of coefficients $t_i = E/E_t$, related to the fluorine ion transference number in the samples. As results from Table 3 for all samples, except of that containing 5.0 m/o, t_i assumes the values that are close to unity. Similar behaviour was found for the samples sintered from the mixture of CaF_2 and α-Al_2O_3 with α-alumina content in the range of 0–2.5 m/o. Thus, the materials prepared behave like good solid electrolytes in concentrations of α-Al_2O_3 up to 2.5 m/o.

Table 3. Emf of the cell (11), *E*, and the effective ionic transference numbers (E/E_t) at temperatures 700, 800 and 900°C

m/o α-Al_2O_3	E (mV)			E/E_t		
	700°C	800°C	900°C	700°C	800°C	900°C
0	262.9	264.3	263.4	0.97	0.99	1.00
0.5	265.6	261.7	260.5	0.98	0.98	0.99
1.0	262.8	259.0	260.3	0.97	0.97	0.99
1.5	268.3	266.3	262.8	0.99	0.99	1.00
2.0	268.5	266.4	263.2	0.99	0.99	1.00
2.5	271.1	268.0	263.3	1.00	1.00	1.00
5.0	257.4	253.8	252.5	0.95	0.95	0.96

4.4 The determination of the Gibbs free energy of formation (from oxides) for $CaSiO_3$

As a solid electrolyte in the cell (11), a CaF_2 sample containing 2.5 m/o Al_2O_3 was applied. The reactions in the cell (11) can be written as:

a left half cell :

$$CaF_2 + \frac{1}{2} O_2 + 2e^- = CaO + 2F^- \qquad (18a)$$

a right half cell :

$$\begin{aligned} 2CaO + SiO_2 + 2F^- &= \\ CaF_2 + CaSiO_3 + \frac{1}{2} O_2 + 2e^- & \end{aligned} \qquad (18b)$$

the overal cell reaction :

$$CaO + SiO_2 = CaSiO_3. \qquad (19)$$

Thus, the cell reaction is the reaction of formation of 1 mol $CaSiO_3$ from oxides, and the respective standard molar Gibbs free energy, $\Delta_f G^0{}_{ox}$ ($CaSiO_3$), can be calculated on the basis of the emf values of the cell (11), E_{11}, from a formula:

$$\Delta_f G^0_{ox}(CaSiO_3) = 2 \cdot F \cdot E_{11} \qquad (20)$$

In Table 4, $\Delta_f G^0$ox ($CaSiO_3$) determined at 700°C is presented and compared with other literature data.[33,36–38] The values taken from Refs 33 and 36 were determined from emf measurements of galvanic cells involving various solid electrolytes. The results obtained by us do not differ significantly from those presented in the cited papers.

5 CONCLUSIONS

The conducting properties of CaF_2 electrolyte might be improved by an introduction of α-Al_2O_3 as a disperse phase. The properties of the composite electrolytes prepared by two methods differed from each other. The samples in which α-Al_2O_3 was obtained from an organic precursor exhibited higher electrical conductivities than those of the same composition, prepared by direct sintering the mixture of CaF_2 and α-Al_2O_3 powders. The conductivities appeared to be purely ionic and depended markedly on the α-Al_2O_3 content. A significant increase (up to two orders of magnitude) in conductivity in the range 0–2.5 m/o α-Al_2O_3 for both series of the samples prepared was observed. Although the materials prepared were fluorine ion conductors, they were applied successfully in solid-state oxide galvanic cells in the temperature range of 700–900°C. Thus, the CaF_2 based composites containing up to 2.5 m/o α-Al_2O_3 disperse phase seem to be promising electrolytes for electrochemical devices working at moderate and higher temperatures.

Table 4. Standard free enthalpy of $CaSiO_3$ formation (from CaO and SiO_2 oxides), $\Delta_f G_{ox}{}^0$ ($CaSiO_3$) at a temperature of 700°C

Reference	$-\Delta_f G_{ox}{}^0$ ($CaSiO_3$) (kJ.mol^{-1})
This work	89.0±2.9
33	89.7±2.1
36	88.7±0.8
37	91.2±4.2
38	85.6±4.0

ACKNOWLEDGEMENT

This work was carried out under contract no. 7 TO8D 013 08 with the Polish Scientific Research Committee.

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