

The mobility of oxygen ions in CaF₂

R. AKILA, K. T. JACOB

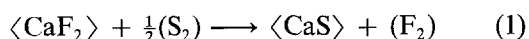
Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India

Received 30 January 1989; revised 9 June 1989

The a.c. conductivity of CaF₂ samples containing a fine dispersion of CaO particles has been measured in the temperature range 630 to 1100 K. The conductivity of the dispersed solid electrolyte is two orders of magnitude higher than that for pure polycrystalline CaF₂ in the middle of the temperature range. Transport measurements on pure single crystals of CaF₂ and polycrystalline samples, with and without CaO dispersion, using Fe + FeO and pure Fe as electrodes, clearly indicate that fluorine ions are the only migrating ionic species with a transport number of almost unity, contrary to the suggestion of Chou and Rapp [1, 2]. The enhanced conductivity of the dispersed solid electrolyte probably arises from two effects. A small solubility of oxygen in CaF₂ results in an increase in the fluorine vacancy concentration and conductivity. Adsorption of fluorine ions on the surface of the dispersed particles of CaO results in a space charge region around each particle with enhanced conductivity. Measurements on a galvanic cell incorporating CaF₂ as the solid electrolyte and oxide electrodes show that the e.m.f. is a function of the activity of CaO at the electrode/electrolyte interface. The response to an oxygen potential gradient is, therefore, through an exchange reaction, which establishes an equivalent fluorine potential at the electrode/electrolyte interface.

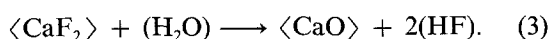
1. Introduction

Calcium fluoride is a solid electrolyte in which the mobility of fluorine interstitials and vacancies is much higher than that of calcium ions [1-5]. Calcium fluoride has been extensively used in galvanic cells for the measurement of fluorine potential [6, 7]. It has also been employed in solid state cells for the measurement of chemical potentials of oxygen [8-10] and sulphur [11]. The response to sulphur is accomplished by the use of CaS as an auxiliary electrode. The mutual solubility between CaF₂ and CaS is negligible. The chemical potential of sulphur is converted into an equivalent chemical potential of fluorine by virtue of the exchange reaction

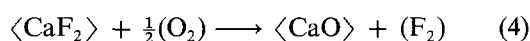


$$\Delta\mu_{\text{F}_2} = \frac{1}{2}\Delta\mu_{\text{S}_2} - \Delta G_1^0 \quad (2)$$

where the symbol $\langle \rangle$ denotes a solid, $()$ represents a gas and ΔG_1^0 is the standard Gibbs' energy change for Reaction 1. Even when CaO is not used intentionally as an auxiliary electrode, cells based on CaF₂ give a Nernstian response to an oxygen potential difference at the electrodes [8-10]. Following the mechanism suggested by Jacob *et al.* [11] for the sulphur sensor, Ramanarayanan *et al.* [10] have suggested that in oxygen containing atmospheres at high temperature, a small amount of CaO is formed *in situ* on the electrolyte surface. Fine precipitates of CaO are also often present in translucent single crystals of CaF₂. Energetically the most likely reaction producing CaO precipitates is



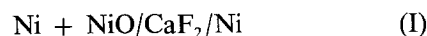
When CaO is present, it can act as an auxiliary electrode, converting the partial pressure of oxygen into an equivalent partial pressure of fluorine, by virtue of the exchange reaction



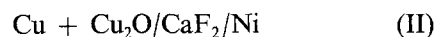
$$P_{\text{F}_2} = K_4 P_{\text{O}_2}^{1/2} \quad (5)$$

where K_4 is the equilibrium constant for Reaction 4.

On the contrary, Chou and Rapp [8, 9] have suggested that in oxygen bearing atmospheres, oxygen ions substitute for fluorine ions in the CaF₂ lattice, producing fluorine vacancies for charge compensation. According to Chou and Rapp, the oxygen ions are mobile in CaF₂ and are responsible for the e.m.f. when an oxygen potential difference is established across the electrolyte. Their conclusion is based on titration experiments using the cells [9].



and



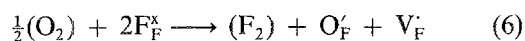
where the Ni electrode was positive. After the titration, green NiO was found on the Ni electrode. An oxygen transport number of 0.31 at 1235 K was calculated.

Complex admittance measurements in argon and oxygen atmospheres in the frequency range 20 Hz to 20 kHz were also performed by Chou and Rapp [9] using the cell arrangement



In the temperature range from 625 to 1250 K, the bulk conductivity of single crystal CaF₂ was higher in argon atmosphere ($P_{\text{O}_2} \approx 10$ Pa) than in argon

($P_{O_2} \approx 10^{-10}$ Pa). The highest conductivity was shown by a CaF₂ crystal preheated in pure oxygen at 1161 K for 3 days and measured in an argon atmosphere. In d.c. experiments, where the variation of current with time was recorded for a fixed d.c. voltage across the CaF₂ electrolyte, an increasing current was measured as the oxygen partial pressure at one of the electrodes was increased. It was suggested that in oxygen atmosphere, oxygen enters the CaF₂ crystal through the following redox reaction on the Pt electrode



The increased current was attributed to the conduction of oxygen ions or an electronic species in CaF₂.

The influence of the oxygen partial pressure on the electrical conductivity of single crystal CaF₂ has also been studied by Levitskii *et al.* [12]. The atmosphere around the cell varied between a reducing CO/CO₂ environment to one of pure oxygen at unit atmospheric pressure. The electrical conductivity of pure CaF₂ was found to increase as the oxygen partial pressure of the atmosphere increased. The conductivity increase has been suggested to result from an increased fluorine vacancy concentration caused by the substitution of oxygen for fluorine ions in the CaF₂ lattice.

Recent investigations [13–15] have shown that the electrical conductivity of pure CaF₂ can also be enhanced by dispersion of second phase insulating oxides in the CaF₂ matrix. Addition of 2 mol % Al₂O₃ increased the conductivity of pure single crystal CaF₂ by about two orders of magnitude at 650 K. An enhancement by about three orders of magnitude was obtained by the addition of 2 mol % CeO_{2-x} [15]. Following the explanation of Maier [16, 17] for silver halides containing oxide dispersions, Vaidehi *et al.* [15] have suggested that the enhancement effect in oxide dispersed CaF₂ is due to the conductivity contribution from the space charge regions around the second phase particles. These regions contain an increased concentration of fluorine ion vacancies. Hence an enhancement in conductivity of CaF₂ may arise from an increase in fluorine defect species, produced by homogeneous doping, and/or dispersion of a secondary oxide phase in the CaF₂ matrix.

If oxygen ions entering the CaF₂ lattice are indeed mobile, CaF₂ can be used in fuel cells. It is therefore important to establish firmly whether mixed anionic (fluorine and oxygen) conduction is possible in CaF₂. Three independent sets of experiments were performed in this study. First the a.c. conductivity of polycrystalline CaF₂, with and without a dispersion of fine CaO particles, was measured as a function of temperature. Next, transport measurements were undertaken using pure single crystals of CaF₂ as well as polycrystalline specimens with and without CaO dispersion. Current was passed from a pure Fe electrode to an Fe + FeO electrode, which provided a source of oxygen at constant partial pressure. The Fe electrode was examined after the titration to identify the migrating ion and the transport number. Finally,

the e.m.f. of a galvanic cell, using pure CaF₂ as the solid electrolyte and Ni + Ni₂SiO₄ + SiO₂ and Ni + NiO as the electrodes, was monitored as a function of time. The three-phase electrode was designed to provide a constant oxygen potential and varying activity of CaO as a result of interaction between SiO₂ and the small CaO precipitates on the surface of the CaF₂ crystal.

2. Experimental

2.1. Materials

Optical grade single-crystal CaF₂ rods 12.7 mm diameter were obtained from Harshaw Chemical Company. Pellets (4 mm thick) were cut from the rods using a diamond wheel. Fine powders of Ni, Fe, Fe₂O₃ and NiO (puratronic grade) were obtained from Johnson Matthey Chemicals and quartz form of silica (99.9% purity) from Ventron. A pellet containing Fe + 'FeO' in the molar ratio 1:2 was prepared by mixing Fe and Fe₂O₃ powders in the appropriate ratio followed by compaction and sintering in argon at 1273 K. Since the dissociation pressure of FeO at 1273 K is 1.33×10^{-10} Pa, loss of oxygen is not expected during sintering in argon. Nickel orthosilicate (Ni₂SiO₄) was prepared from high purity silicic acid and nickel sulphate. Both compounds were heated separately in flowing argon up to 1400 K and their respective mass losses were determined. An intimate mixture of the two compounds was then heated up to 1200 K in a platinum crucible in an atmosphere of argon. After quenching, the mixture was ground under acetone, pelletized and fired at 1750 K. The cycle of quenching, pelletizing and firing at 1750 K was repeated four times. The mixture was held at 1750 K for five days. X-ray diffraction analysis revealed that the product was single-phase Ni₂SiO₄.

To prepare CaF₂ samples containing 2 mol % CaO as a fine dispersion, calcium fluoride and calcium oxide powders in proportionate amounts were ground together to form an intimate mixture, which was then pelletized and sintered under argon. Argon gas was purified by passing over phosphorus pentoxide and then over copper turnings at 750 K and titanium granules at 1150 K. X-ray diffraction of CaF₂ samples containing CaO clearly identified them as two-phase mixtures.

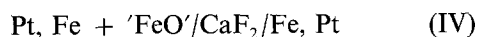
2.2. Cell assembly and experimental procedure

2.2.1. Conductivity measurements. Pellets of pure polycrystalline CaF₂ and of the two-phase CaF₂-2 mol % CaO mixture were prepared by double end compression in a steel die. The cold pressed pellets were sintered at 1100 K in purified argon atmosphere. The grain sizes of the sintered pellets, as determined from SEM measurements, were $\sim 37 \mu\text{m}$ for pure CaF₂ and $\sim 27 \mu\text{m}$ for the two-phase mixture. The oxide particles were mainly dispersed along the grain boundaries.

The electrodes for conductivity measurements were

prepared by coating platinum paste (Engelhardt T 1150) on both flat surfaces of the sintered pellets. The electrodes were then fired in air to burn off organic binders and to promote adhesion. Electrical connections were provided by platinum leads connected to platinum foils which were spring loaded on the electrode surfaces. The conductivity was measured as a function of temperature in the range 630 K to 1100 K at a fixed frequency of 2 kHz in a purified argon atmosphere.

2.2.2. Titration cell. The titration cell was assembled with a CaF_2 pellet, on one side of which was a sputtered Fe layer 10 μm thick. This served as the positive electrode. A sintered electrode pellet containing Fe + 'FeO' in the molar ratio 1:2 served as the negative electrode. The flat surfaces of the pellets were polished to provide good contact. Electrical connections to the two electrodes were provided by Pt foils spring loaded to contact the electrodes. Platinum leads were attached to the foils. The cell arrangement can be represented as



The cell was heated to 1100 K. A steady current of $80 \mu\text{A cm}^{-2}$ was passed through the cell for 6 ks and then switched off. The variation of e.m.f. with time was followed both during and after the passage of current. The cycle was repeated after the open circuit e.m.f. reached a steady-state value. At the end of the experiment, the Fe electrode was subjected to microscopic examination and X-ray diffraction analysis. The experiments were carried out using single crystal CaF_2 , polycrystalline CaF_2 and polycrystalline CaF_2 with a fine dispersion of CaO. Since the sputtered Fe electrode was adherent to the solid electrolyte it was difficult to separate them. In a few experiments

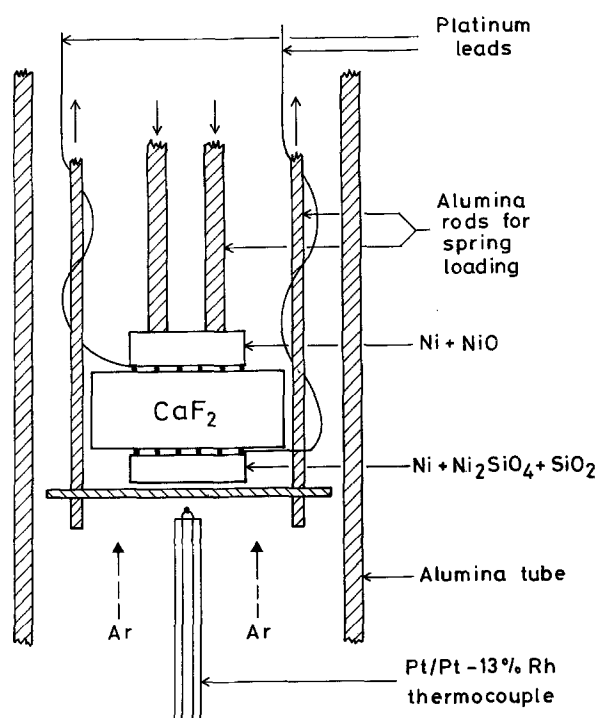
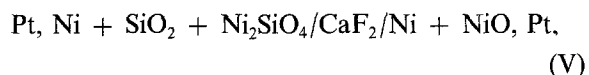


Fig. 1. A schematic diagram of the assembly of Cell V.

designed for quantitative measurement of transport number, two pellets of CaF_2 were used in series and the total weight gain of the CaF_2 pellet with the iron electrode was measured.

2.2.3. E.m.f. cell. A schematic diagram of the cell arrangement used for the e.m.f. study is shown in Fig. 1. the cell comprised a single-crystal CaF_2 pellet sandwiched between a Ni + NiO pellet and a three-phase Ni + SiO_2 + Ni_2SiO_4 pellet. The cell can be represented as



A stacked pellet assembly was used because long CaF_2 tubes were not available. The electrodes were prepared by mixing the components in an equimolar ratio and compacting by double end compression in a steel die. The cold pressed pellets had diameters of 15 mm and thicknesses in the range 2 to 4 mm. The Ni + NiO pellet was sintered for 28 ks at 1400 K and the three-phase electrode was sintered at 1250 K in purified argon. Heat treatment of the three-phase electrode at higher temperature converts high quartz to other crystallographic forms and results in a mixture of allotropic forms of SiO_2 in the pellet. A Pt gauze to which a Pt lead was spot welded was inserted between the electrolyte pellet and the electrodes on either side. The entire cell assembly was spring loaded by a set of alumina rods and slabs.

The assembly was placed in a vertical furnace heated by a resistance winding of Kanthal wire,

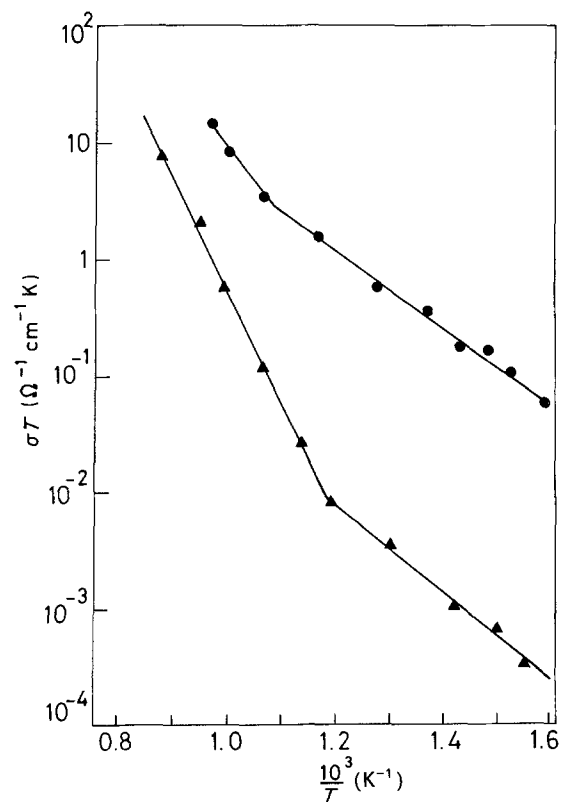


Fig. 2. Variation of conductivity with reciprocal of the absolute temperature for pure polycrystalline CaF_2 (\blacktriangle) and CaF_2 containing a dispersion of 2 mol% CaO (\bullet).

The temperature of the furnace was controlled to within ± 1 K by a proportional controller. Cell temperatures were monitored by a Pt/Pt-13% Rh thermocouple placed close to the cell assembly. Cell e.m.f.'s were measured with a Princeton Applied Research (Model 136) high impedance voltmeter with an input impedance of $10^{14} \Omega$ and a digital display with the least significant digit corresponding to 0.1 mV.

A single stream of purified argon gas flowed over both the electrodes. Mass transport of oxygen via the gas phase was not expected to be significant under the experimental conditions since at each electrode, $P_{\text{O}_2} < 10^{-5}$ Pa at 1300 K. The cell e.m.f. was found to be independent of the flow rate of argon in the range 1 to 4 ml s^{-1} .

Cell reversibility was checked by passing small currents of approximately $10 \mu\text{A}$ through the cell in either direction for ~ 30 s. In each case, the e.m.f. was found to return to the original value before microcoulometric titration, showing that the cell was not polarized. The uniformity of cell temperature was checked by assembling a symmetric cell with Ni + NiO electrodes on both sides. At 1300 K, the e.m.f. across the cell was found to be $0(\pm 0.2)$ mV without any systematic trends, showing that there was no thermal gradient across the cell.

3. Results

3.1. Conductivity measurements

The measured conductivities of pure single and polycrystalline CaF_2 and CaF_2 containing 2 mol % CaO vary with the reciprocal of the absolute temperature as shown in Fig. 2. At 630 K, the enhancement in conductivity of polycrystalline CaF_2 by dispersion of fine particles of CaO (2 mol %) is by a factor of ~ 200 , while at 1100 K, the enhancement is by a factor of ~ 15 . The slope of the 'extrinsic' branch of the conductivity plot for the heterogeneously doped $\text{CaF}_2 + 2 \text{ mol } \% \text{ CaO}$ sample is 0.66 eV.

3.2. Titration studies

The change in the voltage with time across Cell IV, using single crystal CaF_2 , is shown in Fig. 3. The voltage increased during current flow, probably as a result of polarization of the electrodes, and decreased when the current was switched off. A final steady-state e.m.f. of 820 mV was obtained in 1.2 ks. During the second titration cycle, the rate of change of e.m.f. with time was slower, but the final steady-state value was the same. X-ray diffraction of the Fe electrode at the end of the experiment confirmed the presence of FeF_2 at this electrode. The single crystal CaF_2 electrolyte surface which had been in contact with the Fe + FeO electrode was more opaque than the bulk.

Results of coulometric titrations using pure polycrystalline CaF_2 and CaF_2 containing dispersed CaO were similar to that for single crystals. With cells containing two pellets of CaF_2 in series, the weight

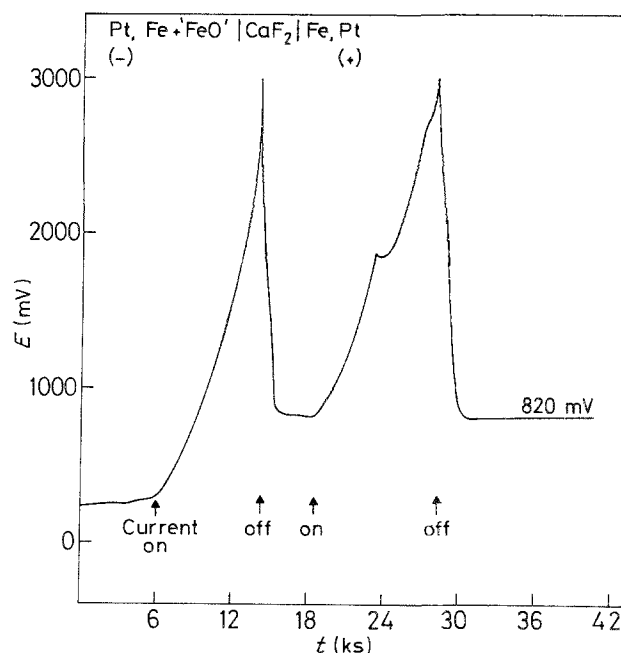


Fig. 3. Variation of the voltage of Cell IV, incorporating single crystal CaF_2 , with time during and after coulometric titration at 1100 K.

gain of the anodic pellet after titration revealed that the transport number of fluorine ions was $1(\pm 0.03)$.

3.3. E.m.f. measurements

A typical plot of the time dependence of the e.m.f. for Cell V at 975 K is shown in Fig. 4. A similar behaviour was seen at higher temperatures. The zero time on the graph corresponds to the time at which the e.m.f. reached a steady-state value at the particular temperature. Initially, the e.m.f. was 20 mV; with the passage of time, it decreased and changed polarity. Three

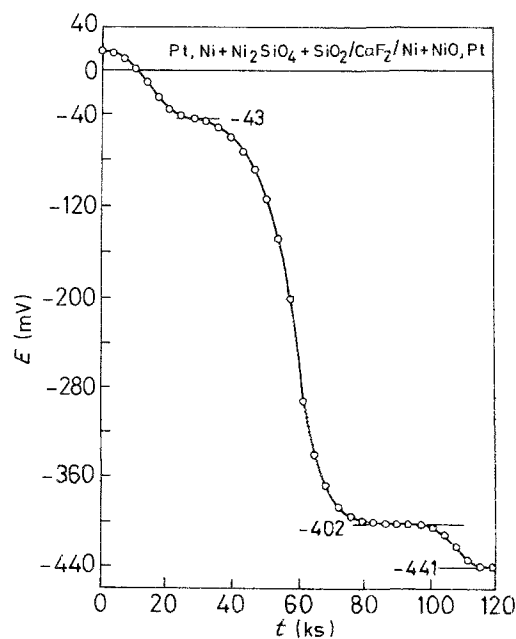


Fig. 4. The complex time dependence of the e.m.f. of Cell V at 975 K. The initial e.m.f. corresponds to the presence of pure CaO at the interface between the electrolyte and the three-phase electrode. The plateau regions correspond to the coexistence of various calcium silicates.

plateau regions were recorded at 975 K, at -43 mV, -402 mV and -441 mV. The e.m.f. remained steady at -441 mV ($+2$ mV) for up to 20 ks. Coulometric titration with currents of $10 \mu\text{A}$ or an increase in cell temperature to 1300 K. resulted in only small changes (± 5 mV) in the final steady-state e.m.f.

At the end of the experiment, the CaF_2 crystal had a milky white appearance and showed the presence of precipitate particles on the electrolyte surface contacting the three-phase electrode. These precipitate particles were identified as CaSiO_3 by selected area electron diffraction.

4. Discussion

4.1. Conductivity measurements

A qualitative explanation of the conductivity enhancement in CaF_2 on addition of 2 mol % CaO may be given based on a theoretical model recently proposed by Maier [16]. The model assumes that in solid electrolytes containing dispersed second phases, the conducting ionic species in the solid electrolyte may be attracted or repelled by the surface of the second phase particles. This results in a space charge region around each second phase particle with an enhanced concentration of vacancies or interstitials as compared to the bulk value. The additional contribution to the conductivity from the space charge region increases the total conductivity. In the present case of CaF_2 containing 2 mol % CaO, the activation energy (0.66 eV) of the 'extrinsic' branch of the conductivity plot is close to the bulk fluorine vacancy migration enthalpy (0.51 eV) [2]. This suggests that fluorine vacancies are the species whose concentration in the space charge region is enhanced and which contribute to an increase in the total conductivity. According to the model, the enhancement effect is significant only at lower temperatures. In the present study, an enhancement in conductivity was seen even at higher temperatures, in contrast to the observed behaviour in silver halides containing oxide phases [16, 17]. The high temperature effect probably arises from a small solubility of oxygen in the CaF_2 lattice, producing charge compensating fluorine vacancies and thereby increasing the total conductivity. Hence the conductivity increase of pure CaF_2 containing a dispersion of 2 mol % CaO may be attributed to an increase in fluorine vacancy concentration both in the bulk and in the space charge regions around the second phase oxide particles.

4.2. Titration studies

Figure 3 shows that during coulometric titration using Cell IV, the e.m.f. increases during the passage of current, probably owing to depletion of fluorine at the cathode which can polarize this electrode. Once the current is switched off, the e.m.f. drops to a steady-state value of ~ 820 mV. If FeO had formed at the sputtered Fe electrode by migration of oxygen ions

from the Fe + FeO cathode during current flow, the final steady-state value should have been zero. However, the e.m.f. showed a constant value of 820 mV. In addition, only Fe and FeF_2 could be detected by X-ray diffraction of the Fe electrode at the conclusion of the experiment.

Since only fluorine was transported through the CaF_2 electrolyte and the electrode did not contain fluorine, the fluorine must have been generated by an exchange reaction between CaF_2 and oxygen from the electrode according to Reaction 4. The oxygen partial pressure at the cathode is fixed by the Fe + FeO coexistence. Assuming unit activities for CaO and CaF_2 and using the values for the free energies of formation of CaO and CaF_2 from Janaf [18] and of 'FeO' from Steele [19] at 1100 K, the chemical potential of fluorine at the cathode is calculated to be $-712810 \text{ J mol}^{-1}$. At the anode the dissociation of FeF_2 establishes a unique fluorine potential corresponding to the Fe + FeF_2 coexistence. This fluorine potential is $-554420 \text{ J mol}^{-1}$ [18]. Using the Nernst expression, the theoretical open circuit e.m.f. across the cell is then obtained as

$$E = \Delta\mu_{\text{F}_2}/2F = 818.7 \text{ mV} \quad (7)$$

The good agreement with the experimental steady-state e.m.f. justifies the validity of the proposed mechanism for the generation of fluorine ions at the Fe + FeO electrode. The milky white appearance of single crystal CaF_2 near the Fe + FeO electrode is probably a result of the precipitation of CaO.

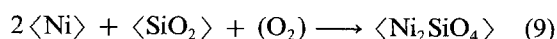
The conclusions drawn from the present experiment are in stark contrast to the results of Chou and Rapp [2], who suggest significant mobility for oxygen ions in CaF_2 . Although the ionic sizes of O^{2-} and F^- ions are close, the higher charge on O^{2-} is likely to result in a higher activation energy for migration, a point overlooked by Chou and Rapp.

4.3. E.m.f. measurements

The initial open circuit e.m.f. (20 mV) of Cell V closely agrees with a value of 19.4 mV obtained with a similar cell using $(\text{Y}_2\text{O}_3)\text{ZrO}_2$ as the solid electrolyte [20] rather than CaF_2 . Yttria-stabilized zirconia is an oxygen ion conductor used for measuring oxygen chemical potential. At the Ni + NiO cathode, the oxygen partial pressure is fixed by the Ni + NiO coexistence. From the free energy of formation of NiO [19]

$$\Delta G_f^0(\text{NiO}) = -234160 + 84.89T (\pm 600) \text{ J mol}^{-1} \quad (8)$$

the equilibrium oxygen partial pressure can be calculated. At the three-phase electrode, the oxygen potential is defined by the reaction



for which Jacob *et al.* [20] give

$$\Delta G_9^0 = -481180 + 175.5T (\pm 1000) \text{ J mol}^{-1} \quad (10)$$

The e.m.f. of Cell V may be explained by assuming the presence of small precipitates of CaO on the surface of CaF₂. The oxygen chemical potential gradient is then converted to an equivalent gradient in fluorine chemical potential, by virtue of Reaction 4. Calcium oxide on the surface of the CaF₂ crystal would initially be at unit activity at both electrodes. Hence, at the beginning of the experiment, the CaF₂ electrolyte correctly responds to the oxygen partial pressure difference at the electrodes.

The time dependence of the e.m.f. shows that a chemical reaction was occurring at one of the electrode/electrolyte interfaces, altering the fluorine chemical potential at that electrode. If CaF₂ was an oxygen ion conductor, the e.m.f. should have remained at the initial value, as the partial pressures of oxygen at the electrodes are not altered. However, if the exchange Reaction 4 is the basis for measurement of oxygen chemical potential by a CaF₂ electrolyte, then a changing activity of CaO at the electrode/electrolyte interface can alter the fluorine chemical potential at this electrode and hence the e.m.f. across the electrolyte.

The calcium oxide present on the CaF₂ crystal at the Ni + NiO electrode would remain at unit activity since the mutual solubilities between NiO, CaO and CaF₂ are negligible. However, at the three-phase electrode, the fine precipitates of CaO can react with the large excess of SiO₂ in the electrode. The phase diagram for the CaO–SiO₂ system [21] shows that three stable silicate phases, Ca₂SiO₄, Ca₃Si₂O₇ and CaSiO₃, can form in the order of increasing silica content. It is reasonable to assume that the small amount of CaO present as fine precipitates in CaF₂ near the electrode/electrolyte interface would gradually disappear by chemical reaction with the much larger quantity of SiO₂ present in the three-phase electrode. The formation of these silicate phases in sequence would decrease the activity of CaO at the three-phase electrode and correspondingly change the equilibrium fluorine chemical potential at this electrode. The activities of CaO in the two-phase fields of the CaO–SiO₂ system at 973 K measured by Benz and Wagner [22] are given in Table 1, along with the corresponding decreases in e.m.f. The sum of the initial e.m.f. and the decrease in e.m.f. due to reduced activity of CaO agrees well (± 2 mV) with the e.m.f. values recorded for each of the plateau regions. This shows that the e.m.f. is dependent on the activity of CaO at the electrode/electrolyte interface. The oxygen potential response of cells using CaF₂ as the solid electrolyte therefore occurs as a result of the exchange reaction which defines an equivalent fluorine potential.

5. Conclusion

The enhanced conductivity of CaF₂ containing a fine dispersion of CaO is predominantly due to the migration of fluorine ions. A small amount of dissolved oxygen increases the fluorine vacancy concentration and hence the bulk conductivity. The adsorption of fluorine ions on the surface of CaO particles results in

Table 1. Chemical potentials of CaO [22] and change in e.m.f. of cell V for different phase mixtures of the CaO–SiO₂ system at the electrode/electrolyte interface at 973 K

Phase mixture	$\Delta\mu_{\text{CaO}}(\text{kJ mol}^{-1})$	$\Delta E(\text{mV})$
CaO + Ca ₂ SiO ₄	0	0
Ca ₂ SiO ₄ + Ca ₃ Si ₂ O ₇	–11.72	–60.7
Ca ₃ Si ₂ O ₇ + CaSiO ₃	–80.75	–418.4
CaSiO ₃ + SiO ₂	–89.12	–461.8

a diffuse space charge region characterized by a higher fluorine vacancy concentration and conductivity. Both mechanism probably contribute to the phenomenal increase in conductivity, with the space charge contribution predominating at lower temperatures.

Calcium fluoride, which is a fluorine ion conductor, can also be used to measure oxygen chemical potentials. Chou and Rapp [1, 2] have suggested that the mobility of oxygen ions in CaF₂ accounts for the Nernstian response of CaF₂ to a gradient in oxygen chemical potential across the electrolyte. In the present study, no evidence for oxygen ion transport in CaF₂ was found. The oxygen potential response is shown to arise from the presence of CaO at the electrode/electrolyte interface, which converts the oxygen potential into an equivalent fluorine potential through an exchange reaction. This hypothesis is proved by the fact that the e.m.f. of a cell with a CaF₂ electrolyte and oxide electrodes is dependent on the activity of CaO established at the interface between the electrode and electrolyte.

References

- [1] R. W. Ure Jr, *J. Chem. Phys.* **26** (1957) 1363.
- [2] W. Bollmann and H. Henninger, *Phys. Stat. Sol. (a)* **11** (1973) 367.
- [3] *Idem, ibid.* **16** (1973) 187.
- [4] L. E. Nagel and M. O'Keefe, in 'Fast Ion Transport in Solids' (edited by W. Van Gool), North Holland, Amsterdam (1973) p. 165.
- [5] J. M. Reau and J. Portier, in 'Solid Electrolytes' (edited by P. Hagenmuller and W. Van Gool), Academic Press, New York (1978) p. 313.
- [6] T. L. Markin, in 'E.m.f. Measurements in High Temperature Systems' (edited by C. B. Alcock), The Institution of Mining and Metallurgy, London (1968) p. 91.
- [7] T. N. Rezhikhina and T. F. Sisoeva, *J. Chem. Thermody.* **11** (1979) 1095.
- [8] S. F. Chou and R. A. Rapp, in 'High Temperature Metal Halide Chemistry' (edited by D. L. Hildenbrand and D. D. Cubicciotti), The Electrochemical Society, N.J. (1978) p. 392.
- [9] *Idem, J. Electrochem. Soc.* **130** (1983) 506.
- [10] T. A. Ramanarayanan, M. L. Narula and W. L. Worrell, *ibid.* **126** (1979) 1360.
- [11] K. T. Jacob, D. B. Rao and H. G. Nelson, *ibid.* **125** (1978) 758.
- [12] V. Levitskii, A. Hammou, M. Dulcot and C. Deportes, *J. Chim. Phys.* **73** (1976) 305.
- [13] S. Fujitsu, M. Miyayama, K. Koumoto, H. Yanagida and T. Kanazawa, *J. Mater. Sci.* **20** (1985) 2103.
- [14] A. Khandkar, V. B. Tare and J. B. Wagner Jr, *Rev. Chim. Minerale* **23** (1986) 274.
- [15] N. Vaidehi, R. Akila, A. K. Shukla and K. T. Jacob, *Mater. Res. Bull.* **21** (1986) 909.
- [16] J. Maier, *J. Phys. Chem. Solids* **46** (1985) 309.
- [17] J. Maier, *Mater. Res. Bull.* **20** (1985) 383.
- [18] D. R. Stull *et al.*, 'JANAF Thermochemical Tables', 2nd

-
- edn, NSRDS-NBS 37, US Dept. of Commerce, Washington D.C. (1971).
- [19] B. C. H. Steele, in 'Electromotive Force Measurements in High Temperature Systems' (edited by C. B. Alcock), The Institution of Mining and Metallurgy, London (1968) p. 3.
- [20] K. T. Jacob, G. M. Kale, R. Akila and A. K. Shukla, *High Temp. Mater. Processes* **7** (1986) 141.
- [21] E. M. Levin and H. F. McMurdie, 'Phase Diagrams for Ceramists', Supplements, Am. Ceram. Soc. (1969) and (1975).
- [22] R. Benz and C. Wagner, *J. Phys. Chem.* **65** (1961) 1308.