MASTER

Fourth Annual Progress Report

Fundamental Studies of Metal Fluorination Reactions

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A. OVERALL PROJECT

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

a) Dr. S.N.S. Reddy has worked 3.5 years on this contract and intends to complete his commitment at OSU in April or May 79. Dr. Reddy has received an immigrant visa and is currently interviewing for an industrial or University position. He has used CaF_2 and BaF_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 and BaF_2 by the Hebb-Wagner polarization method.

b) S.F. Chou has completed three 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 parts of the Ph.D. general examination. He should complete his thesis research on "The Effect of Oxygen on Conduction and Electrochemical Behavior of CaF_2 Electrolytes" in June 1979.

c) B.S. Lee has begun research on the topic, "The Sulfidation of Molybdenum". Mr. Lee passed the general Ph.D. exam in May, 1978. About one additional year of research should be required to complete his Ph.D. theses research.

2. Presentations and Publications of Past Year - A previously reported paper by Fang and Rapp has been published and is attached:

W.C. Fang and R.A. Rapp, "The Electrical Conductivity of $\beta\text{-PbF}_2$ ".

J. Electrochem. Soc., 125, (1978) 683-7.

A previously reported paper by Reddy and Rapp has been published and a reprint is attached:

S.N.S.Reddy and R.A. Rapp, "The Diffusivity and Solubility of Fluorine in Solid Copper", Met. Trans., 9B, (1978)

The most recent work by Reddy and Rapp has been prepared for publication. Preprints or reprints of six papers are attached as part of this progress report:

S.N.S. Reddy and R.A. Rapp, "The Diffusivity and Solubility of Fluorine in Solid Nickel", submitted for publication in Metall. Trans.

S.N.S. Reddy and R.A. Rapp, "Electronic Conductivity of BaF_2 ", submitted for publication in J. Electrochemical Soc.

R.A. Rapp, "Materials Selection and Problems for Molten Carbonate Fuel Cells," Proceedings of DOE-EPRI Workshop on Carbonate Fuel Cells, Oct. 30-Sept.1, 1978.

R.A. Rapp, "The Maturing of High Temperature Corrosion Research", Editorial in Corrosion, 34, Aug. (1978).

During the past contract year a number of presentations of this DOE-sponsored research or participation in DOE-sponsored (or related) corrosion conferences have been made:

Professor Rapp presented, "Mixed Electrode Reactions for Galvanic Cells with CaF_2 and $\text{ZrO}_2(+\text{CaO})$ Electrolytes," at the Second International Meeting of Solid Electrolytes in St. Andrews, Scotland, September 25, 1978.

Professor Rapp presented, "The Diffusivity and Solubility

of Fluorine in Solid Nickel" in a colloquium at Hokkaido University, Hokkaido, Japan on December 11, 1978.

With Professor E. Verink, Professor Rapp presented the AIChE course "Fundamentals of Corrosion" in Philadelphia, June 7-8, 1978.

Professor Rapp presented, "Materials Selection and Problems for Molten Carbonate Fuel Cells" at DOE-EPRI Workshop on Carbonate Fuel Cells, Oak Ridge, Oct. 31, 1978.

Professor Rapp served on a discussion panel at the DOE-EPRI conference "Review of Materials for Coal Gasification Systems", at NBS, Washington, D.C., Oct. 11, 1978.

Professor Rapp served as Co-Chairman (with W.W. Smeltzer) on High Temperature Oxidation Symposium at Electrochemical Society in Seattle, May 22-25, (1978).

During the past year Professor Rapp has presented seminars on differing topics of high temperature corrosion at EXXON Research Laboratory, Wright-Patterson Air Force Base, DECHEMA (Frankfurt, Germany), Imperial College (London, England), Lehigh University, Ohio State University, Case-Western University, Electrochemical Society (Columbus, Ohio), Tokyo Institute of Technology and National Research Institute for Metals (Tokyo, Japan).

Future presentations are scheduled for the Feb. AIME meeting (with Dr. Reddy, "Diffusivity and Solubility of Fluorine in Solid Nickel) in New Orleans, at the 1979 Gordon Conference on Corrosion, at the Fourth (NAVY) Conference on Gas Turbine Materials in the Marine Environment, and at the International Society for Electrochemistry meeting in Trondheim, Norway.

Professor Rapp has completed the first draft for an

Audio course on High-Temperature Corrosion for the American Chemical Society. The final version should consist of about 7.5 hours of taped lecture supported by a 200 page manual.

Professor Rapp has been selected by the NACE Research Committee to organize an International Research Conference on High Temperature Corrosion in 1981.

Report of Research Progress

The status of the individual research tasks of this contract fall into three different stages of completion and will therefore be reported differently. The research of Dr. S.N.S. Reddy is mostly completed and prepared for publication; therefore, these detailed results are presented as two preprint Appendices of papers just recently submitted for publication. Some internal fluoridation of alloys will be completed within the final months of the contract period.

The work of Mr. S.F. Chou is at an intermediate stage where many experimental results are available but detailed analysis and interpretation are still incomplete; these results will be presented as the body of this progress report. Finally, the experimental work of Mr. B.S. Lee is only beginning, following a literature search and a construction stage. Therefore, these aspects of the research will be presented in the proposal, and not in this progress report.

Influence of Oxygen on the Electrical and Electrochemical Behavior of CaF_2 Solid Electrolytes (S.F. Chou)

Introduction

Our earlier work included a study of the electrical conduction and electrochemical behavior of CaF_2 solid electrolytes contacting electrodes of fixed oxygen activities. An oxygen concentration cell I, with a CaF_2 single-crystal solid electrolyte yields an emf value relatable to the oxygen activities of the electrodes.

Our previous coulometric titration work proved that oxygen ions can move in CaF_2 single crystals, probably via fluorine vacancies. The conductivity, σ , of the CaF_2 solid electrolyte measured with pairs of identical electrodes of $\text{Ni} + \text{NiF}_2$, $\text{Ni} + \text{NiO}$ and $\text{Cu} + \text{Cu}_2\text{O}$ were determined at a fixed frequency, 1592Hz at different temperatures. The plot of $\log \sigma T$ vs. $1/T$ showed a high activation energy above 535°C , which may represent the sum of activation energies for the mobility of vacancies and the formation of anti-Frenkel defects. The lower activation energy at low temperatures can be explained in terms of the mobilities of vacancies generated by oxygen doping.

The electronic structure of the fluorine ion is the same as that of the oxygen ion. The radius of oxygen ion is only $0.03\text{\AA}$ larger than that of the fluorine ion¹. Presumably oxygen can be incorporated into a CaF_2 lattice and migrate readily over fluorine vacancies. V.A. Levitski, et al², observed a higher bulk conductivity for the CaF_2 electrolyte in an oxygen environment, $\sigma \propto P_{\text{O}_2}^{1/4}$, and they suggested that oxygen interacts with the CaF_2 lattice and generates vacancies according to the following reaction:

where $\text{V}_\text{F}^\cdot$ is a fluorine vacancy, $\text{F}_\text{F}^\text{x}$ is a normal fluorine lattice site and $\text{O}_\text{F}^\cdot$ is an oxygen ion replacing a fluorine ion in the lattice.

Our recent work suggests that at the interface between a metal-

metal oxide electrode and the CaF_2 electrolyte oxygen reacts with the CaF_2 lattice as follows:

At the oxide electrode/ CaF_2 electrolyte interface, the surface defect structure is determined by the electrical potential drop and the oxygen pressure according to Eq. (2). But theoretically, in contact with oxygen electrodes, the bulk of the CaF_2 electrolyte has its intrinsic character at high temperatures. At intermediate temperatures, since oxygen irreversibly incorporates in the CaF_2 lattice, extrinsic character dominates. At low temperatures, the association of fluorine vacancies and oxygen dopants reduces the conductivity significantly, since the neutral complex does not contribute to the electrical conduction.

Because the ac conductivity measurement at a fixed frequency does not separate the interfacial phenomena from that of the bulk, an ac impedance (or admittance) analysis technique over a frequency range from 20 to 20 KHz was applied over the past year. In order to investigate the effects of oxygen on the electrical characteristics of the bulk and the electrode/electrolyte interface of CaF_2 electrochemical cells separately, the equivalent electrical circuits for the following cells were determined, and the geometric capacitances, the double-layer capacitances, the bulk conductivities and the interface conductivities were examined.

After understanding the behavior of oxygen at the electrode/ electrolyte interface and in the bulk of a CaF_2 electrochemical cell, a theory was developed to rationalize the emf values of cell I.

Two more titration experiments were repeated to investigate the transport of oxygen in CaF_2 crystals more quantitatively.

Theory for Complex Admittance (Impedance) Measurements

An electrochemical cell, similar to cells II through IV can be replaced by an equivalent circuit of resistors and capacitors. For a non-blocking electrode, which permits finite current passage in addition to an interface capacitance, the equivalent circuit ^{3,4} is described by Fig. 1. The bulk capacitance, R_b , is proportional to the geometric factor A/ℓ , where ℓ is the thickness of the electrolyte, and A is the cross-sectional area of the electrolyte. The geometric capacitance, C_g , arises from the finite dielectric constant of the electrolyte. The geometric capacitance of the cell is expressed by ⁴

$$C_g = \frac{\epsilon_0 \epsilon_r A}{\ell} \quad (3)$$

where ϵ_0 is the permittivity of a vacuum, and ϵ_r is the dielectric constant of the electrolyte (low frequency limit).

The double-layer capacitance, C_{dl} , at the metal/electrolyte interface is a series combination ⁵ of a diffusion layer capacitance, C_d , and an inner layer capacitance, C_i ,

$$C_{dl}^{-1} = C_d^{-1} + C_i^{-1} \quad (4)$$

the inner layer is the first ion layer of the electrolyte next to

the metal surface. The inner layer capacitance is dependent on the charge density of the layer and the finite size of the ions. The interface charge-transfer resistance, R_{ct} , is proportional to the interfacial area between the electrode and the electrolyte.

When a time-dependent sinusoidal potential

$$E = E_0 \sin \omega t \quad (5)$$

is applied across the equivalent circuit of Fig. 1, a sinusoidal current

$$I = I_0 \sin(\omega t + \alpha) \quad (6)$$

will flow as a consequence. Here α is a phase angle corresponding to the phase difference between the potential and the current, and ω is the angular frequency. The voltage and the current are related by a complex impedance,

$$Z = \frac{E}{I} \quad (7)$$

The impedance of Circuit 1 in Fig. 1 is

$$\begin{aligned} Z &= (C_g \omega j + \frac{1}{R_b})^{-1} + (C_{dl} \omega j + \frac{1}{R_{ct}})^{-1} \\ &= Z' - Z'' j \end{aligned} \quad (8)$$

where Z' and Z'' are the real and imaginary parts of the complex impedance, and

$$j = (-1)^{1/2}$$

The admittance of the circuit is

$$\begin{aligned} Y &= \frac{1}{Z} \\ &= [(C_g \omega j + \frac{1}{R_b})^{-1} + (C_{dl} \omega j + \frac{1}{R_{ct}})^{-1}]^{-1} \\ &= Y' + Y'' j \end{aligned} \quad (9)$$

where Y' and Y'' are the real and the imaginary parts of the admittance, respectively.

Equivalent Circuit 1 can also be transformed into the circuit in Fig. 2 to which the Wayne-Kerr conductivity bridge was calibrated. Here C_p and R_p^{-1} are the readings from the bridge directly. These readings can be transformed into real and imaginary parts of equivalent Circuit 1 through the following transformation formulae⁶

$$\tan \theta = \omega R_p C_p \quad (10)$$

$$Z' = R_p \cos^2 \theta \quad (11)$$

$$Z'' = R_p \sin \theta \cos \theta \quad (12)$$

$$Y' = R_p^{-1} \quad Y'' = \omega C_p \quad (13), (14)$$

When plotting the real part and imaginary part of the impedance on a complex plane, the figure is two semi-circles with one common joint, as shown in Fig. 3a, where the magnitude of the impedance decreases with frequency. The frequencies ω_1 and ω_2 at the maxima of the semi-circles in Fig. 3a are related to C_g , R_b , C_{dl} and R_{ct} by³

$$C_g R_b \omega_1 = 1 \quad (15)$$

$$C_{dl} R_{ct} \omega_2 = 1 \quad (16)$$

The centers of the circles are on the real axis. The intercepts of the circles and the real axis represent the bulk resistance and the sum of the bulk and the interface resistances. When the interface resistance is much greater than that of the bulk, $R_b + R_{ct}$ approximates R_{ct} . The smaller circle passes through the origin, since when the frequency approaches infinity the impedance approaches zero.

Figure 3b shows the plotting of the real and imaginary parts of the admittance on a complex plane at different frequencies. The admittance increases with frequency. The curve rises rapidly in the high frequency region. When the frequency approaches infinity, the imaginary part of the admittance, i.e., ωC , approaches infinity. The intersections of the circles and the real axis represent $(R_b + R_{ct})^{-1}$ and R_b^{-1} . When $R_b \ll R_{ct}$, $(R_b + R_{ct})^{-1}$ approaches R_{ct}^{-1} . The semi-circle does not pass through the origin until R_{ct} approaches infinity. In both plottings 3a and 3b, the low-frequency dispersion corresponds to the electrode and the high frequency dispersion corresponds to the electrolyte.

When the geometric capacitance is removed from Circuit 1, as shown in Fig. 4, then

$$Z = R_b + (C_{dl}\omega j + R_{ct}^{-1})^{-1} \quad (17)$$

$$Y = [R_b + (C_{dl}\omega j + R_{ct}^{-1})^{-1}]^{-1} \quad (18)$$

The impedance and admittance plots on the complex plane are shown in Figs. 5a and 5b. Equation (16) still holds.

3. Experimental Procedure

A. Complex Admittance Measurement

A Wayne-Kerr a.c. conductivity bridge combined with a General Radio tuned-amplifier and a Hewlett-Packard oscillator were used to read conductance, $\frac{1}{R_p}$, and capacitance, C_p , spontaneously over a frequency range from 20 to 20 KHz. A time-dependent sinusoidal potential $E_0 \sin \omega t$ was applied across the electrochemical cell during the measurement, where E_0 was 260 mv to 600 mv, which is much less than the decomposition potential of CaF_2 . Test circuits

4 and 5 in Fig. 6 were set up from known electrical components used to assure the proper functioning of the bridge. The real and imaginary impedances of circuit (4) at different frequencies were calculated from Eqs. (10)-(12). Figure 7 shows a plot of Z' vs Z'' on a complex plane for the test circuit of Fig. 6(a). The corresponding real and imaginary admittances calculated by Eq. (13) and (14) are plotted in Fig. 8.

The electrolytes were rough-cut, optical-grade cylindrical CaF_2 single crystal disks from Harshaw. The desired electrolyte thickness was obtained by polishing down the original crystal, 0.3 cm thick and 1.25 cm diameter, or stacking two crystals together. Cells with different electrodes, $\text{Ni} + \text{NiF}_2$, $\text{Ni} + \text{NiO}$, and $\text{Cu} + \text{Cu}_2\text{O}$, and different electrolyte thicknesses were tested. Cell II-1 has $\text{Ni} + \text{NiF}_2$ electrodes, and the electrolyte is 0.3 cm thick. Cell II-2 has the same $\text{Ni} + \text{NiF}_2$ electrodes, but the electrolyte is made of two 0.3 cm thick CaF_2 crystals.

Cell III-1 has $\text{Ni} + \text{NiO}$ electrodes, and the electrolyte is a 0.19 cm thick crystal. Cell III-2 has $\text{Ni} + \text{NiO}$ electrodes, and the electrolyte is the double-thickness one used in Cell II-2, now sintered together, and polished to 0.58 cm thick. Cells IV-1 and IV-2 have $\text{Cu} + \text{Cu}_2\text{O}$ electrodes, and the electrolytes are 0.30 and 0.60 cm thick, respectively. The diameter of all the electrolytes is 1.25 cm. The resistance is about 1Ω for all the electrodes.

B. Titration Experiment

A constant current of 200 μA , was passed from a $\text{Ni} + \text{NiO}$ electrode, through the CaF_2 single crystal electrolyte, to a pure nickel electrode, as shown in Fig. 9, over a period

of five days. A regulated high-voltage supply, Keithley Instruments, in series with a $10^6 \Omega$ resistor was used to produce the constant current. The operating temperature was between 950°C and 1000°C . The potential drop across the electrolyte during the titration varied from 800 mv to 1500 mv, which is much lower than the decomposition voltage of CaF_2 .

Results and Discussion

A. Titration Experiment

The x-ray diffraction pattern confirms that the green film produced at electrode/electrolyte interface is nickel oxide. Other exposed surfaces of the electrode were not oxidized. The nickel oxide film was present on both the surface of the CaF_2 crystal and on that of the nickel electrode. In the first run, the weight of NiO calculated by Faraday's Law was 43.0 mg, while the amount of NiO on the CaF_2 crystal determined by an atomic absorption analysis technique was 11.5 mg. The oxygen transference number, t_0 , is then at least greater than 0.26, since there was some NiO formed on the electrode too. In the second run, more NiO was formed on Ni electrode; the weight of NiO calculated by Faraday's law was 55.1 mg, while the film on the CaF_2 crystal weighed 7.5 mg. The attempt to separate the NiO film from the Ni electrode was not successful. The results demonstrate that at the Ni + NiO electrode | CaF_2 electrolyte interface, oxygen is incorporated into the CaF_2 lattice by an electrochemical process described by Eq. (2). The vacancy current in the CaF_2 electrolyte can support either the oxygen ion or fluorine ion. If the fluorine vacancies conduct fluorine ions, i.e. $t_0 = 0$, then the NiO film

cannot be produced in the titration experiment. If the vacancies carry only fluorine ions, then the CaF_2 crystals should remain unaffected during the titration. Instead, the crystals became milky after the titration. A similar milky crystal was produced when oxidizing the crystal in the air at 800°C for 36 hr; obviously some oxygen ions were left in the lattice.

B. Complex Admittance (Impedance) Measurement

The complex admittance plots of cells II-1 and II-2 at different temperatures are shown in Figs. 10-16. In Fig. 13 the largest two similar semi-circles represent two runs for cell II-1 tested at 647°C . The equivalent circuit of the cell at this temperature is described in Fig. 4. The intersection of the semi-circle with the real axis in the high-frequency region represents the bulk conductivity, $155 \mu\text{Mho}$, while that in the low-frequency region represents the charge transfer conductivity across the electrode/electrolyte interface, around $5 \mu\text{Mho}$. The interface charge transfer reaction is the following

Figure 13 also shows the complex admittance plot of cell II-2 at 647°C . Figure 17 describes the equivalent circuit of cell II-2 at 647°C . The interface between two contacting CaF_2 solid electrolyte crystals produces extra interface capacitance, C_{int} , and interface resistance, R_{int} . The electrical circuit analysis from Bauerle⁷ confirms this model. According to Bauerle's equivalent circuit analysis, C_{int} , C_{dl} , R_{int} and R_{ct} in cell II are related by the following equations:

$$R_{ct} = \frac{1}{G_1} - \frac{1}{G_2} \quad (20)$$

$$R_{int} = \frac{1}{G_2} - \frac{1}{G_3} \quad (21)$$

$$R_b = \frac{1}{G_3} \quad (22)$$

$$C_{dl} = \frac{G_2^2}{\omega_1 (G_2 - G_1)} \quad (23)$$

$$C_{int} = \frac{G_3^2}{\omega_1 (G_3 - G_2)} \quad (24)$$

where G_1 , G_2 and G_3 are the electrode/electrolyte interface, electrolyte/electrolyte interface and the bulk conductivities, respectively. These can be obtained directly from the complex admittance diagram in Fig. 13, where ω_1 and ω_1' are the peak angular frequencies. When G_3 is close to G_2 and much greater than G_1 , Eqs. (20) and (23) are reduced to the following forms:

$$R_{ct} = \frac{1}{G_1} \quad (25)$$

$$C_{dl} = \frac{G_2}{\omega_1} \quad (26)$$

Cell I -2 was tested at 647°C twice. The values of G_1 , G_2 , G_3 , C_{dl} and C_{int} for cell II-1-a and II-1-b at 647°C are listed in Tables I, II and III. The conductivity of the electrolyte/electrolyte interface, around 70 μ Mho, is close to that of the bulk, around 80 μ Mho, while the conductivity of the electrode/electrolyte interface is much lower, around 5 μ Mho. The capacitance of the electrode/electrolyte interface is 5.5×10^{-7} F while that of electrolyte/electrolyte interface is only 6×10^{-9} F. The much lower charge separation between two CaF_2 single crystals, resulting in diminished interface capacitance, is reasonable. For the later runs, sintering of the two crystals makes the small semi-circle

corresponding to the electrolyte/electrolyte interface disappear.

Figure 13 shows that the bulk conductivity of Cell II-1 is consistently twice that of Cell II-2, clearly because the electrolyte thickness of the latter is twice that of the former. The interface charge transfer reaction is proportional to the interface area. Since all electrodes have the same contacting area, Cell II-1 and Cell II-2 read the same interface conductivity for each run; the large semi-circle and the intermediate one in Fig. (13) intersect the real axis at the same point in the low-frequency region. Cell II-1 does not have a second semi-circle, for there is no electrolyte/electrolyte interface. The electrode/electrolyte interfaces of Cell II-1 and Cell II-2 possess the same physical contact area and same chemical composition; therefore the interfacial capacitances of Cell II-1 and Cell II-2 are close, 5.0×10^{-7} F and 5.5×10^{-7} F, respectively.

Cells II-1 and II-2 at temperatures 598°C, 746°C, 792°C and 853°C in Figs. 12 and 14-16 follow the same arguments described above, except that the second semi-circle representing electrolyte/electrolyte interface for Cell II-2 disappears. The equivalent circuit is described by Fig. 4. The bulk conductivities, the interface conductivities, and the interfacial capacitances are all listed in Table I, II, and III.

The results of Cell II-1 and Cell II-2 at lower temperatures 502°C and 548°C are shown in Figs. 10 and 11. The rapid rise of the curve on the complex plane in the high-frequency region demonstrates an additional capacitance phenomenon. The equivalent circuit is described by Circuit 1. The bulk conductivities, the interface conductivities, the interface capacitances and the geometric capacitances are listed in Tables I, II, and III.

The complex admittance plots for Cells III-1 and III-2 at various temperatures, from 398°C to 845°C, are shown in Figs. 18 to 29. At a given temperature, the bulk conductivity of Cell III-1 is consistently three times that of Cell III-2, for the electrolyte thickness of Cell III-2 is three times that of Cell III-1; as expected, the interface conductivities of each cells are the same. Above 400°C, the equivalent circuit is Circuit 3 in Fig. 4. The equivalent circuit is Circuit 1 at 398°C; an additional capacitance is introduced.

For both Cells II and III, the additional capacitance introduced at lower temperatures is the geometric capacitance resulting from the dielectric polarization of the bulk of the CaF_2 crystal. An electrical field exerts a force on charged particles. If such particles in a substance can move unhindered through it, the induced phenomenon is a continuous current. In an electrochemical cell, this current is by definition the Faraday current. If, on the other hand, the charge carriers are not free, i.e., bound to certain regions, they will move until a counterforce is generated and the resulting effect is a dielectric polarization. Polarization effects appear, particularly in ac experiments, when the charge carriers move through a cell which has regions of differing conductivity behavior. For instance, for an irreversible electrode, the interface conductivity is less than that of the bulk of the electrolyte; therefore, interface polarization exists. The polarization also occurs in the bulk of the electrolyte, which introduces a geometric capacitance.

Born⁸ described the dielectric polarization of alkali halide crystals in terms of two contributions: One electronic arising

from the distortion of electron clouds of individual ions relative to their nuclei, and the other atomic polarization arising from the displacement of positive and negative ions relative to each other. Since the resonance frequencies of electronic motions lie in the visible or ultraviolet region, and those for ionic motions lie in the infrared region, both far from the range of ordinary electrical measurements, it is anticipated that a dielectric constant independent of frequency and accompanied by very small losses should be observed. In this study, the applied frequencies, 20 to 20 KHz, actually could not activate these two processes. In other words, they appear as insulators in the equivalent circuits.

Breckenridge^{9, 10} first related the dielectric losses in alkali halide crystals to the motion of coupled defects in crystals, and was able to calculate the activation energy for the motion of defects accordingly. The experiments were carried out at low temperatures, below 250°C, where defects associate, at the audiofrequencies. It should be noted that in pure crystals in the equilibrium state, i.e., without any additional defects from a quenching process, the dielectric loss of this type has never been found¹¹.

Accordingly to Levitskii's² data, the transition temperature where the defect association occurs is 530°C (for a pure CaF_2 crystal at low P_{O_2} defined by CO/CO_2 mixture). In an argon atmosphere, $P_{\text{O}_2} = 10^{-6}$ atm, the transition temperature is 478°C according to Levitskii's² study. For Cells II-1 and II-2, with $\text{Ni} + \text{NiF}_2$ electrodes, the geometric capacitance appears at 548°C or below. For Cells III-1 and III-2, P_{O_2} is defined by $\text{Ni} + \text{NiO}$ electrodes, and the geometric capacitance appears around 400°C.

The geometric capacitance is probably caused by the association of fluorine vacancies and oxygen dopant ions. Cells II-1 and II-2 were not studied in an oxygen environment, but the electrolyte had previously contacted oxide electrodes. The magnitude of the geometric capacitance can be determined by the frequency at the maximum point of the semicircle in the impedance diagram.

The complex admittance plots for Cell IV-1 and IV-2 at different temperatures, from 646°C to 821°C, are shown in Figs. 30 to 36. Because of the limited frequency range available here, not all the measurements enable the plotting of semi-circles; therefore, not all the capacitances and interface conductivities could be determined. The equivalent circuits will be described later when the impedance diagrams are introduced. The bulk conductivities, the interface conductivities, the interface capacitances and the geometric capacitances of Cells IV-1 and IV-2 are listed in Tables I, II, and III. The geometric capacitance appears at rather high temperatures, 700°C or below.

The plot of $\log \sigma T$ vs. $\frac{1}{T}$ for Cells II-1, III-1, and IV-1 is shown in Fig. 37 where σ is the bulk conductivity of the electrolyte. Above 597°C, the data for Cells II-1 and III-1 fall on the same line which is consistent with the results of earlier workers¹². The calculated activation energy for the bulk conduction process is 1.89 eV, very close to Levitskii's² result, 1.92 eV. For Cell 4, the absolute magnitude of the bulk conductivity is slightly higher, probably because of a highly conductive surface¹³ through a non-activated process, but the activation energy remains the same. At temperatures below 597°C, the bulk conductivity of Cell III-1 is much higher

than that of Cell II-1 because the extrinsic interaction between the CaF_2 lattice and dopant oxygen creates more anion vacancies for Cell III-1. At higher temperature, the intrinsic defect concentration overcomes this effect.

The equivalent circuit in Fig. 38 has a Warburg impedance representing a diffusion process. The complete description of this circuit is the following¹³:

$$\begin{aligned}
 Z &= Z' - jZ'' \\
 &= R_b + \frac{R_{ct} + K\omega^{-1/2}}{(C_{de}K\omega^{1/2} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + K\omega^{-1/2})^2} \\
 &\quad - j \frac{\omega C_{dl} (R_{ct} + K\omega^{-1/2})^2 + K\omega^{-1/2} (\omega^{1/2} C_{dl} K + 1)}{C_{dl} K \omega^{1/2} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + K\omega^{-1/2})^2} \quad (27)
 \end{aligned}$$

This rather complicated formula can be simplified according to its two limiting cases¹³:

1. At low frequencies the impedance reduces to

$$Z = R_b + R_{ct} + K\omega^{-1/2} - j(K\omega^{-1/2} + K^2 C_{dl}) \quad (28)$$

where K is a constant in a Warburg impedance, W, expression:

$$W = K\omega^{-1/2} - jK\omega^{-1/2} \quad (29)$$

When plotting Z'' against Z' , a straight line of 45° slope is obtained, curve A in Fig. 39.

2. If diffusion polarization, W, can be neglected, i.e., at higher frequencies, a rather irreversible electrode-reaction, Eq. (27) reduces to

$$Z = R_b + \frac{R_{ct}}{1 - \omega^2 C_{dl}^2 R_{ct}^2} - j \frac{\omega C_{dl} R_{ct}^2}{1 + \omega^2 C_{dl}^2 R_{ct}^2} \quad (30)$$

If, in this case, the imaginary and real parts are plotted against each other a semicircle is obtained, curve B in Fig. 39; this can be demonstrated by elimination of ω between Z' and Z'' , leading to

$$(Z' - R_b - \frac{R_{ct}}{2})^2 + (Z'')^2 = (\frac{R_{ct}}{2})^2 \quad (31)$$

Again, Eq. (16) determines the double-layer capacitance, C_{dl} , from the frequency at the top of the semicircle. The interface charge transfer resistance, R_{ct} , can be obtained directly from the radius of the semicircle.

Figures 40 and 44 demonstrate that a Warburg impedance acts in Cell IV-1 and IV-2. At low frequencies, the slopes of the lines from the impedance diagram are close to 45° . Armstrong⁴ demonstrated that a Warburg impedance can not occur in a blocking electrode, but it arises when a solid electrolyte has immobile anions and two different sorts of cations, one of which is present at a low concentration, where the two ions have similar mobilities. Such an electrolyte might be Na- β -alumina with a small fraction of the sodium ions substituted by silver ions; sodium ions act as a supporting electrolyte for Ag^+ . In Cells IV-1 and IV-2, a small fraction of the fluorine ions in the lattice should be substituted by oxygen ions; oxygen ions then act as second conduction ions. The titration experiment suggests that oxygen ions have significant mobility compared to that of fluorine vacancies, while calcium cations are immobile.

After recognizing the presence of the Warburg impedance

in Cells IV-1 and IV-2, the interface conductivity is determined by measuring the radius of the semicircle in the impedance diagram. The semicircle intersects the real axis at the points R_b and $R_b + R_{ct}$, while the straight line intersects the real axis at the point $R_b + R_{ct} - 2K^2C_{dl}$. The interface conductivity, R_{ct} , is close to that of the bulk. The rather slight change of conductivity reading, R_p^{-1} , from the bridge, over a frequency range from 20 to 20 KHz also suggests that the interface conductivity is close to that of the bulk.

For Cells II-1 and II-2, presumably, the rate of electrode reaction defined by Eq. (19) determines the interface conductivity. For Cells III-1, III-2, IV-1, and IV-2 the rate of electrode reaction defined by Eq. (2) determines their interface conductivities. When plotting $\log (R_{ct})^{-1}$ vs. $1/T$, as shown in Fig. 45, the slope represents the activation energy for the process. The interface conductivity of Cell IV-1 is much greater than that of Cell III-1 even though they both have a similar electrode reaction defined by Eq. (2), since the oxygen activity in $Cu + Cu_2O$ electrode is much greater than that in $Ni + NiO$ electrode. The interface conductivity of Cell II measures the rate of electrode reaction involving fluorine. The reaction rate is higher than that of Cell III and lower than that of Cell IV. For Cell III, the empirical activation energy is 1.80 ev above $717^\circ C$ and 0.70 ev below $717^\circ C$. For Cell II, the activation energy is 2.0 ev above $680^\circ C$ and 0.70 ev below. The different activation energies at low and high temperatures probably results from the extrinsic and intrinsic nature of the vacancies which are involved in each

electrode reaction. The limited data for Cell IV does not allow the determination of its activation energy.

When there is no electrical potential drop, the equilibrium Frenkel space-charge double layer does not exist; positive and negative defects are of equal concentration. When the electrical potential drop exists, for instance at the electrode/electrolyte interface, the concentrations of positive and negative defects are no longer the same, which therefore creates the double layer¹⁴. Raleigh¹⁵ also explains that the surface of an electrolyte has a specific defect structure with high defect concentration which defines a specific capacitance¹⁵. Calcium fluoride has the anti-Frenkel defect structure. The electrical neutrality condition is satisfied in the bulk of the electrolyte. But, at the surface, either the concentration of fluorine vacancies, V_F° , is greater than that of fluorine interstitials or vice-versa:

$$\text{or} \quad [V_F^\circ] > [F_i'] \quad (32)$$

$$[V_F^\circ] < [F_i'] \quad (33)$$

Thus, an electrical potential drop is generated across the electrode-electrolyte interface. The capacitance of the interface is determined by the charge density, q , at the interface, and the electrical potential drop V :

$$C = \frac{q}{V} \quad (34)$$

The charge density is determined by the interface defect structure. Raleigh¹⁶ has suggested that for the pt/AgBr interface a specific layer of adsorbed silver ions was formed on the Pt electrode. The nature of this layer is independent of the state and the conductivity.

of the electrolyte. Therefore, the double layer capacitance remained nearly the same despite a 40-fold decrease in electrolyte conductivity. Armstrong¹⁷ also suggested this is true to some extent for Pt-Ag₄Rb₄I₅. The double-layer capacitance of Cells II-1 and II-2 increases by factors of 4.5 and 8, respectively, over a temperature range from 598°C to 853°C, while the bulk conductivity increases 260-fold. For Cell II-1 the capacitance increases from 1.9×10^{-7} F to 8.6×10^{-7} F from 598°C to 853°C, while for Cell III-1 over a temperature range from 598°C to 842°C, the capacitance increases from 8×10^{-9} F to 2.2×10^{-7} F. At high temperatures, the capacitances of Cell IV-1 approach that of Cell II-1. A similar situation occurs for Cells II-2 and IV-2, shown in Table III. The double layer capacitance of Cell II probably results from a specific surface defect structure of high vacancy concentration. The nature of this surface defect structure is insensitive to variation in temperature or bulk conductivity. For Cells IV-1 and III-2, when introducing oxygen to the system, the nature of the surface defect structure changes. At high temperatures, above 800°C, the double layer capacitance of Cell IV is close to that of Cell II, and at low temperatures it is much less. Similar to the character of the bulk of the CaF₂ crystals, oxygen starts to influence the surface defect structure, now according to Eq. (2), at low temperatures. At high temperatures, the intrinsic defect concentration overcomes the concentration of dopant oxygen in the double layer, therefore the double-layer capacitance approaches that of Cell II.

The interface capacitance of Cells IV-1 and IV-2 are higher than those of Cells II and IV, possibly because the surface condition

for a $\text{Cu} + \text{Cu}_2\text{O}$ electrode is much different from that of $\text{Ni} + \text{NiO}$ or $\text{Ni} + \text{NiF}_2$ electrodes.

The complex impedance plots of Cells II, and III given in Figs. 46 to 53 are consistent with the suggested equivalent circuits at different temperatures.

3. Oxygen Concentration Cell with CaF_2 Solid Electrolyte

When galvanic Cell 1 reaches equilibrium during open-circuit emf measurement, the electrochemical potential of the fluorine vacancy, which is the most mobile defect in a pure CaF_2 crystal, is constant throughout the electrolyte.

$$d\eta_{V_F}^\circ = d\mu_{V_F}^\circ + Fd\phi = 0 \quad (35)$$

where $\eta_{V_F}^\circ$ is the electrochemical potential of V_F° , $\mu_{V_F}^\circ$ is the chemical potential of V_F° , F is the Faraday constant, and ϕ is the electrical potential. In the bulk of the electrolyte, for a virgin crystal, the following equation holds

$$[V_F^\circ] = [F_i'] = K^{1/2} \quad (36)$$

where K is the equilibrium constant for the following reaction:

$$\text{with } \mu_{V_F}^\circ = \mu_{V_F}^\circ + RT \ln \gamma_{V_F}^\circ [V_F^\circ] \quad (38)$$

where $\gamma_{V_F}^\circ$ is the activity coefficient of F_F°

$$\text{therefore } d\mu_{V_F}^\circ = RT d \ln \gamma_{V_F}^\circ + RT d \ln [V_F^\circ] \quad (39)$$

Since $[V_F^\circ] = K^{1/2}$, and $\gamma_{V_F}^\circ$ is constant for a dilute concentration across the electrolyte, then $d\mu_{V_F}^\circ = 0$ (40)

With Eqs. (35) and (40), the electrical potential is constant in

the bulk of the electrolyte:

$$d\phi = 0 \quad (41)$$

At the electrode/electrolyte interface, the electrical neutrality condition is no longer locally satisfied according to Eq. (36). The excess charge is compensated by a charged electrode surface. Since $d\eta_{V_F^\circ} = 0$, the interfacial electrical potential drop defines a chemical potential drop of V_F° in the double layer, as shown in Fig. (54).

Because the oxygen ion is readily mobile over fluorine vacancies, $t_O > 0.26$, the electrochemical potential of O_F° is also constant in the equilibrium state. In the bulk of the electrolyte, the electrical potential is constant, and the chemical potential of O_F° , which is determined by residual oxygen content in CaF_2 crystal, is also constant. At the interface, the electrical potential gradient cancels the chemical potential gradient of O_F° , resulting in a constant electrochemical potential of O_F° , as shown in Fig. 54. The Warburg impedance observed in Cell IV is a strong evidence that the oxygen diffusion layer exists and that oxygen ions are rather mobile in the double layer.

The following equations describe the equilibrium conditions at the two interfaces according to Eq. 2:

$$\eta_{V_F^\circ} (R) + 1/2 \mu_{O_2} (R) + 2\eta_e (R) = \eta_{O_F^\circ} (R) \quad (42)$$

$$\eta_{V_F^\circ} (L) + 1/2 \mu_{O_2} (L) + 2\eta_e (L) = \eta_{O_F^\circ} (L) \quad (43)$$

where η_e represents the electrochemical potential of electrons, R represents $\text{Cu} + \text{Cu}_2\text{O}$ (right-hand) electrode, L represent $\text{Ni} + \text{NiO}$ (left-hand) electrode, and μ_{O_2} is the chemical potential of oxygen.

Subtracting Eq. (43) from Eq. (42):

$$\begin{aligned} \eta_{V_F^\circ}(R) - \eta_{V_F^\circ}(L) + 1/2(\mu_{O_2}(R) - \mu_{O_2}(L)) + 2(\eta_e(R) - \eta_e(L)) \\ = \eta_{O_F'}(R) - \eta_{O_F'}(L) \end{aligned} \quad (44)$$

With $\eta_{V_F^\circ}(R) = \eta_{V_F^\circ}(L)$ and

$$\eta_{O_F'}(R) = \eta_{O_F'}(L)$$

$$\text{therefore } 1/2(\mu_{O_2}(R) - \mu_{O_2}(L)) + 2(\eta_e(R) - \eta_e(L)) = 0 \quad (45)$$

The electrochemical potential of electron can be expressed as

$$\eta_e(R) = \mu_e(R) - F\phi(R) \quad (46)$$

$$\eta_e(L) = \mu_e(L) - F\phi(L) \quad (47)$$

where μ_e is the chemical potential of electrons, and ϕ is the electrical potential in the electrode. Substituting Eqs. (46) and (47) into Eq. (45):

$$\begin{aligned} 1/2(\mu_{O_2}(R) - \mu_{O_2}(L)) + 2(\mu_e(R) - F\phi(R)) - \\ (\mu_e(L) - F\phi(L)) = 0 \end{aligned} \quad (48)$$

The chemical potential of electron is the same when both electrodes are connected to the platinum leads:

$$\mu_e(R) = \mu_e(L) \quad (49)$$

(Equation (48) can be simplified;

$$1/2(\mu_{O_2}(R) - \mu_{O_2}(L)) - 2(F\phi(R) - F\phi(L)) = 0 \quad (50)$$

$$\begin{aligned} \text{or } \mu_{O_2}(R) - \mu_{O_2}(L) &= 4F(\phi(R) - \phi(L)) \\ &= 4FE \end{aligned} \quad (51)$$

The emf values obtained from Cell I confirms Eq. (51).

Conclusions

The interaction of oxygen with a CaF_2 crystal changes the bulk and the interface characteristics of the crystal. Equation(1) describes the chemical reaction which affects mostly the bulk of the electrolyte. Equation(2) describes the electrochemical reaction at the electrode/electrolyte interface and affects the surface defect structure. The plot of $\log \sigma T$ vs. $1/T$ of Cell III suggests that the effects from oxygen are important only at lower temperatures, below 597°C . The double-layer capacitances of Cells II and III vary differently with temperature, because the $\text{Ni} + \text{NiO}$ electrode of Cell III change its surface defect structure at lower temperatures. At high temperatures, because the intrinsic character of the bulk and the surface prevail, the action from oxygen diminishes. The bulk defect structure also determines the crystal geometric capacitance. For Cell III, this geometric capacitance is probably attributed to the association of oxygen dopants and the fluorine vacancies. For Cell II, it is possibly attributed to the association of fluorine vacancies and the residual oxygen dopants from processing or other impurities such as Al^{+3} .

Complex impedance analysis is a successful technique to separate the interface phenomena from the bulk phenomena. Equivalent circuits were established for Cells II, III and IV at different temperatures. The Warburg impedance observed in Cell IV shows that the oxygen ion has a mobility similar to the fluorine ion in the double layer; the oxygen diffusion layer exists in the double layer where fluorine vacancies act as supporting conducting species. In Cell IV, the electrode reaction is a rather rapid reaction defined by Eq. (2). The titration experiment is a direct proof that oxygen

ions have significant mobility in the CaF_2 lattice, $t_0 > 0.26$.

Oxygen can, not only incorporate into the CaF_2 lattice through chemical or electrochemical processes, but also move readily over fluorine vacancies. Then through synchronized movement of fluorine vacancies and oxygen ions Cell I reaches its equilibrium state when both fluorine vacancy and dopant oxygen establish constant electrochemical potentials in the cell. At that time, Cell I reads emf values corresponding to the oxygen activities in the electrodes.

Future Work

In order to determine the importance of the contribution of oxygen to the geometric capacitance through the vacancy-oxygen ion association model, the geometric capacitances of a virgin CaF_2 crystal and an oxygen-saturated CaF_2 crystal will be studied by the complex impedance analysis technique. The electrodes will be Pt blocking electrodes.

The virgin crystal should not have any significant geometric capacitance, since it should not have any oxygen ions associated with fluorine vacancies. Also, a virgin CaF_2 crystal should have a very low concentration of any associated defects. The oxygen-saturated crystal can be prepared by sintering a CaF_2 crystal in the air, at various high temperatures, then quenching it to the room temperature. The geometric capacitance will be calculated from the frequency at the top of the semicircle in a impedance diagram. At this frequency the motion of the associated defects is activated. By studying the

resonant frequency, f , for different temperatures, the activation energy, E , for the motion of oxygen ions over fluorine vacancies can be determined.

$$f \propto e^{-E/RT}$$

The complex impedance study of Cells II, III, IV will be carried to low temperatures. The following cell will also be studied:

These works will clarify the influence of oxygen over the nature of the double-layer capacitance.

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- Fig. 18. Complex Plane Admittance Plots for Cells with Ni + NiO Electrodes at 398°C; o Cell III-1; Δ Cell III-2.
- Fig. 19. Complex Plane Admittance Plots for Cells with Ni + NiO Electrodes at 508°C; o Cell III-1; Δ Cell III-2.
- Fig. 20. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 546°C; o Cell III-1; Δ Cell III-2.
- Fig. 21. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 598°C; o Cell III-1; Δ Cell III-2.
- Fig. 22. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 646°C; o Cell III-1; Δ Cell III-2.
- Fig. 23. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 648°C; o Cell III-1; Δ Cell III-2.
- Fig. 24. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 740°C; o Cell III-1, Δ Cell III-2.
- Fig. 25. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 744°C; Δ Cell III-1, o Cell III-2.
- Fig. 26. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 839°C; o Cell III-1; Δ Cell III-2.
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- Fig. 29. Complex Plane Admittance Diagrams of Cells with Ni+NiO Electrodes at 646°C; o Cell III-1; Δ Cell III-2.
- Fig. 30. Complex Plane Admittance Diagrams of Cells with Cu + Cu₂O Electrodes at 646°C; o Cell IV-1; Δ Cell IV-2.
- Fig. 31. Complex Plane Admittance Plot for Cell with Cu + Cu₂O Electrodes at 649°C.
- Fig. 32. Complex Plane Admittance Plot of Cell with Cu + Cu₂O Electrodes.
- Fig. 33. Complex Plane Admittance Plots for Cells with Cu + Cu₂O Electrodes at 699°C; o Cell IV-1; Δ Cell IV-2.
- Fig. 34. Complex Plane Admittance Plots for Cells with Cu + Cu₂O Electrodes at 750°C; Δ Cell IV-1; Cell IV-2.
- Fig. 35. Complex Plane Admittance Plots for Cells with Cu + Cu₂O Electrodes at 791°C; Δ Cell IV-1; o Cell IV-2.

- Fig. 36. Complex Plane Admittance Plots for Cells with Cu + Cu₂O Electrodes at 821°C; Δ Cell IV-1; Cell IV-2.
- Fig. 37. The plots of $\log T/R_p$ vs. $1/T$ for Cells with Ni + NiF₂, Ni + NiO, and Cu + Cu₂O Electrodes.
- Fig. 38. Diagram of Equivalent Circuit 7 for Cells with Cu + Cu₂O Electrodes.
- Fig. 39. Complex Plane Impedance Plots of Equivalent Circuit 7.
- Fig. 40. Complex Plane Impedance Plots for Cells with Cu + Cu₂O Electrodes at 791°C; Δ Cell IV-1; o Cell IV-2.
- Fig. 41. Complex Plane Impedance Plots for Cells with Cu + Cu₂O Electrodes at 750°C; o Cell IV-1; Δ Cell IV-2.
- Fig. 42. Complex Plane Impedance Plots for Cell with Cu + Cu₂O Electrodes at 649°C; Cell IV-2.
- Fig. 43. Complex Plane Impedance Plots for Cells with Cu + Cu₂O Electrodes at 646°C; Δ Cell IV-1; o Cell IV-2.
- Fig. 44. Complex Plane Impedance Plots for Cell with Cu + Cu₂O Electrodes at 649°C; Cell IV-1.
- Fig. 45. The Plots of $\log 1/R_{ct}$ vs. $1/T$ for Cells with Ni + NiF₂, Ni + NiO and Cu + Cu₂O Electrodes.
- Fig. 46. Complex Plane Impedance Plots of Cells with Ni + NiF₂ Electrodes at 792°C; o represents scale 0 to 1000 Ω and Δ represents scale 0 to 5000 Ω on the real axis.
- Fig. 47. Complex Plane Impedance Plots for Cells with Ni + NiF₂ Electrodes at 502°C; Δ Cell II-1; o Cell II-2.
- Fig. 48. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes at 398°C; Δ III-1; o III-2.
- Fig. 49. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes at 744°C; Cell III-1 Δ on a 5000 Ω scale; on a 25000 Ω scale on real axis, Cell III-2 o on a 5000 Ω scale.
- Fig. 50. Complex Plane Impedance Plots for Cell with Ni + NiO Electrodes, III-1, at 648°C.
- Fig. 51. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes at 845°C; Cell III-1 on a 1000 Ω scale, Δ on a 5000 Ω scale on real axis; Cell III-2 o on a 1000 Ω scale.
- Fig. 52. Complex Plane Impedance Plots for Cell with Ni + NiO Electrodes at 840°C; Δ Cell III-1; o Cell III-2.

Fig. 53. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes; Δ Cell III-1 Δ on a 12 Ω scale on real axis, o on a 70 Ω scale; Cell III-2 on a 12 Ω scale, Δ on a 70 Ω scale.

Fig. 54. Profiles of fluorine vacancy concentration, $[V_F]$, oxygen substitute concentration $[O_F]$, electrical potential, ϕ , electrochemical potential of fluorine vacancy, η_V , and electrochemical potential of oxygen dopant η_O , V_F across the CaF_2 solid electrolyte in Cell 1, on V_F arbitrary energy and concentration scales.

Table I Bulk conductivities in μMhO , of Cells II-1, II-2, III-2, IV-1, and IV-2 at Various temperatures.

Table II Electrode-Electrolyte interface conductivities, in μMhO , of Cells II-1, II-2, III-1, III-2, IV-1 and IV-2 at various temperatures.

Table III Electrode-Electrolyte interface capacitances, geometric capacitances and Electrolyte-Electrolyte interface capacitances of Cells II-1, II-2, III-1, III-2, IV-1 and IV-2 at various temperatures.

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Fig. 1. Diagram of Equivalent Circuit 1 for Electrochemical Cell with Identical Electrodes.

Fig. 2. Diagram of Equivalent Circuit 2; Build-in Circuit for Wayne-Kerr Bridge, C_p ; Capacitor, R_p ; Resistor.

(a)

(b)

Fig. 3. (a) Impedance plot of the real part against the imaginary part, and (b) Admittance plot of the real part against the imaginary part for circuit 1.

Fig. 4. Diagram of Equivalent Circuit 3, without a geometric capacitor.

(a)

(b)

Fig. 5. (a) Impedance plot of the real part against the imaginary part, and (b) Admittance plot of the real part against the imaginary part for circuit 3.

Fig. 6. Diagrams of Test Circuits 4, (a), and 5, (b), as used to insure the proper functioning of Wayne-Kerr Bridge.

Fig. 7. Impedance plot of the real part against the imaginary part for Circuit 4.

Fig. 8. Admittance plot of the real part against the imaginary part for circuit 5.

Fig. 9. Titration Experiment Schematic.

Fig. 10. Complex Plane Admittance Plots for Cells II-1, °, and II-2, °, at 502°C.

Fig. 11 Complex Plane Admittance Plots for Cells II-1, , and II-2, °, at 548°C.

Fig. 12. Complex Plane Admittance Plots for Ce-1s II-1, Δ , and II-2, at 598°C.

Fig. 13. Complex Plane Admittance Plots for Cells II-1 and II-2 at 647°C. ($\bullet$ represents cell II-1 Run a; $\circ$ cell II-2, Run a; $\square$ cell II-1, Run b; Δ cell II-2, Run b.)

Fig. 14. Complex Plane Admittance Plots for Cell II-1, Δ , and Cell II-2, $\circ$, at 746°C.

Fig. 15. Complex Plane Admittance Plots for Cells with Ni + NiF₂ Electrodes at 792°C; o Cell II-1; Δ Cell II-2.

Fig. 16. Complex Plane Admittance Plots for Cells with Ni + NiF₂ Electrodes at 853°C, Cell II-1; Δ Cell II-2; Run a; $\circ$ Cell II-2, Run b.

Fig. 17. Diagram of Equivalent Circuit 6 for cell with Ni + NiO Electrodes and two CaF_2 crystals as Electrolyte.

Fig. 18. Complex Plane Admittance Plots for Cells with Ni + NiO Electrodes at 398°C; o Cell III-1; Δ Cell III-2.

Fig. 19. Complex Plane Admittance Plots for Cells with Ni + NiO Electrodes at 508°C; o Cell III-1; Δ Cell III-2.

Fig. 20. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 546°C; o Cell III-1; Δ Cell III-2.

Fig. 21. Complex Plane Admittance Diagrams of Cells with Ni + NiO. Electrodes at 598°C; o Cell III-1; Δ Cell III-2.

Fig. 22. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 646°C; o Cell III-1; Δ Cell III-2.

Fig. 23. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 648°C; o Cell III-1; Δ Cell III-2.

Fig. 24. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 740°C; o Cell III-1, Δ Cell III-2.

Fig. 25. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 744°C; Δ Cell III-1; o Cell III-2.

Fig. 26. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 839°C; o Cell III-1; Δ Cell III-2.

Fig. 27. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 840°C; Δ Cell III-1; o Cell III-2.

Fig. 28. Complex Plane Admittance Diagrams of Cells with Ni + NiO Electrodes at 842°C; Δ Cell III-1; $\bullet$ Cell III-2.

Fig. 29. Complex Plane Admittance Diagrams of Cells with Ni+NiO Electrodes at 646°C; o Cell III-1; Δ Cell III-2.

Fig. 30. Complex Plane Admittance Diagrams of Cells with Cu + Cu₂O Electrodes at 646°C; o Cell IV-1; Δ Cell IV-2.

Fig. 31. Complex Plane Admittance Plot for Cell with Cu + Cu₂O Electrodes at 649°C.

Fig. 32. Complex Plane Admittance Plot of Cell with Cu + Cu₂O Electrodes.

Fig. 33. Complex Plane Admittance Plots for Cells with Cu + Cu₂O Electrodes at 699°C; ○, Cell IV-1; Δ, Cell IV-2.

Fig. 34. Complex Plane Admittance Plots for Cells with $\text{Cu} + \text{Cu}_2\text{O}$
Electrodes at 750°C ; Δ Cell IV-1; $\bullet$ Cell IV-2.

Fig. 36. Complex Plane Admittance Plots for Cells with Cu + Cu₂O Electrodes at 821°C; Δ Cell IV-1; $\bullet$ Cell IV-2.

Fig. 37. The plots of $\log T/R$ vs. $1/T$ for Cells with Ni + NiF₂, Ni + NiO, and Cu + Cu₂O Electrodes.

Fig. 38. Diagram of Equivalent Circuit 7 for Cells with $\text{Cu} + \text{Cu}_2\text{O}$ Electrodes.

Fig. 39. Complex Plane Impedance Plots of Equivalent Circuit 7.

Fig. 40. Complex Plane Impedance Plots for Cells with Cu + Cu₂O Electrodes at 791°C; Δ Cell IV-1; o Cell IV-2.

Fig. 41. Complex Plane Impedance Plots for Cells with Cu + Cu₂O Electrodes at 750°C; o Cell IV-1; Δ Cell IV-2.

Fig. 42. Complex Plane Impedance Plots for Cell with Cu + Cu₂O Electrodes at 649°C; Cell IV-2.

Fig. 43. Complex Plane Impedance Plots for Cells with Cu + Cu₂O Electrodes at 646°C; Δ Cell IV-1; o Cell IV-2.

Fig. 45. The Plots of $\log 1/R_{ct}$ vs. $1/T$ for Cells with Ni + NiF₂, Ni + NiO and Cu + Cu₂O Electrodes.

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Fig. 47. Complex Plane Impedance Plots for Cells with Ni + NiF₂ Electrodes at 502°C; Δ Cell II-1; o Cell II-2.

Fig. 48. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes at 398°C; Δ III-1; o III-2.

Fig. 49. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes at 744°C; Cell III-1Δ on a 5000 Ω scale; on a 25000 Ω scale on real axis; Cell III-2 o on a 5000 Ω scale.

Fig. 50. Complex Plane Impedance Plots for Cell with Ni + NiO Electrodes, III-1, at 648°C.

Fig. 51. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes at 845°C; Cell III-1 on a 1000 Ω scale, Δ on a 5000 Ω scale on real axis; Cell III-2 o on a 1000 Ω scale.

Fig. 52. Complex Plane Impedance Plots for Cell with Ni + NiO Electrodes at 840°C; Δ Cell III-1; o Cell III-2.

Fig. 53. Complex Plane Impedance Plots for Cells with Ni + NiO Electrodes; Δ Cell III-1 Δ on a 12 Ω scale on real axis, $\circ$ on a 70 Ω scale; Cell III-2 on a 12 Ω scale, Δ on a 70 Ω scale.

Fig. 54. Profiles of fluorine vacancy concentration, $[V_F^\bullet]$, oxygen substitute concentration $[O_F]$, electrical potential, ϕ , electrochemical potential of fluorine vacancy, $\eta_{V^\bullet}$, and electrochemical potential of oxygen dopant $\eta_{O^\bullet}$, F across the CaF_2 solid electrolyte in Cell 1, on F arbitrary energy² and concentration scales.

Temp °C	Cell II-1	Cell II-2	Cell III-1	Cell III-2	Cell IV-1	Cell IV-2
398°C			5.0	2.05		
502°C	3.5	1.63				
508			29.4	10.5		
546			50.2	17.0		
548	9.25	4.5				
598	35.7	17.6	133	40		
646			260	81	193	44
647	a) 156 b) 156	a) 81 b) 83				
648			298	97		
649					212	47.5
699					640	190
740			1600	525		
744			1635	560		
746	1000	500				
750					2100	460
791					4750	1090
792	2800	1500				
821					8850	2250
839			12800	4100		
840			8500	3500		
842			11100	3650		
845				3430		
853	9150	4550				

Table I Bulk conductivities in $\mu\text{M h } \Omega$, of Cells II-1, II-2, III-2, IV-1, and IV-2 at Various temperatures.

Temp °C	Cell II-1	Cell II-2	Cell III-1	Cell III-2	Cell IV-1	Cell IV-2
398			0.08	0.09		
502						
508			0.32	0.36		
546			0.8	0.9		
548						
598	3.5	3.5	1.3	1.7		
646			2.0	2.0		
647	a) 6 b) 3	a) 6 b) 3				
648			2	1.8		
649						
694						
696			3.2	3.4		
699					225	92
740			6	5.6		
744			7.0	6.0		
746	35	35				
750						
791					400	
792	100	100				
821					1100	
839			45	48		
840			a) 44 b) 32	a) 30 b) 28		
842			42	33		
845				26		
853	300	300				

Table II Electrode-Electrolyte interface conductivities, in μMhO , of Cells II-1, II-2, III-1, III-2, IV-1 and IV-2 at various temperatures.

Electrode - Electrolyte Interface Capacitance	Temp °C	Cell II-1	Cell II-2	Cell III-1	Cell III-2	Cell IV-1	Cell IV-2
	398			$1.33 \times 10^{-9} F$	$1.6 \times 10^{-9} F$		
	502						
	508			$4.8 \times 10^{-9} F$	$5.0 \times 10^{-9} F$		
	546			$8 \times 10^{-9} F$	$5.6 \times 10^{-9} F$		
	548	$5.3 \times 10^{-8} F$					
	598	$1.9 \times 10^{-7} F$	$0.9 \times 10^{-7} F$	$8 \times 10^{-9} F$	$8 \times 10^{-9} F$		
	646			$2.8 \times 10^{-8} F$	$3.2 \times 10^{-8} F$		
	647	5×10^{-7}	$5.5 \times 10^{-7} F$				
	648			$2.4 \times 10^{-8} F$	$1.9 \times 10^{-8} F$		
	649						
	694						
	696						
	699					$2 \times 10^{-6} F$	$1.4 \times 10^{-6} F$
	740			$10 \times 10^{-8} F$	$8.4 \times 10^{-8} F$		
	744			$6.5 \times 10^{-8} F$	$6.0 \times 10^{-8} F$		
	746	$5.3 \times 10^{-7} F$	$4 \times 10^{-7} F$				
	750						
	791					$1.1 \times 10^{-5} F$	
	792	$4.5 \times 10^{-7} F$	$2.4 \times 10^{-7} F$				
	821					$9.2 \times 10^{-6} F$	$4.8 \times 10^{-6} F$
	839			$2.7 \times 10^{-7} F$	$3.2 \times 10^{-7} F$		
	840			$9.0 \times 10^{-8} F$	$8.0 \times 10^{-8} F$		
	842			$2.2 \times 10^{-7} F$	$1.9 \times 10^{-7} F$		
	845				$4.2 \times 10^{-8} F$		
	853	8.6×10^{-7}	7.2×10^{-7}				
Geometric Capacitance	398			$3.9 \times 10^{-11} F$	$6.3 \times 10^{-11} F$		
	502		$1.3 \times 10^{-11} F$				
Electrolyte-Electrolyte Interface Capacitance	649						
	647		a) $6.0 \times 10^{-11} F$ b) $6.8 \times 10^{-9} F$				

Table III Electrode-Electrolyte interface capacitances, geometric capacitances and Electrolyte-Electrolyte interface capacitances of Cells II-1, II-2, II-1, II-2, IV-1 and IV-2 at various temperatures.