MASTER

Third Annual Progress Report

Fundamental Studies of Metal Fluorination Reactions

DOE contract No. EY-76-S-02-2671 A001

Principal Investigator:

Professor Robert A. Rapp

Research Associate:

Dr. S.N.S. Reddy

Research Assistants:

S.F. Chou

B.S. Lee

Department of Metallurgical Engineering
The Ohio State University
Columbus, Ohio 43210

January 1978

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EB
2 36376
12

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A. OVERALL PROJECT

1. Personnel - In addition to the Principal Investigator, Professor Robert A. Rapp, five researchers have received full or partial support on this contract during the past year:

a) Dr. S.N.S. Reddy has worked 2.5 years on this contract and intends to complete his commitment at OSU in April or May 78. Dr. Reddy has applied for an immigrant visa and is currently interviewing for an industrial or University position. He has worked with CaF_2 -electrolyte cells to determine the diffusivity and solubility of fluorine in copper and in nickel. He has established the partial electronic conductivities in CaF_2 by the Hebb-Wagner polarization method.

b) W.C. Fang received his M.S. degree in September, 1977 and is currently working at General Electric Corporate Research Laboratory in Schenectady. His visa will permit permanent residency in the United States. His M.S. thesis was entitled, "Electrical Conductivities of Beta-Lead Fluoride." Mr. Fang is currently engaged in electrochemical studies of hot corrosion at G.E.

c) S.F. Chou has completed two years of research on the topic, "Mixed Electrode Reactions in Solid Electrolyte Cells." In October 1977, Mr. Chou successfully passed both the written and oral portions of the Ph.D. general examination. He should complete his thesis research on "Mixed Electrode Reactions" in about another year.

d) B.S. Lee has conducted research on the topic, "Point Defects and Conduction in Pure and Doped Nickel Difluoride" for six months. Mr. Lee entered OSU with an M.S. degree in Materials Science from North Carolina State University. He plans to take the Ph.D. general examination in May 1978. Upon passing this exam, about one additional year of research would be required to complete his Ph.D. thesis research.

e) L.E. Lent entered OSU in the Autumn Quarter 1977 with a BS in Metallurgy from Minnesota University. For his three months on the project, he reviewed the literature on scale growth on pure metals, with the intention to initiate experiments with an SEM hot stage. In January 1978, Mr. Lent decided to quit graduate school and seek employment. Insufficient interest (lack of motivation) was given as the reason for the change in plans.

2. Presentations and Publications of Past Year - At the October 1977 meeting of the Electrochemical Society, personnel of this contract presented three papers, each of which have already been submitted as ERDA-427 Form reports:

W.C. Fang and R.A. Rapp, "Electrical Conductivity of Beta Lead Fluoride," (report No. COO-2671-6),

S.N.S. Reddy and R.A. Rapp, "Electronic Conduction in CaF_2 Electrolyte," (report No. COO-2671-4),

S.F. Chou and R.A. Rapp, "Dual Ionic Conductivity in Solid Electrolytes CaF_2 and ZrO_2 (+ CaO)" (report No. COO-2671-5).

Each of these papers has been accepted for publication in the ECS paperback "Proceedings of the Symposium on Metal-Halide

Reactions," Editor D. Cubicciotti (1977).

In addition, an extended version of the paper by Fang and Rapp has been accepted for publication in the Journal Electrochemical Society, and has been previously submitted as ERDA report No. COO-2671-3.

At the October meeting of the ASM-AIME, the following paper was presented:

S.N.S. Reddy and R.A. Rapp, "The Diffusivity and Solubility of Fluorine in Solid Copper." The submission of this paper to Metallurgical Transactions is anticipated in the near future.

Professor Rapp presented, "A Review of Electrical Measurements on Solid Electrolytes" at a ERDA-sponsored workshop on Solid-Electrolyte Fuel Cells at Brookhaven Nat. Lab., May 5-6, 1977.

Professor Rapp presented, "A Review of Corrosion at Elevated Temperatures," at Argonne Nat. Lab on Jan. 13, 1978.

With Professor R.W. Staehle, Professor Rapp presented the AIChE course "Fundamentals of Corrosion" in Houston, March 23-24 and in New York, November 12-13, 1978.

Professor Rapp presented seminars on the topic "High-Temperature Corrosion," to the Cleveland local AIME chapter on April 21, to the University of Delaware on April 26, and to Penn. State University on May 13, 1977.

Professor Rapp was chairman of the Gordon Research Conference on Corrosion in New London, N.H., July 18-22, 1977.

3. Results of Major Significance

(a) Solubility and Diffusivity of Fluorine in Solid-Copper—Dr. S.N.S. Reddy.

In the past year, Dr. Reddy established that the CaF_2 solid electrolyte could be used for kinetic studies. He has

completed potentiostatic electrochemical measurements of fluorine diffusivity in solid copper. These results are given by the equation:

$$D_F^{\text{Cu}} (\text{cm}^2/\text{sec}) = 9.32 \exp\left(\frac{-23,600}{RT}\right)$$

Coulometric titration measurements did not provide sufficiently reproducible values for the solubility of fluorine in solid copper, so again the potentiostatic electrochemical method was used to obtain the values:

$$N_F^{\text{Cu}} (\text{atom fraction}) = 0.98 \exp\left(\frac{-19,000}{RT}\right)$$

These data are the first values for solubility and diffusivity of any halogen in any metal, and therefore represent a significant scientific advance which will assist in further theoretical interpretation of the behavior of gases in metals.

From a practical standpoint, these values for the solubility and diffusivity of fluorine in solid copper are unexpectedly high, comparable to the values for oxygen in solid copper. In the high-temperature reaction of copper-base alloys with fluorine-containing gases, a deleterious internal precipitation of internal fluoride particles must be expected.

(b) The Electronic Conductivity of CaF_2 Electrolyte—Dr. S.N.S. Reddy.

Through the use of the potentiostatic electrochemical method for three different reference electrodes, both the p-type and n-type electronic conductivities have been established for

single crystals of CaF_2 . From a scientific viewpoint, the high magnitude of p-type electronic conduction is unexpected in view of the large band gap energy for CaF_2 .

From the practical standpoint, any electrochemical fuel cell, or battery or machine intended to operate with a cathode at relatively high PF_2 will experience a loss in power and high electrode polarization as a result of the p-type electronic conduction.

(c) Mixed Electrode Reactions in Solid Electrolyte Cells—
S.F. Chou.

Galvanic cells involving the CaF_2 (fluorine-conducting) electrolyte function as oxygen cells when provided with electrodes of differing oxygen potential. Likewise, the oxygen conducting electrolyte ZrO_2 (+CaO) functions as a fluorine electrolyte when provided with electrodes of differing fluorine potential. From a scientific standpoint, such behavior has not been previously studied or explained. Experiments involving electrodes fixing both fluorine and oxygen potentials, as well as conductivity studies, have contributed to a partial understanding of these unusual phenomena. The results are explained in terms of a coupled transport of charged vacancies and neutral anion-vacancy complexes.

From a practical viewpoint, the contamination of a galvanic cell in the laboratory, or of an electrochemical monitor or a high-temperature battery by a second mobile ion in the electrolyte can result in voltage changes, for worse, or perhaps better.

B. TASK SUMMARIES

1. Solubility and Diffusivity of Fluorine in Solid Metals, and Related Experiments (S.N.S. Reddy).

For the past year 1977-78, the electrochemical determination of the solubility N_F and the diffusivity D_F in solid copper and nickel was proposed. Internal fluorination kinetic studies of Cu and Ni alloys were proposed to establish the $N_F D_F$ product. Further, a d.c. polarization method was proposed to establish the partial electronic conductivities of the nominally pure CaF_2 electrolyte.

During this period, accurate and reproducible values for the solubility and diffusivity of fluorine in solid copper were measured by the electrochemical potentiostatic technique. The electronic conductivity of CaF_2 (both p-type and n-type) was measured using d.c. polarization cells.

The problems associated with the initial solubility-diffusivity measurements were caused by electrode polarization, and by non-uniform contact between the metal electrode and the CaF_2 electrolyte. As a result, non-reproducible values for the solubility of fluorine in solid copper were initially obtained. However, the addition of 10 to 15 vol. % CaF_2 to the $\text{Ni}+\text{NiF}_2$ reference electrode minimized the polarization. Bonding of Cu to the CaF_2 electrolyte at temperatures very close to the melting point of Cu resulted in uniform electrode/electrolyte contact.

At this point, we recognize that the use of a BaF_2 electrolyte (because of its lower melting point) instead of CaF_2 , may be better suited for the future determination of the solubility and diffusivity of fluorine in solid nickel. Bonding at temperatures just below the melting point of BaF_2 should provide uniform Ni/BaF_2 contact. This work is currently in progress.

Internal fluoridation kinetic studies encountered major experimental difficulties. Some dilute Cu-Ni alloys and powdered $\text{Cu}+\text{CuF}_2$ were encapsulated within evacuated quartz capules. However, CuF_2 reacted with the quartz at high temperatures, resulting in SiF_4 vapor. Thus, the procedure was changed. Currently, internal fluorination studies are being conducted inside Al_2O_3 crucibles with tightly closed lids. These results should be available in a couple months.

In the next year, this task shall seek to obtain accurate and reproducible data for the solubility and diffusivity of fluorine in solid nickel. Internal fluorination kinetic studies for Cu- and Ni- base alloys will be completed. Finally, CaF_2 electrolytes will be doped with soluble concentrations of LiF and YF_3 and both the ionic and electronic conductivities will be established by a.c. and d.c. methods, respectively. These data can be interpreted to obtain the concentrations and mobilities of native point defects and electronic defects in CaF_2 . Such information would relate directly to the galvanic cell studies of mixed electrode reactions by Mr. S.F. Chou.

2. Conductivity Studies of NiF_2 and $\beta\text{-PbF}_2$ (W.C. Fang, B.S. Lee).

For the past year 1977-78, the completion of a.c. and d.c. studies of the conductivity of $\beta\text{-PbF}_2$ was proposed. Similar studies and galvanic cell studies to establish the ionic transference number for NiF_2 were proposed.

The electrical studies of $\beta\text{-PbF}_2$ by Mr. Fang were highly successful as reported in the last annual report. In addition to the valuable results, certain new methods were developed for the attachment of Pt electrodes and for the introduction of some CaF_2 into reversible $\text{Ni}+\text{NiF}_2$ electrodes to minimize polarization.

In the more recent conductivity measurements for NiF_2 as a function of PF_2 and temperature, the values of current were not stable. In galvanic cell emf measurements, the migration of impurity oxygen was found to cause irreproducible results. X-ray diffraction shows that NiF_2 is contaminated by moisture even upon storage in a desiccator. A 99.99% purity NiF_2 powder was contaminated severely by oxygen, while 99.8% pure NiF_2 was relatively contamination-free. The ionic transference number of 99.8% NiF_2 was obtained as a function of temperature using the galvanic cell emf measurements. (Fig. 1)

Attempts were made to rid the NiF_2 of oxygen. Sintering $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$ in a vacuum could not remove all of H_2O ; instead oxygen reacted with NiF_2 presumably creating $\text{V}_\text{F}^\dagger$ ionic defects. In addition to the use of a CaO -stabilized zirconia tube to pump out O_2 from the reaction chamber, all the possible cell

Fig. 1 - Transference number of NiF_2 as function of temperature.

preparation must be done in a dry box filled with Ar.

Some preliminary galvanic cell measurements were made for NiF_2 doped with LiF or YF_3 . Further measurements of this sort, in combination with conductivity studies should clarify and discount the role of oxygen contamination in the behavior of NiF_2 .

3. The Use of CaF_2 in Open-Circuit Galvanic Cells—S.F. Chou

For the past year 1977-78, a more extensive study of the mixed potential developed by oxygen contaminated CaF_2 -electrolyte galvanic cells was proposed. An interpretation for these phenomena and the experimental redetermination of Gibbs energies of formation of fluorides using YF_3 -or LiF -doped CaF_2 electrolytes were proposed.

In this reporting period, considerable experimental and theoretical progress has been made toward the understanding of solid-electrolyte galvanic cells exhibiting mixed reactions. The phenomenon of mixed reactions from the presence of oxygen on CaF_2 cells was also discovered for the presence of fluorine in $\text{ZrO}_2(+\text{CaO})$ electrolyte cells. As seen in Fig. 2, measurements for a fluorine concentration cell with the CaF_2 electrolyte (filled circles) agree with those involving the ZrO_2 electrolyte. Further, the voltage of CaF_2 cells involving three-phase electrodes which fix both the oxygen and fluorine activities simultaneously shift from agreement with the oxygen cell at low temperatures to agreement with the fluorine cell

Figure 2 - Emf Values of Galvanic Cells as a Function of Temperature.

at high temperatures (open triangles). Conductivity data of Fig. 3 for two-phase or three-phase electrodes complement these results. Theoretically, the cell voltages can be understood in terms of a coupled transport between charged anion vacancies and neutral vacancy-impurity complexes at the lower temperatures. At higher temperatures, most of the oxygen is not complexed to the fluorine vacancies. Future work will further define the intrinsic, extrinsic and associated temperature regions.

Because of an insufficient number of experimental stations (only three for four researchers), the redetermination of $\Delta G_{\text{formation}}^{\circ}$ for fluorides did not progress.

Fig. 3 - A.C. Conductivity of CaF_2 Involving Differing Electrodes.

C. EXTENDED DISCUSSION1. Diffusivity and Solubility of Fluorine in Solid Copper—(S.N.S Reddy)

The diffusivity and solubility of fluorine in solid copper was determined by an electrochemical potentiostatic titration technique using the cell:

Initially, the values for the solubility of fluorine in solid copper were not reproducible, primarily because of polarization of the $\text{Ni}+\text{NiF}_2$ reference electrodes and inadequate contact between the copper electrode and the CaF_2 electrolytes. Numerous preliminary experiments were required to overcome these problems and refine the experimental technique. In the past year, accurate and reproducible values for the diffusivity and solubility of fluorine in copper were obtained.

The diffusivity of fluorine in solid copper is shown in Fig. 4 as a function of reciprocal temperature. In the temperature range 757-920°C, the diffusivity values are given by the equation

$$D_F^{\text{Cu}} = 9.32 \times 10^{-2} \left(\begin{smallmatrix} +0.16 \\ -0.06 \end{smallmatrix} \right) \exp \left(\frac{-23,600 \pm 2200}{RT} \right)$$

Unfortunately, no values for the diffusivity of fluorine in copper are available in the literature to compare with those obtained

Fig. 4 - Diffusivity of fluorine in solid copper as a function of reciprocal temperature.

in this work. However, Pastorek and Rapp¹ have determined the diffusivity of oxygen in copper as

$$D_0^{\text{Cu}} = 1.7 \times 10^{-2} \exp \left(\frac{-16,000}{RT} \right)$$

Oxygen is inferred to dissolve in copper as interstitial atoms. The similarity of activation energies for oxygen and fluorine in solid copper shows that fluorine also diffuses by an interstitial mechanism. But between the temperatures of 757-920°C, the diffusivity of fluorine is smaller than the diffusivity of oxygen in solid copper.

The solubility of fluorine in solid copper was determined between temperatures 757-920°C. The dissolution of fluorine in copper as a function of fluorine pressure obeys Sieverts' law (Henrian behavior), indicating negligible interaction among fluorine atoms in copper. The equilibrium condition for the dissolution reaction

may be written as

$$\ln K = \ln N_{\text{F}} - \frac{1}{2} \ln P_{\text{F}_2}$$

using a standard state for dissolved fluorine such that the activity of fluorine equals the atomic fraction as the atomic fraction tends to zero.

The saturation solubility of fluorine in copper, N_{F}^{S} , is obtained by substituting the value for P_{F_2} corresponding to (Cu + CuF₂) equilibrium.

Figure 5 represents the variation of $\ln K$ vs $1/T$.

A least-squares analysis of the data leads to the expression:

$$\ln K = (-7.0 \pm 3.2) + \left(\frac{20,600 \pm 3600}{T} \right)$$

Using the relations:

$$\Delta G^\circ = -RT \ln K$$

and

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

the following expression was obtained for the dissolution of 1 gram-atom of fluorine into solid copper:

$$\Delta G^\circ (\text{cal/mole F}) = -40,900 + 13.9T$$

From this expression, $\Delta H^\circ = -40,900 \text{ cal/mole}$ and $\Delta S^\circ = -13.9 \text{ mol/K}$.

Figure 6 represents the saturation solubility, N_F^S , of fluorine in copper as a function of temperature. Again, other data for the solubility of fluorine in copper are not available in the literature to compare with the values obtained in this work.

2. Electronic Conductivity of Solid CaF_2 Electrolyte—

(S.N.S. Reddy).

The low-level electronic conduction in solid CaF_2 was determined for the first time in this work, using the Hebb-Wagner polarization cell:

Fig. 5 - Equilibrium constant, K , for the dissolution of fluorine in solid copper as a function of reciprocal temperature ($N_F = KP_{F_2}^{1/2}$)

Fig. 6 - Solubility of fluorine in copper as a function of temperature

where M+MF_x represents reversible electrodes consisting of Ni+NiF_2 , Co+CoF_2 and Y+YF_3 .

For the d.c. polarization cell, the electronic current-applied voltage relationships are:

For p-type conduction only, i.e., $\sigma_{\Theta}^{\circ} \gg \sigma_{\Theta}^{\circ}$

$$\log I_e = \frac{RTA\sigma_{\Theta}^{\circ}}{L} + \frac{E}{2.303RT}$$

For n-type conduction only, i.e., $\sigma_{\Theta}^{\circ} \gg \sigma_{\Theta}^{\circ}$

$$I_e = \frac{RTA\sigma_{\Theta}^{\circ}}{L}$$

The results of the d.c. polarization studies are summarized as follows:

(i) Total conductivity of solid CaF_2 was found to be independent of fluorine activity for PF_2 ranging from the Y+YF_3 to the Ni+NiF_2 reversible electrodes.

(ii) For the polarization cells with Ni+NiF_2 and Co+CoF_2 electrodes, the electronic currents exhibited an exponential dependence on applied voltage. This current-applied potential relationship indicated p-type electronic conduction. Table I shows the p-type conductivity and electronic transference numbers of CaF_2 at various temperatures.

(iii) For the polarization cell using Y+YF_3 electrode, the electronic currents reached a plateau value at large applied potentials, indicating n-type electronic conduction. Table I

shows n-type electronic conductivity and electronic transference numbers between the temperatures 600-900°C.

The existence of n-type electronic conduction in CaF_2 at low fluorine pressures (or high Ca activities) was recognized in the literature. Wagner² estimated electronic transference numbers based on color center migration data. Our results indicate that Wagner's estimation was high. Recently, Delcet, Heus & Egan³ have measured n-type conduction at various Ca activities in the temperature range 800-950°C. At 800°C, the n-type electronic transference number obtained from the current work and that from Delcet et al³ agrees very well.

The significant contribution of the present polarization studies is the determination of p-type electronic conduction in CaF_2 at comparatively high fluorine pressures, which would limit the use of CaF_2 as a solid electrolyte at higher fluorine pressures. This factor has not been previously recognized in the literature.

References

1. R.L. Pastorek and R.A. Rapp, Trans. Met., Soc., AIME, 245 (1969) 1711.
2. C. Wagner, J. Electrochem. Soc., 115, (1968) 933.
3. J. Delcet, R.G. Heus and J.J. Egan, Brookhaven National Laboratory, personal communication.

Table 6 - Electronic Conductivity of CaF₂

Reversible Electrode	Temperature °C	σ_{θ}° (ohm-cm) ⁻¹	σ_{θ}° (ohm-cm) ⁻¹	t_e
Ni + NiF ₂	550	--	6.7×10^{-9}	6.1×10^{-5}
	600	--	5.3×10^{-8}	2.7×10^{-4}
	650	--	1.5×10^{-7}	3.4×10^{-4}
	700	--	3.0×10^{-7}	2.7×10^{-4}
Co + CoF ₂	600	--	1.1×10^{-8}	5.6×10^{-5}
	700	--	1.2×10^{-7}	1.1×10^{-4}
Y + YF ₃	600	2.3×10^{-6}	--	1.1×10^{-2}
	700	1.1×10^{-5}	--	9.5×10^{-3}
	800	2.2×10^{-5}	--	1.0×10^{-2}

2. Electrical and Electrochemical Behavior of NiF₂—

B.S. Lee.

Conductivity measurements can provide information concerning the type of defects, the concentrations and mobilities of mobile defects as well as various enthalpies of defect formation, migration, and association in NiF₂.

Galvanic cell measurements are related to ionic transference numbers which derive from conductivity measurements. The open-circuit emf measurements can therefore be used to check the values obtained from conductivity measurements.

To elucidate, for the fluorine concentration cell, Wagner's equation may be expressed as

$$E = - \frac{1}{2F} \int_{\mu_{F_2}'}^{\mu_{F_2}''} (t_{ion}) d\mu_{F_2} \quad (1)$$

where F is Faraday's constant, and μ_{F_2}' and μ_{F_2}'' are the chemical potentials of fluorine in the reversible cathode and anode, respectively, and t_{ion} is the ionic transference number. By measuring partial conductivity as a function of P_{F_2} , one can evaluate t_{ion} as a function of P_{F_2} . Then the E from Eq. (1) can be calculated and compared with the experimental value of emf. From the emf measurement of the galvanic cell, the average ionic transference number t_{ion} of NiF₂ as a function of temperature can be calculated from the relation:

$$\bar{t}_{ion} = \frac{E_{o.c.} \text{ (measured using NiF}_2 \text{ electrolyte)}}{E_{o.c.} \text{ (measured using CaF}_2 \text{ electrolyte)}} \quad (2)$$

Galvanic cell emf measurements were conducted using pure and doped NiF₂ as electrolytes during the past year and this

study will be followed by conductivity measurements in the succeeding year.

Experiment

Two grades of NiF_2 of different purities were used; 99.99%-purity NiF_2 and 99.8%-purity NiF_2 were purchased from Atomergic Chemicals and ESPI*, respectively. The galvanic cell arrangement $\text{Ni}|\text{NiF}_2|\text{Cu}+\text{CuF}_2$ as shown in Fig. 7 was used with electrolyte and electrodes pressed in a 1.3cm dia. steel die. The $\text{Cu}+\text{CuF}_2$ coexistence electrode was made by mixing Cu , CuF_2 and CaF_2 with the ratio of 2:2:1.

NiF_2 electrolytes doped with monovalent and trivalent impurities also were used. Ultra-pure LiF was used for monovalent doping, and YF_3 for trivalent doping. Dopants (2.5 m/o and 5.0 m/o of dopants in powder form) were mixed with NiF_2 and sintered at 600°C for 12 hrs in a zirconia tube, followed by crushing into powder and repressing into electrolytes.

Results and Discussion

The open-circuit emf for the galvanic cell

is shown in Fig. 8. For curves (1) and (2), the initial "heating" emf's are not the equilibrium values, while curve (3) was obtained after heating the cell at 650°C for 2 days to finally obtain equilibrium values.

*Electronic Space Products, Inc.

Fig. 7 - Cell arrangement for galvanic cell measurements using NiF₂ as an electrolyte.

Fig. 8 - Open-circuit voltage for the galvanic cell $\text{Ni}|\text{NiF}_2|\text{Cu}+\text{CuF}_2$.

The high value of t_{ion} in the temperature range of 500°C - 800°C can result either from the intrinsic defects or from the effect of impurities. The use of ultra-pure NiF_2 (e.g. 99.99%) should eliminate the second possibility, but there exists experimental difficulties which will be mentioned later.

Curve (2) which was heated to 800°C showed a higher emf. This result might arise because of a quenching effect, i.e., when NiF_2 is heated at 800°C it creates a high concentration of native defects, and these could be quenched in when the cell is cooled down. However, the phenomenon is less likely with the sintered powder electrolyte.

Because the electrolyte was pressed from the powder, the mechanical strength at the higher temperature of 700°C to 800°C is very low. Using a single crystal would solve this problem and also perhaps an oxygen contamination problem, but obtaining a NiF_2 single crystal seems impossible at this point. However, hot-pressing could be helpful to increase the mechanical strength of the pressed electrolyte.

From Fig. 8, the 99.8% purity NiF_2 shows significant ionic conduction which is a function of temperature. The calculated F_{ion} is shown in Fig. 9.

Apparently, NiF_2 is an electronic conductor up to the temperature 400°C, and becomes an ionic conductor at temperatures higher than 600°C, as do the cuprous halides which at room temperature and below are exclusively electronic conductors, and above 400°C are essentially pure cation conductors.

Fig. 9 - Transference number of NiF_2 as function of temperature.

When NiF_2 of 99.99% purity was used as the electrolyte, galvanic cell emf values were very unstable and sometimes went to a negative value. Later, x-ray diffraction showed that initially the NiF_2 was mostly in the form of nickel fluoride hydrate ($\text{NiF}_2 \cdot 4\text{H}_2\text{O}$). The sintering of NiF_2 in vacuum at around 400°C did not eliminate oxygen and at higher temperatures; apparently the oxygen reacted with NiF_2 to act as a monovalent dopant.

Stangely, 99.99% NiF_2 formed $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$ even in the desiccator, while 99.8% NiF_2 did not. Extreme care must be taken to prepare oxygen-free electrolytes.

To test the effect of contaminant oxygen on galvanic cell values, NiF_2 of 99.99% purity was exposed in the air prior to use as an electrolyte. Oxygen was the only impurity in this electrolyte.

Figure 10 is a plot of $E_{\text{o.c.}}$ vs temperature for the cell involving an oxygen-contaminated NiF_2 as the electrolyte. After some time the emf values were very stable. In fact, the electrodes of this cell became three-phase electrodes upon reaction with the electrolyte:

These preliminary indications of the effect of oxygen on the ionic transference number must be correlated to the current work of S.F. Chou.

Fig. 10 - EMF values for a galvanic cell using NiF_2 exposed to air as an electrolyte.

When NiF_2 is doped with LiF , two kinds of dissolution reaction must be considered:

where reaction (1) produces fluorine vacancies and (2) produces interstitial Li^{+} and fluorine ions.

Preliminary galvanic cell studies for doped NiF_2 -electrolyte cells with $\text{Cu}+\text{CuF}_2$ and $\text{Ni}+\text{NiF}_2$ electrodes are reported in Fig. 11. However, the NiF_2 used in this study was known to be contaminated by oxygen. The unusual shapes of the curves are believed to result from oxygen dissolution in the electrolyte. After the cells were cooled from 600°C , all cells showed very low emf's and the interface between NiF_2 and $\text{Cu}+\text{CuF}_2$ was covered with Cu_2O . Further experimentation is obviously needed.

When NiF_2 is doped with YF_3 , the expected reaction is:

The galvanic cell emf measurements of Fig. 5 showed that YF_3 supported electrolytic behavior, but the complicated results require further interpretation.

Park and Nowick¹ studied the conductivities of MnF_2 and MgF_2 and concluded that these crystals have anti-Frenkel defects. The two mobile defects are fluorine vacancies, $\text{V}_{\text{F}}^{\bullet}$ and the anion interstitial ion, F_i' . It is reasonable to assume that NiF_2 also has anti-Frenkel defects, because NiF_2 has the same structure (rutile) and the ionic size of Ni^{2+} is very close

Fig. 11 - EMF values for galvanic cells using doped-NiF₂ as electrolytes.

to that of Mn^{2+} or Mg^{2+} .

References

1. D.S. Park and A.S. Nowick, J. Phys. Chem. Solids, 37, (1976) 607.

3. Mixed Electrode Reactions in Solid Electrolyte

Cells—S.F. Chou.

Upon the initiation of this research in 1975-6, the measurement of fluorine activities at elevated temperatures by means of a CaF_2 -solid electrolyte galvanic cell was set forth as a goal for one research task. The possibility that residual oxygen in a gaseous fluorine environment might affect the voltage of such a cell measurement was immediately realized. In fact, previous results¹ of a CaF_2 cell determination of the standard Gibbs energies of formation of many fluorides differed significantly from values established by calorimetry. Oxygen contamination of the CaF_2 electrolyte was suspected.

To know and limit the residual oxygen activities in the gaseous environments of this work, the CaF_2 -electrolyte cells have been enclosed in closed-end, impervious, stabilized zirconia electrolyte tubes which were painted with four porous platinum electrodes to provide an oxygen pump and gauge for the titrative removal and monitoring of residual oxygen, respectively.² In fact, the open-circuit voltages of CaF_2 -electrolyte cells provided with differing metal/metal fluoride electrodes were found to depend upon the residual oxygen activity of the environment. Thus, the research planned for the past year 1977-8 was intended to clarify the role of oxygen solute on CaF_2 -cell measurements.

The open-circuit voltages of four galvanic cells were reported:

The results are summarized in Figs. 12 and 13. The data for cell (I) for an oxygen-free environment provided the cell voltages corresponding to the virtual reaction $\text{Ni} + \text{CuF}_2 \rightarrow \text{NiF}_2 + \text{Cu}$. The data for cell (II) were in exact agreement with well known values of ΔG° for the reaction $\text{Ni} + \text{Cu}_2\text{O} \rightarrow \text{NiO} + 2\text{Cu}$ from 800-1000°C. Thus, surprisingly, for electrodes of fixed oxygen activity and in the absence of definitely fixed fluorine activities, CaF_2 functioned exactly as an exclusive oxygen-ion conducting electrolyte. Likewise, cell (IV) with electrodes of fixed fluorine activity provided cell voltages in agreement with those of cell (I), although zirconia is normally an oxygen ion conductor. Cell (III) was studied from 580-740°C to establish the behavior of the CaF_2 electrolyte in contact with electrodes fixing both the fluorine and the oxygen activities. At temperatures above about 680°C, the cell voltage agreed approximately with that for cell (I), but below 680°C, the voltage dropped to about 300 mv, a value approaching that for cell (II).

The authors have prepared a yet-unpublished theory to interpret the results for cells (II), (IV), and especially (III). The theory supposes that two species, in this case a charged anion vacancy and a neutral oxygen-vacancy complex are

Figure 12 - e.m.f. Value of Cell 20 as a Function of Temperature.

Figure 13 - Emf Values of Galvanic Cells as a Function of Temperature.

necessarily coupled in their motion through the electrolyte (like ambipolar diffusion) because of the redox reactions at each electrode interface. For cell (II), at the anode, the oxidation reaction is

At the cathode, the reduction reaction is

Thus, for the transport of one gm-atom of oxygen via a neutral $(\text{V}_\text{F}\text{O}_\text{F}^\text{x})$ complex from the cathode to the anode, two gm-atoms of unassociated anion vacancies must diffuse from the anode to the cathode (corresponding to two gm-atoms of fluorine ions diffusing from the cathode to the anode). This interpretation applies only at the low temperature region where the oxygen and anion vacancies are predominantly associated or complexed. To the authors' knowledge, this interpretation represents the first description of coupled transport between a neutral species $(\text{V}_\text{F}\text{O}_\text{F}^\text{x})$ and a charged species $\text{V}_\text{F}^\bullet$ in solid-state electrochemistry. As driving forces for these species, the neutral complex $(\text{V}_\text{F}\text{O}_\text{F}^\text{x})$ can only respond to a concentration gradient, while the anion vacancies can respond to both concentration and electrical gradients. Because the transport of these species is coupled, a force on either of the species will generate a force and a corresponding migration of the other species. At steady-state for cell (III), for example, the steady-state condition by this theory is

equivalent to co-current fluxes of oxygen and fluorine through CaF_2 . Because both the fluorine and oxygen activities of the $\text{Cu} + \text{Cu}_2\text{O} + \text{CuF}_2$ electrode exceed those for the $\text{Ni} + \text{NiO} + \text{NiF}_2$ electrode, at steady-state, both fluorine and oxygen ions would migrate down their respective activity gradients from the $\text{Cu} + \text{Cu}_2\text{O} + \text{CuF}_2$ electrode to the $\text{Ni} + \text{NiO} + \text{NiF}_2$ electrode. The theoretical expectation for cell voltage according to this model is given by:

$$E_{\text{o.c.}} = \bar{t}_F \frac{RT}{2F} \ln \frac{P'_F}{P''_F} + \bar{t}_O \frac{RT}{4F} \ln \frac{P'_O}{P''_O} \quad (1)$$

where $\bar{t}_F$ and $\bar{t}_O$ are not the usual transference numbers, but rather they are each fractions describing the fractional equivalents of fluorine and oxygen involved in redox reactions per equivalent of charge passed through the external circuit.

To test the necessary condition that oxygen is mobile in CaF_2 , the Tubandt-type cell (V) was constructed and run at 800°C

where an impressed d.c. voltage was intended to drive oxygen from the $\text{Cu, Cu}_2\text{O}$ source electrode to the Ni sink. After passing current at 800°C for one week in the O_2 -getter system, an obvious green layer of NiO (identified by x-ray diffraction) was found at the Ni/electrolyte interface although other surfaces of the Ni were free of oxide. An analogous attempt to drive fluorine ions through zirconia from a Cu, CuF_2 source to a Ni sink was not immediately successful and needs

to be repeated.

For cell III, at high temperatures, the concentration of intrinsic anion vacancies exceeds by far that generated in compensation of the oxygen dopant. Then most of the oxygen ions are not complexed. However, under these conditions the migration of oxygen over intrinsic vacancies via nearly random formation and dissociation of complexes does indeed carry a current. However, if the electrodes allow redox reactions for the fluorine species, the fluorine current should exceed by far that for oxygen. For this reason, the galvanic cell voltage for cell (III) at high temperatures approximated that for the fluorine cell alone.

In an attempt to establish the oxygen and fluorine transference numbers independently through a.c. conductivity measurements at 1592 cps, CaF_2 was provided with identical electrodes as given by the symmetric cells (VI) and (VII).

As shown in Fig. 14, from three self-consistent conductivity runs for cell (VI) from 512-844°C, a conductivity activation energy of 33.2 Kcal/mole (1.44 eV/mole) was found for the oxide electrodes. For two runs from 375-770°C, the three-phase electrode cell (VIII) showed a transition in conduction behavior, with the high-temperature conductivity exhibiting an activation energy of 41.3 kcal/mole (1.79 eV/mole) above

Figure 14 - A.C. Conductivity of CaF₂ Involving Differing Electrodes.

about 527°C and the low temperature conductivity exhibiting 20.3 kcal/mole (0.88eV/mole) below about 527°C. Thus, differing magnitudes and activation energies were observed for the conductivities of cells (VI) and (VII).

The conductivities of oxygen-doped CaF_2 crystals provided with Cu or Pt electrodes have been previously investigated over broad temperature ranges. Bollmann, et al³ studied the analogous solutions NaF- and CaO-doped CaF_2 ; each dopant generates compensating anion vacancies. At the highest temperatures, intrinsic ionic conduction exceeded that introduced by the oxygen dopant. At lower temperatures, in a dissociation region, the dopant-created vacancy concentration exceeded the intrinsic defects, but the oxygen and the vacancies were mostly not associated on adjacent anion sites. At quite low temperatures, the $(\text{V}_\text{F}\text{O}_\text{F}^\text{x})$ complexes were predominant. The results of the studies by Bollmann, et al³ and Levitskii, et al⁴ are summarized with the current results in Table I. The conductivity results from the three-phase electrode cell VII do not correlate well to the oxygen-doped CaF_2 data. On the other hand, this particular measurement has also not been previously attempted.

The interpretation of the conductivity results is still incomplete, and more work needs to be done. Further, the significance of these data to the open-circuit emf results is also yet uncertain. The results are complicated because the measurements at the lowest temperatures probably encompass an association reaction

to form a neutral complex or association ($V_F O_F^X$). Because oxygen ions can only migrate via anion vacancies, oxygen diffusion at low temperatures is only accomplished by the migration of neutral ($V_F O_F^X$) complexes, and these species do not contribute to the electrical conductivity. But at higher temperatures all conductivity measurements from cell VI and VII should correspond to fluorine conduction over vacant anion sites. A question still remains concerning the temperature above which the CaF_2 can equilibrate with the oxygen activities of the electrodes, and below which the oxygen is frozen into the lattice.

In an intermediate temperature range, the ($V_F O_F^X$) complexes are mostly dissociated, although the resulting concentration of free $V_F^\bullet$ sites is fixed by the concentration of free O_F' ions. In this case, all the vacancies should contribute to fluorine conduction, and the oxygen should be relatively immobile because of the lack of complexes. The temperature range where CaF_2 is shown to behave as an oxygen electrolyte (800-1000°C) is either in this dissociation region or else the intrinsic ionic conduction region. In either case, the oxygen anions can only move as minority dynamically formed complexes, which are very low in concentration.

In the next year, further conductivity measurements will be conducted with $\text{Ni}+\text{NiO}$ and $\text{Ni}+\text{NiO}+\text{NiF}_2$ electrodes. The identification of the detailed conduction mechanism will be learned. Galvanic cells will be constructed with oxygen and

three-phase electrodes using electrolytes of CaF_2 doped with NaF or YF_3 . In this case, the oxygen dopant should represent a minority impurity in the electrolyte.

Theoretically, there seems to be no fundamental reason why neutral $(\text{V}_\text{F}\text{O}_\text{F}^\text{x})$ complexes cannot support reversible redox reactions at the electrodes of a galvanic cell. Then transport of the complexes must be driven by a concentration (and not electrical) gradient through the electrolyte. These future studies should clarify the unusual mixed electrode reactions in the solid electrolyte cells.

Table I - Conduction Activation Energies for Oxygen Doped CaF₂

Authors	Electrodes	Intrinsic Region		Dissociation Region		Association Region	
		Q (eV/mole)	T Range	Q (eV/mole)	T Range	Q (eV/mole)	T Range
Bollman, et al ³	evap. Cu, oxygen from melt	1.92		0.55		0.99	
Levitskii, et al ⁴	porous Pt P _{O₂} =2x10 ⁻⁶	1.92	>660°C	0.64	600>T T>480°C	1.30	<480°C
	porous Pt CO ₂ /CO=9 low P _{O₂}	2.0	>527°C				
	porous Pt P _{O₂} =1 atm	2.10	>910°C	0.63	910>T T>800°C	1.30	<800°C
current work Chou & Rapp	cell VI Cu/Cu ₂ O	1.44	844>T T>512°C				
	cell VII Cu/Cu ₂ O/CuF ₂	1.79	770>T T>527°C	0.88	527>T T>375°C		

References

1. W.H. Skelton and J.W. Patterson, J. Less Comm. Metals, 31, (1973) 47.
2. Y.K. Agrawal, D.W. Short, R. Gruenke, and R.A. Rapp, J. Electrochem. Soc.,
3. W. Bollmann, P. Gorlich, W. Hauk and H. Mothes, Phys. Stat. Sol. A2, (1970) 157.
4. V. Levitskii, A. Hammon, M. Duclot, and C. Deportes, J. Chim. Phys., 73, (1976) 305.