C00-2671-2

MASTER

FUNDAMENTAL STUDIES OF METAL FLUORINATION REACTIONS

Progress Report
for Period May 1, 1976-April 31, 1977

Robert A. Rapp

Ohio State University
Columbus, Ohio 43210

January 1977

Prepared For
The U.S. Energy Research and Development Administration
Under Contract No. EY-76-S-02-2671

INTRODUCTION

The present research is being undertaken to study some fundamental thermodynamic and transport properties and detailed mechanisms pertinent to metal fluorination reactions. The program consists of determining the following properties using solid-state, CaF_2-electrolyte galvanic cells: (A) solubility and diffusivity of fluorine in metals, specifically nickel, and (B) the nature of the point defects (type, concentration and mobility) in metal fluorides as a function of fluorine partial pressure, temperature and impurity concentration. The latter study encompasses the study of the electrical conductivity of metal fluorides under thermodynamically well-defined conditions. Another objective of the program is: (C) to design and construct a fluorine probe for the measure of fluorine chemical potentials in gaseous environments. The probe must be evaluated in oxygen-containing atmospheres which might limit its accuracy and lifetime.

For several technical reasons, the specific experimentation has deviated somewhat from that originally proposed. For two reasons, a probable phase change in CaF_2 at a temperature around 1175°C and a thermal expansion coefficient which differs greatly from solid nickel, CaF_2 single crystal electrolytes could not yet be interfaced perfectly to solid nickel for electrochemical studies. However, these problems were avoided by the successful substitution of copper for nickel in the studies of solubility and diffusivity. Some problems also arose in the study of the electrical conductivity of NiF_2, namely, only relatively impure NiF_2 was available, and NiF_2 exhibited poor mechanical stability as electrodes. Therefore, the proposed methods were used mostly for the study of β-PbF_2, for which previous studies also provided values for comparison. With the experience gained form the work reported here, future experimentation in the next year with nickel metal and NiF_2 should be successful.

The principal investigator (R. Rapp) has devoted about 25% of his time (15% ERDA support, 10% OSU matching support) to this research and to the guidance of Dr. Reddy and graduate students W. C. Fang and S. F. Chou. This level of support will continue for the remainder of the current term. Several publications and presentations for the research results of this project are contemplated within the next year. The principal investigator (R. Rapp) is also receiving Federal support from the National Science Foundation at 15% during the academic year and 50% over two summer months for a research grant to study, "Hot Corrosion of Alloys."

I. The Electrochemical Measurement of the Solubility and Diffusivity of of Fluorine in Solid Copper (S. Reddy)

A. Introduction

Many chemical and extractive metallurgical processes, including the gaseous diffusion isotope separation method, involve halogen gases and volatile metal halide species. In such high-temperature halide processes, metals are generally required as the materials for the fabrication of hardware. A recent review[1] has been published, surveying the characteristics of the high-temperature halogenation of metals. In comparison to the oxidation of metals and alloys, the detailed mechanisms of halogenation are very poorly characterized. The literature contains no information concerning the magnitudes of the solubility and diffusivity of any halogen in any metal.

In this report, electrochemical experiments to determine the solubility and diffusivity of fluorine in solid copper at temperatures 800-1000°C are discussed. The present results represent the very first determination of the magnitudes of solubility and diffusivity of fluorine in copper. In addition, this is the first time that the CaF_2 solid electrolyte has been used in kinetic experiments.

The original purpose of this investigation was to determine the solubility and diffusivity of fluorine in solid nickel, because, in fluorine-containing environments, the important alloys of industrial use are generally nickel-base. However, for reasons discussed later, electrochemical experiments with solid nickel were found to be difficult, and it was felt that attempts should first be made with solid copper. With the experimental insights gained by using solid copper, further experiments are presently underway to determine the solubility and diffusivity of fluorine in solid nickel.

B. Theory

A potentiostatic electrochemical experiment involving the CaF_2 solid electrolyte was used for the determination of diffusivity and solubility of fluorine in copper. The method is similar to that used by Pastorek and Rapp[2] for the determination of solubility and diffusivity of oxygen in solid copper using the oxygen-ion-conducting, stabilized-zirconia electrolyte. The experimental arrangement consists of a double-cell arrangement shown in Figure 1.

The experimental procedure was based on the premise that for the cell

$$\mathrm{Ni} + \mathrm{NiF_2} \,\Big|\, \mathrm{CaF_2} \,\Big|\, \mathrm{Cu} + \mathrm{F}\ (\text{dissolved})$$

the cell voltage E can be related to the activity of fluorine atoms (a_F) in the copper electrode at the electrode/electrolyte interface according to the expression:

$$E - I_{ion}\,\Omega_{ion} = \frac{1}{F}\left(\mu_F' - \mu_F''\right) = \frac{RT}{F}\ \ln\ \frac{a'(\mathrm{Cu})}{a_F''(\mathrm{Ni} + \mathrm{NiF_2})} \qquad (1)$$

where I_{ion} is the ionic current, Ω_{ion} is the ionic electrical resistance of the electrolyte and μ_F is the chemical potential of fluorine atoms. The standard state for fluorine atoms is defined by the expression

$$a_F \equiv f_{F_2}^{\frac{1}{2}} \approx P_{F_2}^{\frac{1}{2}} \tag{2}$$

where f_{F_2} is the fugacity of fluorine molecules and P_{F_2} the partial pressure.

The ionic current passing through the CaF_2 electrolyte is carried by fluorine ions. From Ficks' first law, the ionic cell current is related to the gradient in fluorine atom concentration at the electrolyte/copper interface by the expression

$$\left(\frac{\partial N_F}{\partial x}\right)_{x=0} = \frac{-I_{ion} V_{Cu}}{F\ A\ D_F} \tag{3}$$

where N_F is the atom fraction of fluorine in copper, V_{Cu} the molar volume of copper, A the cross-sectional area of the electrode, and x the distance in the copper from the electrolyte/copper interface.

Initially, the potentiostat of Figure 1 was set at a voltage E_1 and the copper was brought to equilibrium at a well defined fluorine activity somewhat higher than Ni-NiF_2 coexistence. At the start of an experimental run, the electromotive force was jumped to a new value E_2, which was yet too low to form CuF_2 at the copper/electrolyte interface. The diffusion of fluorine atoms was monitored by a continuous recording of the cell current. From the solution of the diffusion equation and the time-dependence of the current, values for the solubility and diffusivity of oxygen in solid copper can be derived as follows.

For a concentration-independent diffusion coefficient, Fick's second law for one-dimensional diffusion of fluorine into the finite copper specimen is

$$\frac{\partial N_F}{\partial t} = D_F \frac{\partial^2 N_F}{\partial x^2} \tag{4}$$

The initial condition is:

$$N_F = N_F(E_1) \text{ for } o < x < \ell,\ t = o$$

and the boundary conditions are:

$$N_F = N_F(E_2) \text{ for } x = o, \ell \text{ and } t > o$$

$$N_F = N_F(E_2) \text{ for } o \leq x \leq \ell \text{ and } t = \infty$$

where ℓ is the thickness of the copper specimen and $N_F(E_1)$ is the equilibrium atom fraction of fluorine in copper at an oxygen activity $a_F(E_1)$ when a voltage E_1 is applied to the cell according to Eq. (1).

For a truly potentiostatic experiment, $I_{ion}\ \Omega_{ion}$ must be restricted to values much smaller than the applied E throughout the pumping transient so that the activity of fluorine atoms at the copper/electrolyte interfaces is essentially time-independent. This is nearly the case in this experiment. For example, from the conductivity measurements for CaF_2 of Hinze and Patterson[3], the ionic conductivity of single crystal CaF_2 is 1.58×10^{-3} $(\text{ohm-cm})^{-1}$ at 800°C. If the electrolyte thickness is 0.2 cm, and diameter is 1.27 cm, the value of $I_{ion}\ \Omega_{ion}$ would be 1.0 mv for $I_{ion} = 10\mu a$. At higher temperatures, the value of $I_{ion}\ \Omega_{ion}$ would be no more important compared to ΔE.

The solution of Eg. (4) is given by

$$N_F(x,t) = N_F(E_1) - [N_F(E_1) - N_F(E_1)] \sum^{\infty} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{\ell}\right) \exp\left(\frac{-n^2\pi^2 D_F t}{\ell^2}\right) \quad (5)$$

$$n = 1,3,5,\ldots\ldots$$

Differentiating Eq. (5) with respect to x and substituting into Eq. (3), the instantaneous ionic current for the two cells is given by

$$I_{ion} = B\sum^{\infty} \exp\left(\frac{-n^2\pi^2 D_F t}{\ell^2}\right) \qquad (6)$$

$$n = 1,3,5$$

where $B = \left(\frac{8FAD_F}{\ell V_{Cu}}\right) [N_F(E_2) - N_F(E_1)]$

Defining a characteristic time τ as $\tau = \frac{\ell^2}{\pi^2 D_F}$, for long times $(\frac{t}{\tau} \geqslant 0.5)$, Eq. (6) reduces to

$$I_{ion} \approx B \exp\left(\frac{-t}{\tau}\right) \qquad (7)$$

A plot of log I_{ion} vs t should approach linear behavior with a slope of $\frac{-1}{2.303\tau}$ and intercept of log B. Thus, a value for D_F is obtained from the slope. The change in equilibrium fluorine content of copper, $\Delta N_F = N_F(E_2)-N_F(E_1)$, can be calculated from the now known value of D_F and the intercept value of log B.

If Sieverts' law is obeyed (i.e., Henrian behavior for the dissolution of fluorine in solid Cu)

$$\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}} = \text{constant at constant T}$$

where $\Delta P_{F_2}^{\frac{1}{2}} = \left|P_{F_2}^{\frac{1}{2}}(E_2) - P_{F_2}^{\frac{1}{2}}(E_1)\right|$

By knowing the Gibbs energy of formation of CuF_2 (or $P_{F_2}(Cu + CuF_2)$), the saturation solubility of fluorine in copper can be calculated according to the expression

$$N_F^{(s)} = \left(\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}\right) P_{F_2}^{\frac{1}{2}}(Cu + CuF_2) \qquad (8)$$

C. Experimental Materials and Apparatus

The CaF_2 solid electrolytes were purchased from Harshaw Chemical Company as optically pure single crystals of cylindrical geometry, 12.7 mm diameter and 2 mm thickness. The non-reversible copper electrode was obtained from Materials Research Corporation as a 19 mm diameter polycrystalline rod of 99.999% purity. Cylindrical specimens of 2 mm thickness and 11 mm diameter were machined from this rod. The faces of the specimens were ground flat with avoidance of rounded corners, then mechanically polished through 600-grit SiC paper and finally polished with 0.5μ alumina abrasive. The specimens were then rinsed in distilled water and ultrasonically cleaned in acetone. The final thickness and diameter of the copper specimens were measured to 0.003 mm accuracy using a micrometer.

The voltage applied to the cell consisted of the output from a Wenking potentiostat minus the voltage drop across a small standard resistor used to measure the current. A Speedomax-H strip-chart recorder was connected to the terminals of the standard resistor and the voltage was recorded as a function of time.

The cell was suspended vertically in a spring-loaded ceramic holder which was described in the previous report. Temperatures were indicated by a calibrated Pt/Pt + 10%Rh thermocouple. The cell temperature was held constant to 10.5°C in a single diffusion run and ±1°C during experimentation at a given isotherm. The Ar-gas surrounding the cell was purified free of moisture and CO_2; the P_{O_2} of the gas was set by passing it over Ti chips held at 850°C.

The preliminary bonding of the copper electrode and the CaF_2 electrolyte was performed to insure that the copper specimen adhered with intimate contact to the electrolyte. The copper specimen, with an electrolyte superimposed on each face was assembled in the cell holder and placed under spring pressure. This assembly was then heated slowly in flowing purified Ar gas and held at 1075°C (melting point of Cu is 1083°C) for 6 hours to achieve a suitable bond. The cell assembly was then slowly cooled (50°C/hour) to room temperature. The bonding between the electrolyte and copper was strong and attempts to break the bond resulted in fracture through the electrolyte. Also, no chemical interaction was observed visually between Cu and CaF_2. In order to prevent the cylindrical surfaces of the copper specimen from interacting with the surrounding gas phase, these surfaces were coated with alumina cement, and dried in an oven at 100°C.

In the preliminary experiments, the reversible electrodes consisted of Ni and NiF_2 powder mixture in a volume ratio of approximately 4 to 1. The polarization characteristics of this electrode were determined by measuring the I-V characteristics of the symmetric cell $Ni\text{-}NiF_2|CaF_2|Ni\text{-}NiF_2$. The results of the measurements were reported in the previous progress report. For example, the electrode was found to be essentially reversible up to 50μa at 850°C, 100μa at 900°C and 300μa at 950°C. However, repeated use of this electrode resulted in the formation of a thin layer of nickel metal at the electrode/electrolyte interface with accompanying irreversibility (polarization).

The addition of some CaF_2 powder into the $Ni\text{-}NiF_2$ electrode prevented the formation of the Ni layer at the electrode/electrolyte interface. The composition of the reversible electrode used in the present investigation was 2 parts Ni powder, 2 parts NiF_2 powder and 1 part CaF_2 powder. This electrode was found to be reversible in the range of ionic currents observed in the present investigation. The electrode powders were mixed by grinding in a porcelain mortar and pressed in a steel die to form 1.3 cm dia. discs. The electrodes were sintered in situ during heating to 800°C.

E. Experimental Procedure

The cell was assembled in the furnace and flushed with purified argon. The cell chamber was then evacuated and the furnace temperature raised to 250°C in order to outgas the system for 1 hour. At this time, purified argon was introduced to the cell at a low flow rate and the furnace was slowly heated to 800°C and held at this temperature.

In preparation for a run, a predetermined emf E_1 was applied to the cell, with the copper electrode at positive polarity. The cell was then held at temperature long enough to allow volume diffusion to occur (i.e., times in excess of the relation $t = \frac{x^2}{4D_F}$), and allow equilibration of the copper at $N_F(E_1)$. This insured the necessary initial condition of a homogeneous fluorine content, $N_F(E_1)$, throughout the copper specimen. Then an emf E_2 (greater or less than E_1), which was too low to form CuF_2 on the copper electrode, was applied to the cell and values of the current and elapsed time were recorded. The potentiostatic experiment was repeated at different temperatures between 802 and 995°C with various values of applied emf.

One of the difficulties associated with this study is the high vapor pressure of NiF_2 which at 800°C equals 2.8×10^{-6} atm; it reaches 10^{-4} atm at 939°C. In an open system with flowing Ar gas, the loss of NiF_2 by evaporation from the reference electrode could affect the diffusion currents. For example, at 800°C, flowing Ar gas did not affect appreciably either the diffusion current or steady-state current. However, at higher temperatures, increasing the Ar gas flow rate increased the cell current.

For this reason, during diffusion runs, the cell chamber was filled with argon gas at 1 atm pressure and subsequently closed. Also, the cell chamber was periodically flushed and refilled with argon before making diffusion runs at each temperature. With this precaution, the effect of NiF_2 evaporation on the diffusion currents was minimized. A set of potentiostatic experiments with a copper specimen were completed in about 5 days.

G. Results and Discussion

(i) Cell current-time relationship

The experimental data consisted of recorded plots of cell current vs time. Figures 2 and 3 represent the variation of cell current at 803.4°C and 940.4°C, when the applied emf was changed from E_1 to E_2. From an initial high value at short times, the cell current decreased rapidly. At very long times, when fluorine diffusion in copper was complete, the cell current reached a steady-state value which remained constant with time. This steady-state current is interpreted to be essentially electronic current at the applied emf E_2.

The steady-state electronic current was subtracted from the total cell current to obtain the ionic currents associated with fluorine diffusion in the copper specimen. In Figures 4 and 5, log I_{ion} is plotted versus time. At long times, the logarithm of the ionic current becomes a linear function of time in accordance with Eg. (7). In Figures 4 and 5, discrete points have been taken from the continuous recorded current-time plots at regular time intervals. The diffusivities and change in fluorine contents of the copper specimen were calculated from the slopes and intercepts, respectively, in accordance with the preceeding theory.

(ii) Steady-state currents

If the CaF_2 electrolyte were a perfect ionic conductor, the steady-state currents at the end of diffusion run would be zero. However, whenever the applied voltage was non-zero, the steady-state current was finite and increased with increasing voltage. The steady-state current can either result from electronic conductivity of CaF_2 or from the interaction of the Cu electrode with the gas phase. Since there was intimate contact between the Cu and the electrolyte and since the cylindrical surfaces of the Cu were coated with alumina cement, the interaction of Cu with the gas phase was minimized. Also, when the applied voltage was zero, the steady-state cell current was essentially zero.* For this reason, the steady-state currents are considered to be essentially totally electronic.

For the cell $(-)\mathrm{Ni} + \mathrm{NiF_2}|\mathrm{CaF_2}|\mathrm{Cu}(+)$, Wagner[4] has shown that the steady-state electronic current is related to applied potential by the following expression:

$$I_e = I_{\ominus} + I_{\oplus} = \frac{RTA}{LF}\left[\sigma^{\circ}_{\ominus}\left\{1-\exp\left(\frac{-EF}{RT}\right)\right\} + \sigma^{\circ}_{\oplus}\left\{\exp\left(\frac{EF}{RT}\right)-1\right\}\right] \tag{9}$$

where $\sigma^{\circ}_{\ominus}$ is the n-type electronic conductivity of CaF_2 in equilibrium with $Ni + NiF_2$, $\sigma^{\circ}_{\oplus}$ the p-type electronic conductivity of CaF_2 in equilibrium with $Ni + NiF_2$, and A and L are the area and thickness of the CaF_2 electrolyte, respectively.

If CaF_2 has essentially only p-type conductivity in equilibrium with $Ni + NiF_2$, Eq. (9) can be reduced to

$$Ie = \frac{RTA}{FL}\left[\sigma^{\circ}_{\oplus}\exp\left(\frac{EF}{RT}\right)\right] \quad \text{for } EF \gg RT \tag{10}$$

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*In a few cases where the contact between the Cu and the electrolyte was not intimate, the steady-state current was non-zero at applied zero voltage. Such cells were discarded from potentiostatic study.

According to Eq. (10), a plot of log I_e vs E should be a straight line with a slope of $\frac{F}{2.303RT}$. Figure 6 shows the plot of log I (steady-state) vs E for the cell Ni + $NiF_2|CaF_2|$Cu at 802°C. The experimental slope is 4.70 $(\text{volt})^{-1}$ which is in excellent agreement with the theoretical slope of 4.74 $(\text{volt})^{-1}$. The p-type electronic conductivity of CaF_2 in equilibrium with Ni + NiF_2 is obtained from the intercept as $\sigma_{\oplus}^{\circ} = 4.21 \times 10^{-6}$ $(\text{ohm-cm})^{-1}$. From Hinze and Patterson[3], the ionic conductivity of a CaF_2 single crystal at 800°C is 1.58×10^{-3} $(\text{ohm-cm})^{-1}$. Thus, the electronic transference number of single crystal CaF_2 at about 800°C and $P_{F_2} = P_{F_2}(Ni + NiF_2)$ is obtained as $t_e \approx 2.66 \times 10^{-3}$.

At higher temperatures, the plot of log I (steady-state) vs E gave a slope which was less than the theoretical slope. This was probably caused by the high vapor pressure of NiF_2 at higher temperatures which provide some steady-state loss of NiF_2 (v) from the Ni.

(iii) Diffusivity of fluorine in solid copper

The diffusivities of fluorine in solid copper, D_F, obtained from potentiostatic experiments between temperatures 802.5°C and 995.0°C, are given in Table I. In Figure 7, the values of log D_F are plotted vs $\frac{1}{T}$. The error bars in Figure 7 represent the values for the individual standard deviations at each temperature. The best fit line can be expressed as

$$D_F = 3.8 \times 10^{-1} \exp\left(\frac{-24,600}{RT}\right) \text{cm}^2/\text{sec}. \qquad (11)$$

This is compared to the diffusivity of oxygen in solid copper reported by Pastorek and Rapp[2] as

$$D_O = 1.7 \times 10^{-2} \exp\left(\frac{-16,000}{RT}\right) \text{cm}^2/\text{sec}. \qquad (12)$$

Table I: Diffusivity of fluorine and change of equilibrium fluorine content in solid copper as determined from potentiostatic electrochemical experiments.

Temperature °C	E_1 MV	E_2 MV	$D_F \times 10^5$ $cm^2(sec)^{-1}$	$\frac{\Delta N_F}{(\Delta P_{F_2})^{1/2}} \times 10^{11}$ (atomic ppm)$(atm)^{-1/2}$
802.5±1	275.6	317.4	0.405	7.74
	399.1	431.8	0.316	7.65
	361.1	399.1	0.492	3.33
	431.8	455.1	0.349	2.15
849.0±1	344.3	388.7	0.762	2.365
	304.5	344.3	0.474	3.89
	276.6	304.5	0.500	4.13
	188.1	208.4	0.796	3.13
	208.4	238.5	0.703	2.90
	238.1	276.6	0.644	2.78
902.5±1	367.5	416.3	1.52	0.55
	416.3	460.4	1.00	1.30
	330.0	367.5	1.22	0.52
	283.9	330.0	1.02	0.67
	375.9	323.7	0.908	0.63
	415.8	375.9	1.22	0.79
941.0±1	439.9	401.5	1.25	1.40
	401.5	364.0	1.25	1.12
	364.0	325.2	1.53	0.735
	325.2	291.4	1.71	0.62
	373.2	414.6	1.44	1.00
	291.4	344.8	1.355	0.77
	344.8	373.2	1.26	1.08
995.0±1	352.9	335.5	1.76	0.79
	221.8	183.1	2.81	0.47
	307.7	267.3	2.495	0.51
	267.3	221.8	2.43	0.485
	335.5	307.4	1.84	0.715

Between temperatures 802°C and 995°C, the diffusivity of fluorine at a given temperature is smaller than the diffusivity of oxygen in solid copper. Also, the activation energy for fluorine diffusion is higher than the activation energy for oxygen diffusion in solid copper.

(iv) Solubility of fluorine in solid copper

The equilibrium condition for the reaction

$$\tfrac{1}{2}F_2(g) = \underline{F}\ (\text{in Cu}) \tag{13}$$

may be written as

$$P_{F_2}^{\frac{1}{2}} = N_F\gamma_F \tag{14}$$

where N_F is the atom fraction of $\underline{F}$ in copper and γ_F the activity coefficient. For F_2 molecules in the gas phase, $f_{F_2} = 1$ atm is the standard state. If the concentration of fluorine in copper is very small ($N_F \ll 1$) and the energetic interaction among $\underline{F}$ atoms in copper is negligible, Henrian behavior is expected in which γ_F is independent of N_F and depends only on the temperature. Under such conditions the value of $\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}$ is constant at a given temperature and independent of N_F. The values of $\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}$ are given in Table I for temperatures between 802°C and 995°C. Henrian behavior is valid within the scatter for the values $\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}$. A plot of $\log\left(\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}\right)$ vs $\frac{1}{T}$ should be linear and the slope can be related to the heat of solution of fluorine in copper (reaction (13)).

The present results indicate that a plot of $\log\left(\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}\right)$ vs $\frac{1}{T}$ is linear except for data at 902°C. Currently, potentiostatic experiments are being repeated to determin values of $\left(\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}\right)$ as a function of temperature more accurately. For this reason, the discussion of the thermodynamics of fluorine dissolution in solid copper is deferred for the present.

The saturation solubility (solvus line) for fluorine in solid copper, N_F^S can be calculated as

$$N_F^S = \left(\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}\right) P_{F_2}^{\frac{1}{2}}(Cu+CuF_2) = \left(\frac{\Delta N_F}{\Delta P_{F_2}^{\frac{1}{2}}}\right)\exp\left(\frac{2\Delta G^\circ_{CuF_2}}{RT}\right)$$

The melting point of CuF_2 is 950°C and the equilibrium between Cu and CuF_2 can be represented as:

$$Cu(s) + F_2(g) = CuF_2(s) \ ; \ T < 950°C \qquad (15)$$

$$Cu(s) + F_2(g) = CuF_2(l) \ ; \ 950 < T \leq 1083°C \qquad (16)$$

There are no free-energy data available in the literature for reaction (16). For reaction (15), there are four Gibbs energy values reported in the literature[5,6,7,8], all differing from each other. The most recent value for reaction (15) is reported by Skelton and Patterson[8] as ΔG_f° (15) = -130,000 + 28.46 T(°K) cal./mole F_2. Using this value, the saturation solubility of fluorine in copper is calculated and reported in Table II. It should be noted that the values reported in Table II are only tentative. Experiments are currently underway to determine more accurately the standard Gibbs energies for reactions (15) and (16). A more detailed discussion of the solubility of fluorine in solid copper will follow the completion of these experiments.

Table II: Saturation solubility N_F^S of fluorine in solid copper (using standard free-energy for formation of $CuF_2(s)$ from ref. (8)).

Temperature °C	Solubility, N_F^S atomic ppm
802.5	41 ± 23
849.0	90 ± 19
902.5	78 ± 31
941.0	245 ± 69

H. Summary

A potentiostatic electrochemical experiment has been used to determine the diffusivity D_F and the solubility N_F^S of fluorine in solid copper. The diffusivity of fluorine in solid copper can be represented by the expression

$$D_F = 3.8 \times 10^{-1} \exp\left(\frac{-24,600}{RT}\right) cm^2 (sec)^{-1}$$

Using the standard Gibbs energy of formation of CuF_2 from ref. 8, the solubility of fluorine in solid copper was found to increase from 41 atomic ppm at 802°C to 245 atomic ppm at 941°C.

CaF_2 solid electrolyte in equilibrium with Ni + NiF_2 exhibited considerable p-type electronic conductivity at high temperatures. At 800°C, the electronic transference number of CaF_2 in equilibrium with Ni + NiF_2 was found to be approximately 10^{-3}.

II. A Conductivity Study of Point Defects in NiF_2 and β-PbF_2 (W. C. Fang)

Three types of experiments have been done in the past year: (a) An extensive series of preliminary experiments were conducted to confirm the fluorine exchange capacity of a porous graphite and a porous platinum foil electrode. (b) The a.c. conductivity of β-PbF_2 was measured as a function of fluorine activity and (c) the electronic conduction of β-PbF_2 was measured using the direct-current polarization technique.

A. Preliminary Experiments

In order to study point defects in NiF_2 and PbF_2, conditions of fixed and known, but variable fluorine activities are required. In the last annual progress report we reported that an electrochemical arrangement using a graphite electrode as a molecular fluorine exchanger was successful at 800°C and 900°C over a short period of time. However, the succeeding, more extensive, series of experiments showed that neither graphite nor perforated platinum can be a satisfactory molecular fluorine exchange electrode when temperatures were below around 800°C. However, platinum has an advantage over graphite in some aspects which will be discussed later.

B. Experimental Materials and Apparatus

Orthorhombic α-PbF_2 powder (99.9% pure) was used. The cubic modification β-PbF_2 was made from α-PbF_2 by heating to over 400°C. A platinum foil of 0.003 cm thickness was perforated by punching hundreds of holes into it.

The reference electrodes in the cell of Figure 9 were prepared from a nickel plus nickel fluoride mixture in volume ratio of approximately 1 to 3 by pressing in a 1.3 cm dia. steel die. Electrolytes were prepared from ultrapure calcium fluoride powder. A Wenking potentiostat was used to supply various voltages ($E_{appl.}$) to the right-hand cell, and the open circuit voltages ($E_{O.C.}$) at the left-hand cell were measured by an L.&N. K-3 potentiometer. A Keithley 153 microvolt-ammeter was used to monitor the current.

B. Results and Discussion

Theoretically, the open-circuit voltages ($E_{O \cdot C \cdot}$) of the right-hand cell should be equal to the applied voltages of the left-hand cell ($E_{appl.}$). In practice, however, deviation was observed because of the following factors:

(a) Polarization of Ni/NiF_2 reference electrodes. As can be seen from Figure 9, for an applied voltage of 1000 mv, $E_{O \cdot C \cdot}$ increases to its maximum value of 960 mv in 3 minutes and then drops slowly to 640 mv in 50 minutes. This characteristic performance was observed whenever the right-hand Ni + NiF_2 electrode was polarized, in other words, whenever a thin film of Ni metal was formed at the electrolyte/electrode interface to block the further supply of F^- ions from the electrode. However, this polarization was eliminated by adding CaF_2 to the reference electrodes. From our experimental tests, the optimum volume ratio of Ni, NiF_2, and CaF_2 for a satisfactory reference electrode is about 6:2.5:2.

(b) Electrical Current. The current in the right-hand cell of Figure 8 indicates the rate of the steady-state fluorine ion discharge process at the interface of the CaF_2 electrolyte and the perforated platinum foil. This discharge process results from fluorine escape through a loose bond between the CaF_2 electrolyte and the platinum foil. A linear relation between the values for the $E_{O \cdot C \cdot}$ and the current for $E_{appl.}$ equal to 1000 mv was observed as shown in Figure 10. Because perforated platinum foil made a better bond than graphite, platinum foil was chosen as a molecular fluorine exchanger in the a.c. conductivity study of β-PbF_2.

(c) Temperature.

Figure 11 shows the open-circuit voltage as a function of temperature at an applied voltage of 500 mv. Deviation of the open-circuit voltage from the applied voltage tends to decrease as temperature increases. The curve in Figure 11 fits the following equation:

$$E_{O \cdot C \cdot} = K\ [1-\exp(-T)] \text{ where K is constant}$$

From the results of these preliminary experiments, the following conclusion can be drawn: at a given temperature, assuming there is no polarization of the reference electrodes, the open-circuit voltage ($E_{O.C.}$) is totally determined by the magnitude of the current in the left-hand cell. Figure 12 shows a plot of $E_{O.C.}$ vs $E_{appl.}$ at different temperatures.

B. A.C. Conductivity of β-PbF_2

The electrical conductivity of β-PbF_2 has been studied by many investigators.[9-14] But none of them was able to study the a.c. conductivity of β-PbF_2 at various fluorine activities. This work attempts to achieve this goal.

(a) Experimental Apparatus and Procedures. The double cell of Figure 12 was comprised of two symmetrical cells with perforated platinum foils as fluorine gas exchange electrodes. The voltages were provided from two potentiostats which had to be plugged into separate power outlets having different groundings. If the two power sockets would have the same grounding, then there is an electrical short-circuit between the two potentiostats, such that the two platinum electrodes used as electrical contacts to measure the a.c. conductivity of β-PbF_2 will always be in a closed circuit.

Measurements of a.c. conductivity were made by using the Wayne-Kerr Universal Bridge B211 at a frequency of 1592 cps. When the conductance of a specimen was higher than 0.1 ohm^{-1}, the measurements were made by use of a Wayne-Kerr Low Impedance Adaptor Q211 in conjunction with the bridge. The resistance of the Ni lead wires was measured independently in the furnace at different temperatures and the β-PbF_2 conductivity measurements were corrected accordingly. The measurement procedure consisted of initially equilibrating the sample at the highest fluorine pressure ($E_{appl.}$ = 1900 mv) and at the highest temperature 600°C. After the measured conductance remained constant over a period of 3 hours the value was recorded, and the applied voltage was lowered to 300 mv. The procedure was then repeated at lower temperatures. Finally the temperature was again raised to 600°C to assure that no change had occurred in the cell during the run.

(b) Results and discussion. The results of a.c. conductivity measurements are plotted in Figure 14 as a function of fluorine pressure at various temperatures. By very careful examination, there is only a very small negative slope for each line. The absolute magnitude of these slopes tends to decrease as temperature decreases. But essentially, the a.c. conductivity of β-PbF_2 is independent of fluorine pressure, indicating that β-PbF_2 is a predominant ionic conductor over a wide range of P_{F_2}. Figure 15 shows that the conductivity tends to increase at increasing fluorine pressure. The temperature dependence shown in Figure 15 will require further study prior to interpretation and publication.

C. Measurements of Partial Electronic Conduction from Polarization Measurements

The d-c polarization technique according to C. Wagner[4] was applied for the determination of $\sigma_{\oplus}$ and $\sigma_{\ominus}$ in the PbF_2 electrolyte at the equilibrium fluorine activity of a Cu + CuF_2 mixture. Figure 15 shows the cell arrangement intended for this study. The cell is subjected to various d.c. potentials below the decomposition potential (2.6 v) of PbF_2 into Pbcs) and $F_2(g)$.. The right-hand reversible electrode at the right is made negative, and under these conditions, no steady-state ionic current can pass because of the blocking electrode on the left. Accordingly, each time the applied potential is changed, a transient ionic current corresponding to a redistribution of the ions in the crystal to the new applied voltage will pass initially, but eventually drop to zero. The completed ionic redistribution cancels out the electric field within the crystal. At this steady-state condition, the total current is composed of electronic and electron hole conduction according to the equation:

$$i_\infty = i_\ominus + i_\oplus = \frac{RT}{LF}\, \sigma^\circ_\oplus[1-\exp(-u)] + \sigma^\circ_\ominus[\exp(u)-1]$$

where L is the cell constant (thickness 1 area), $\sigma^\circ_\oplus$ and $\sigma^\circ_\ominus$ are, respectively, the partial electron hole and electronic conductivities at the equilibrium fluorine activity of the reversible electrode, and $u = EF/RT$, where E is the applied voltage.

If the electrolyte crystal is predominantly an n-type electronic conductor, the equation for the current reduces to

$$i_\infty = i_\ominus = \frac{RT}{LF}\, \sigma^\circ_\ominus[\exp(u)-1] \tag{17}$$

For $\exp(u) \gg 1$, an exponentially increasing current will be observed with increasing potential in a plot of i_∞ vs V, while a linear relationship will be observed in a log $\frac{LF}{RT} i_\infty$ vs V plot. The value for the apparent electronic conductivity $\sigma^\circ_\ominus$ can then be calculated from the intercept of the latter plot as F/2.303RT.

If the electrolyte crystal exhibits predominant p-type electronic conduction, the equation for the current reduces to

$$i_\infty = i_\oplus = \frac{RT}{LF}\sigma^\circ_\oplus[1-\exp(-u)] \qquad (18)$$

In plots of i_∞ vs V and log i_∞ versus V, with increasing voltage, the current increases and tends to the saturation value. The hole conductivity can be calculated from the plateau current value from the log i_∞ vs. V plot.

The d.c. polarization study of electronic conduction in PbF_2 will be undertaken shortly. The results will be compared with previous literature values. Liang and Joshi[12,13] used the cell (-) Pb|PbF_2|graphite (+) to study the d.c. polarization of PbF_2. They reported that PbF_2 was a p-type conductor in the temperature range of 25°C to 300°C. Kennedy, et al[10] also reported that PbF_2 was a p-type conductor at 150°C using a (-) Pb(liq)|PbF_2|C(+), cell. Only Benz[11] using the cell (-)C, Pb(ℓ)|PbF_2|C(+) reported that βPbF_2 was an n-type conductor in the temperature range of 400°C to 600°C.

III. An Electrochemical Probe for the Measurement of Fluorine Activities (S. F. Chou)

In this task a calcium fluoride electrochemical probe was constructed with the intention to measure the fluorine activity in a gaseous phase. Immediately, it was recognized that the influence of oxygen in the gas on the emf of the fluorine probe would need to be established. With these goals in mind, we have uncovered a most unusual behavior for the CaF_2 electrolyte in the presence of oxygen-bearing electrodes.

Calcium fluoride is known to be a predominant ionic conductor of fluorine ions. The electrolytic domain extends to conditions which are at least as reducing as those corresponding to Th, ThF_4 coexistence.[3] According to a recent study of the influence of oxygen on the electrical conductivity of CaF_2 single crystals, CaF_2 also exhibits predominant ionic conductivity in various oxygen environments.[6] However, the ionic conductivity of CaF_2 increases with the dissolution of oxygen into the lattice.[2] The increase was interpreted as resulting from an increased concentration of anion vacancies, $V_F^{\bullet}$, which are generated in electrical compensation of the substitutional dopant oxygen, O_F'.

Our experimentation over the past year has revealed that CaF_2 is a predominant ionic conductor even when the oxygen pressure in the environment is rather low; around 10^{-17} atmosphere. In particular, we have found the CaF_2 can be used as an electrolyte to measure accurately differences in the <u>oxygen</u> activities at low values of P_{O_2}. We are currently working to interpret the details of the electrochemical reactions involved. Since CaF_2 is already known to function well as a fluoride electrolyte, we have begun studies of the open-circuit emf generated in a CaF_2-electrolyte cell when the electrodes maintain known activities for both fluorine and oxygen.

A. Experimental Apparatus and Procedures

Closed-end 4.5 cm and 1.9 cm ID stabilized ZrO_2 tubes from Zircoa, were used as an oxygen pump and oxygen gauge, respectively. Cobalt powder (98%) and nickel powder (99.8%) were obtained from Apache Chemicals, purified copper powder (99%) from Matheson, Coleman and Bell. Nickel difluoride powder (99.8%) was an Electronic Space product. Nickel oxide (99.8%) and cupric oxide (99.9%), which is reduced to cuprous oxide in contact with copper at the experimental temperature range, were obtained from Baker. The CuF_2 was reagent grade obtained from General Electric Company.

The CaF_2 electrolytes were optically pure, randomly oriented, single crystals of CaF_2 purchased from Harshaw Chemical Company, 1.9 cm diameter 0.3 cm thick. Three different fluoride electrodes were used; $Ni+NiF_2$, $Cu+CuF_2$ and $Co+CoF_2$. Fluoride electrodes were prepared from a mixture of metal and metal fluoride in a volume ratio of about 6 to 1, and pressed in a steel die to form pellets 1.3 cm diameter x 0.3 cm thick. The $Cu+Cu_2O$ mixture used as reference electrode in the oxygen cell was prepared in a similar way. Two different three-phase electrodes were used; $Cu+CuF_2+Cu_2O$ and $Ni+NiF_2+NiO$. These mixtures of metal, metal oxide, and metal fluoride were prepared in a 6:2:2 volume ratio. All the metals and metal fluorides were preserved in an argon-atmosphere dry box. Because CuF_2 has a high vapor pressure above 700°C, it was enclosed in an alumina crucible during experimental measurements of cell emf. The mechanical strengths of copper and cobalt pellets were good, while the nickel pellets had rather poor mechanical strength. Platinum foil was used as electrical contact to the electrodes. Nickel wire insulated by an alumina capillary tube was spark welded to the platinum foil, and also used as an electrical lead.

Because the oxygen pressure plays an important role in determining the emf value of a fluorine probe or fluorine concentration cell, a gas purification train described in the previous progress report was used to maintain an argon gas atmosphere free of oxygen and water vapor.

The apparatus shown schematically in Figure 17 was designed to satisfy differing purposes of the experiment. The assembly consisted of two concentric zirconia tubes separated by pressing the zirconia tube (B) against an alumina disk. The fluorine probe or fluorine concentration cell was placed below the alumina disk (G) and maintained in place by means of an alumina sample holder (L) and the springs (N).

The entire assembly was placed inside the zirconia tube (A), 4.4 cm ID and 46 cm long. Both zirconia tubes (A) and (B) were connected by epoxy glue to a brass flange which was sealed by a rubber O-ring. The two chambers were separately flushed with purified argon. A stainless steel cylindrical tube was placed coaxially outside the outer zirconia tube (A) and grounded to prevent electrical pickup during the emf measurements. All the nickel lead wires and thermocouple wires in the cell chamber were insulated by alumina capillary tubes. A Keithley 160 B Digital Multimeter was used to make emf measurements to three significant figures. The cell temperature was maintained to within ±1°C and was indicated by a calibrated Pt- Pt/10%Rh thermocouple.

The inner and outer surfaces of tube (A) and the end part of tube (B) were painted with platinum paste, and sintered at 800°C for 2 hr. The outer tube (A) was connected by lead wires (U) and (X) to a potentiostat (T) to serve as an oxygen pump to control the oxygen activity inside the tube. A suitable voltage was supplied by the potentiostat to pump oxygen out of the zirconia tube (A) at a pumping current of 10-30 mA. A $Cu+Cu_2O$ reference electrode (W) was placed inside the tube (B) which was used as an oxygen probe. The emf between this reference electrode (W) and the Pt electrode (H) corresponding to the oxygen pressure in Tube (A) was around 350 to 450 mV with the $Cu+Cu_2O$ electrode always at positive polarity. Then the calculated oxygen pressure in tube (A) was maintained around 10^{-17} atm.

To initiate an experiment, the cell assembly was closed and evacuated to 10^{-6} torr. The system was alternately flushed with argon and evacuated several times to minimize the oxygen content in the system. Finally, purified argon was passed through the system at a flow rate of 1-3 cm^3/min. The cell was heated slowly to 800°C at a rate of 50°C per hr., because ZrO_2 has very poor tolerance to thermal shock. Because of the high vapor pressure of CuF_2 at elevated temperature, $Cu + CuF_2$ or $Cu + CuF_2 + Cu_2O$ electrodes were encapsulated in an alumina crucible. The equilibrium emf value of the fluorine cell was observed after holding the cell at 800°C for 12 to 24 hrs. The oxygen pump was used continuously to exclude oxygen from tube (A). Thermocouple and oxygen gauge emf values were recorded at the same time when the equilibrium emf values for the fluorine cell were taken.

B. Experimental Results and Discussion

An emf amounting to two volts and drifting down to 400mV after two days was observed in the following cell (19) with the CaF_2 solid electrolyte.

$$Ni + NiF_2 | CaF_2 | Ni + NiO + NiF_2 \qquad (19)$$

The $Ni + NiF_2 + NiO$ electrode always had positive polarity. This result is not consistent with that expected (emf = 0) for a pure fluorine ionic conductor. Some sort of electrode reaction involving oxygen was occurring.

To test the performance of CaF_2 as a pure oxygen electrolyte, the emf was determined for cell (20) involving $Ni + NiO$ and $Cu + Cu_2O$ electrodes and the CaF_2 solid electrolyte:

$$Cu + Cu_2O | CaF_2 | Ni + NiO \qquad (20)$$

For a residual oxygen concentration around 10^{-17} atmosphere read by the oxygen gauge, the cell was heated up to 1050°C, and stayed at that temperature for 24 hr before reaching an equilibrium emf condition. The equilibrium emf values were taken at various temperatures upon decreasing temperature. At each temperature the cell was held for 2 to 4 hr at the equilibrium emf to detect any significant emf drift within ±1mV. The equilibrium state was tested by passing some current through the cell, and the equilibrium emf was re-established again in two minutes. The emf values were measured over a temperature range from 850° to 1050°C. A plot of emf value of Cell (20) vs temperature is shown in Figure 18. The existing equilibrium emf data for cell (20) measured in cells with the stabilized zirconia electrolyte are given by Eq. (21) and are represented by the solid line in Figure 17.

$$E_{20} = 345.6-7.16\text{x}10^{-2}T \text{ mV} \qquad (21)$$

The data from this study using a CaF_2 electrolyte matches the known data remarkably well as shown in Figure 18. From simple thermodynamic calculations it is clear that CaF_2 is stable to oxygen at elevated temperature at even very low P_{F_2}. The exchange reaction of the following type will not occur to any significant extent in our experimental conditions where the oxygen pressure is less than 10^{-17} atmosphere.

$$CaF_2 + 1/2\ O_2 \rightarrow CaO + F_2 \qquad (22)$$

For an oxygen anion conductor, where fluorine transference is zero, one expects the cell emf E to be given as

$$4FE = RT\ln\frac{P_{O_2}(Cu/Cu_2O)}{P_{O_2}(Ni/NiO)} \qquad (23)$$

This study shows that Eq. (23) is obeyed for CaF_2 solid electrolyte. However, it seems unlikely that CaF_2 is predominantly an O^{2-} anion conductor in a low P_{O_2} environment. Nevertheless, it has been found that the conductivity of CaF_2 increased as the oxygen pressure increased at elevated temperature[16]. When the oxygen pressure was in a range $1\text{~}10^{-5}$ atmosphere,[16]

$$\sigma_{CaF_2} = k\, P_{O_2}^{1/4} \qquad (24)$$

In interpretation of these observations, Levitski et al[16] suppose that oxygen ions reside at normal fluorine lattice sites and generate fluorine vacancies according to the reaction

$$1/2O_2 + 2F_F^{*} \rightleftarrows F_F^{\cdot} + O_F^{'} + F_2 \qquad (25)$$

whereby for fixed P_{F_2},

$$[V_F^{\cdot}] = [O_F^{'}] = k' P_{O_2}^{1/4} \qquad (26)$$

Thus, the increase in conductivity was explained as an increase in the concentration of fluorine vacancies.[16]

At the moment, we are not able to describe a cell reaction in detail, i.e., write specific anodic and cathodic half-cell reactions by which the fluorine is the sole conducting species, but the net virtual chemical cell reaction involves only oxygen. We shall emphasize mechanistic interpretation in the future.

Fluorine concentration cells of the following arrangements were also investigated

$$Ni + NiF_2 | CaF_2 | Cu + CuF_2 \qquad (27)$$

$$Co + CoF_2 | CaF_2 | Ni + NiF_2 \qquad (28)$$

The electrode Cu + CuF_2 pellet was encapsulated in an alumina crucible. The initial (high) temperature for both cells was 800°C, and emf values became stable after one day at that temperature. The equilibrium emf values were tested by current passage and emf recovery and also by observing no significant emf change with time, ±2 mV over one to two hours. Cell (27) provided equilibrium emf values over four days of experimentation. Cell (28) did not function long enough to take emf values over a wide range of temperature, and only the emf value of 147 mV at 1002°K was recorded for Cell (28). The Cu + CuF_2 electrode always had positive polarity in Cell (27), and the Ni + NiF_2 electrode had positive polarity in Cell (28). A drift in emf for Cell (27), a continual decrease in emf, was noticed at temperatures lower than 600°C. A more marked drift, an increase to values of 800~900mV, occurred in the temperature range from 750°C to 1000°C. There is no explanation for these observations at the present time. A plot of equilibrium emf values of Cell (27) vs temperature is shown in upper part of Figure 19. Triangles represent the data from the first run in the lower temperature range 540°-600°C, and diamonds represent the data taken from a second run at a higher temperature range (600°C to 900°C). There was no observable oxidation of the electrodes.

The emf value of Cell (27) of about 760mV between 600°C and 750°C, is higher than the values of Skelton and Patterson and other previous studies. The temperature range of the current measurements was also higher. The emf value drifted down to the magnitude of the previous measurement below 600°C. At temperatures higher than 750°C, the emf values were unstable and varied from 800mV to 900mV. At the moment, we feel that our higher emf values may be superior to previous studies, but some further confirmation is required.

The true equilibrium emf value for the fluoride cells can be obtained only when there is no oxygen conductivity in the electrolyte or electrode reactions involving oxygen. Any oxidation of the electrodes and any oxygen present in the atmosphere will cause finite oxygen doping of the electrolyte and therefore perhaps affect the equilibrium emf value. The lone equilibrium emf value for Cell (28), 147 mV at 1002°K, is close to that of existing data.

Because we have observed that CaF_2 can function as a pure ionic conductor (electrolyte) both in oxygen cells as well as in fluorine cells, we decided to contribute important information to the electrochemical behavior of CaF_2, by the investigation of cells which involved three-phase electrodes in which both a definite oxygen activity and fluorine activity were known.

A concentration cell with three-phase (mixed) electrodes Ni + NiF_2+NiO and Cu + CuF_2 + Cu_2O was set in the zirconia tube (A).

$$\mathrm{Ni} + \mathrm{NiF_2} + \mathrm{Ni}\ |\mathrm{CaF_2}|\ \mathrm{Cu} + \mathrm{CuF_2} \tag{29}$$

Because of the high vapor pressure of CuF_2 at elevated temperature, it is encapsulated in an alumina crucible. When emf values were measured, the Cu + CuF_2 + Cu_2O electrode always exhibited the positive polarity. Multiple temperature cycles were carried out. All emf values were recorded when there was no significant change in emf in one hr; ±2 mV. After the passage of current, the cell emf returned to its original value. An emf vs temperature plot is shown in Figure 19; black spots were taken as the temperature was decreased during the first cycle. Temperature was increased after that, and the data taken are represented by empty squares. Then the temperature was decreased again and the data are represented by empty circles. After four days, the cell emf dropped continuously. There was no observable oxidation of the electrodes.

The mixed fluorine and oxygen cell did not develop a single consistent emf value, perhaps because of the polarization of the electrodes occasioned by the electrode reactions which are not yet understood. Probably the virtual cell reaction will require that any current passed through the cell will allow the higher-voltage fluorine reaction to occur in its spontaneous reaction while the lower-voltage oxygen reaction may be forced to occur in the non-spontaneous direction. In other words, perhaps the higher voltage of the fluorine spontaneous reaction will support the "uphill," voltage-driven reaction of oxygen in the non-spontaneous direction. Calculations show that the contact of the Cu + Cu_2O + CuF_2 electrode with CaF_2 should account for a thermodynamic activity of CaO in CaF_2 equal to 6.0×10^{-12}. Likewise, the electrode Ni + NiO + NiF_2 in contact with CaF_2 should establish a thermodynamic activity of CaO in CaF_2 equal to 5.3×10^{-8}. These low values which would fix the extent of oxygen dissolution at these activities do not correspond to significant doping. Thus, the existing experimental results are rather puzzling, and further experiments and interpretation are required.

INTENDED RESEARCH OVER REMAINDER OF CURRENT TERM AND CORRELATION TO PROPOSED TECHNICAL PROGRAM

Within the next month, Dr. Reddy will repeat his studies of N_F and D_F in solid copper, at which time a publication (Metal. Trans.) and presentation (AIME) of the results will be prepared. To avoid the previous problems of perfectly sealing solid nickel to pure CaF_2, the use of YF_3-doped CaF_2 as an electrolyte will be introduced. To substantiate his values for N_F and D_F in copper and future values in nickel, Dr. Reddy will initiate internal fluorination reactions of dilute Cu-base and Ni-base alloys. Finally, Dr. Reddy will establish the level of p-type electronic conduction in CaF_2 through the interpretation of his d.c. polarization experiments.

Within the next couple months, W. C. Fang will conduct open-circuit emf studies to establish the average transference number for NiF_2, which he has already found to approximate 0.3. D.C. polarization studies and a.c.

total conductivity studies as a function of P_{F_2} will provide considerable information about pure NiF_2 and pure β-PbF_2. In March, Mr. Fang should complete his M.S. studies. The publication (J.E.C.S.) and presentation of his work (E.C.S.) is expected.

Over the next several months, Mr. Chou will continue his study of the open-circuit emf cells with CaF_2 electrolytes and electrodes in which both fluorine and oxygen activities are fixed and known. The experiments will serve as a basis for future interpretation and experimentation. The effect of oxygen on LiF and YF_3-doped electrolytes will be studied. These results should be published (J.E.C.S.) and presented (E.C.S.).

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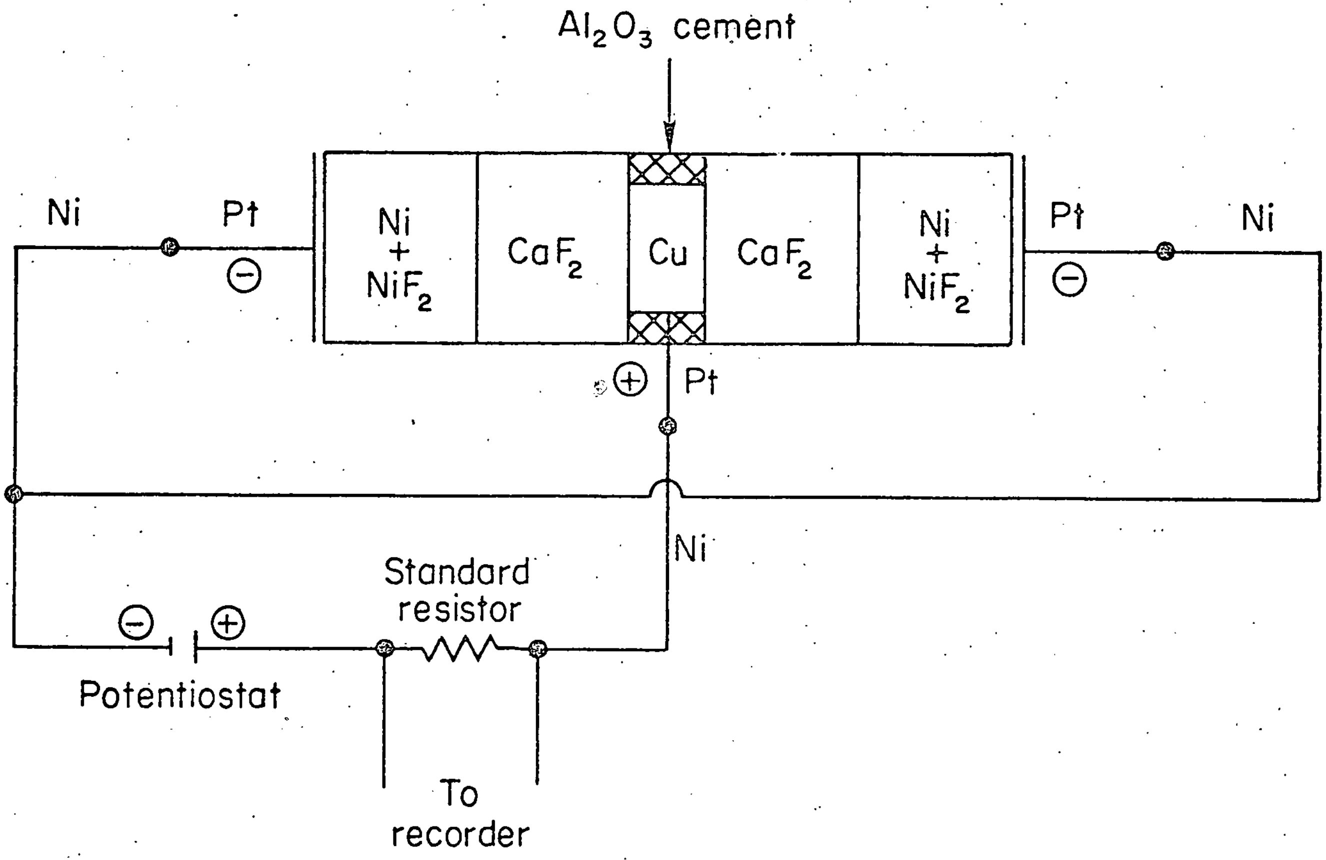

Figure 1 - Electrochemical Cell for the Measurement of Solubility and Diffusivity of Fluorine in Solid Copper.

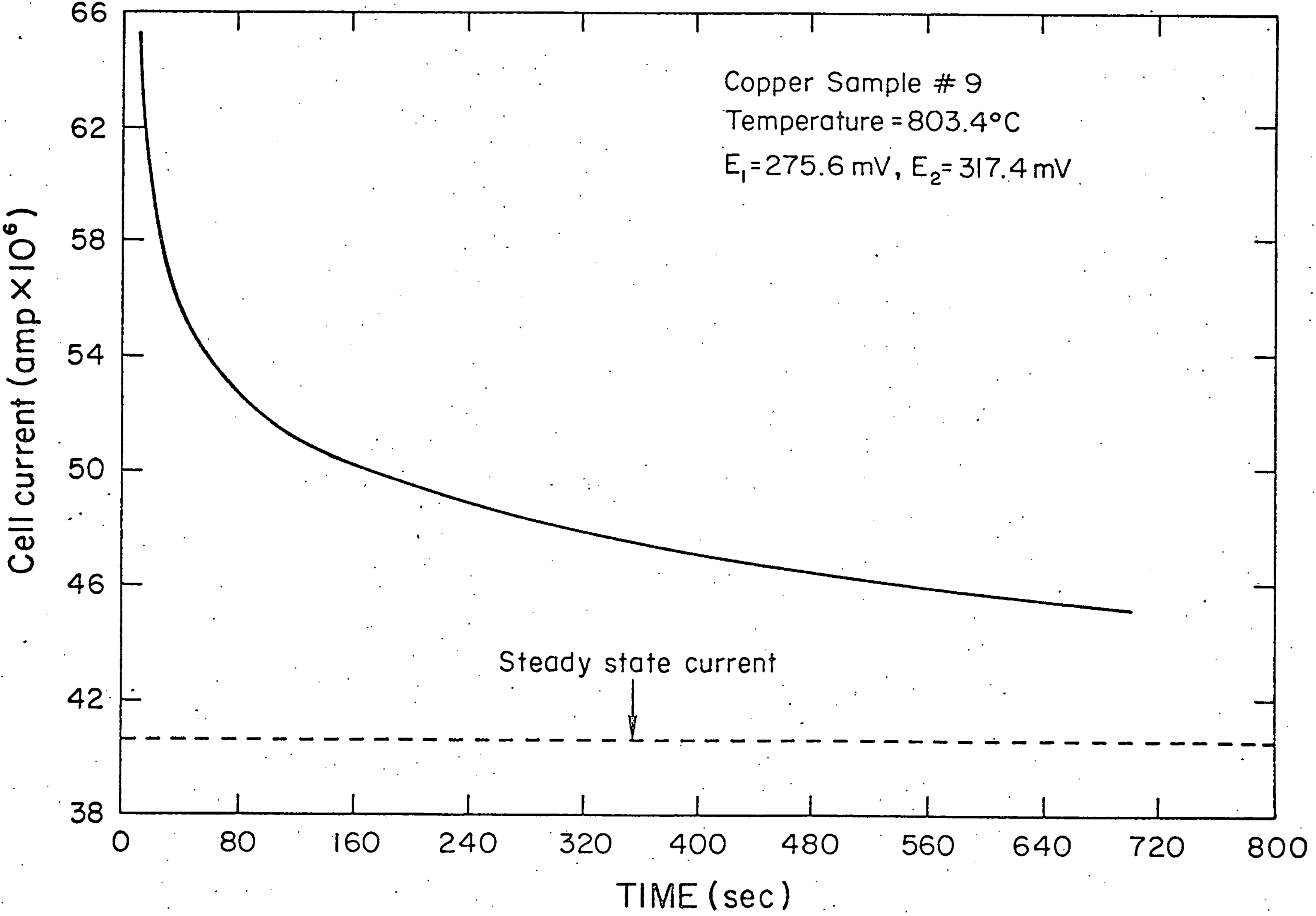

Fig. 2 - Cell current as a function of time in the potentiostatic experiment with solid copper at 803.4 C.

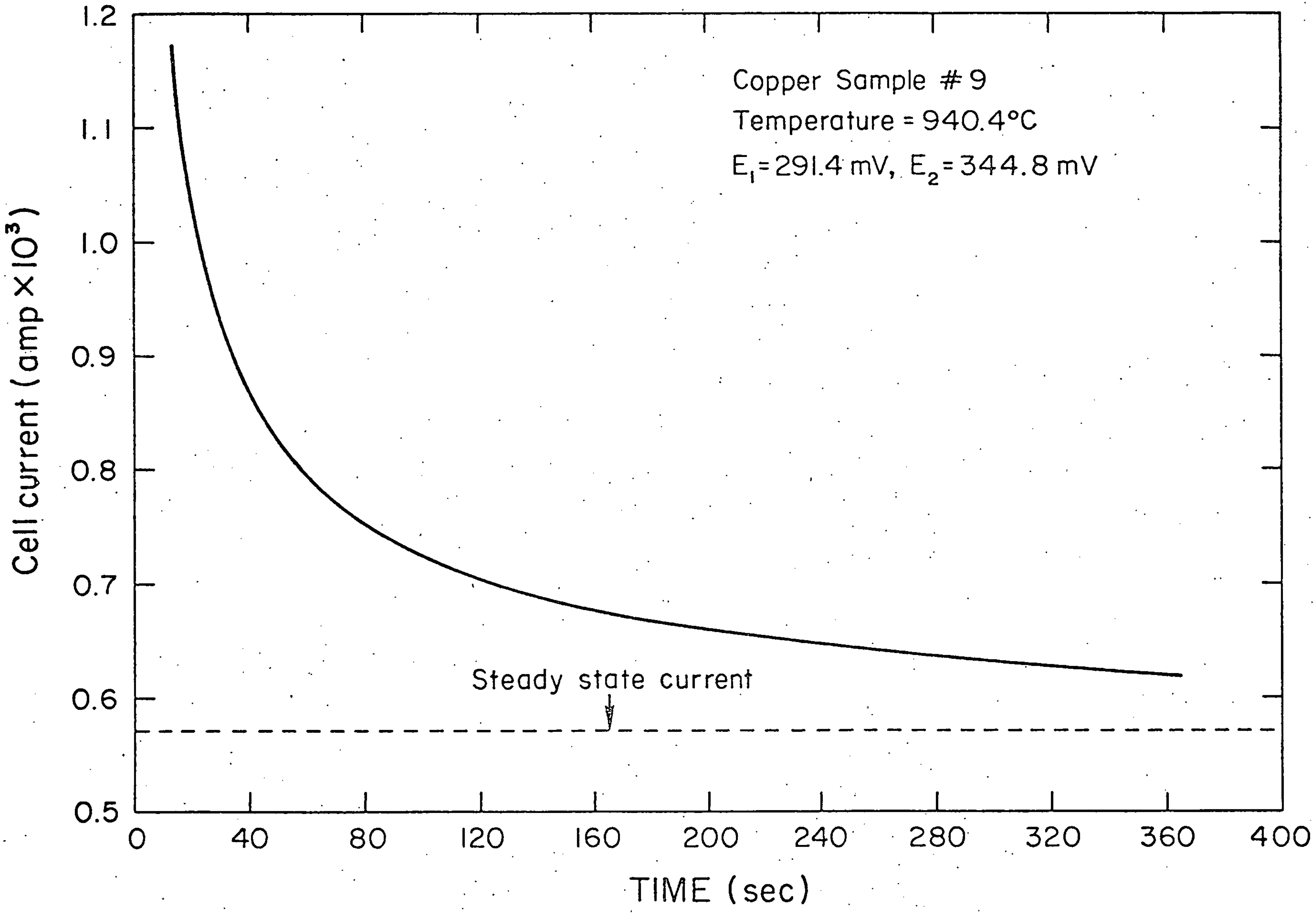

Figure 3 - Cell Current as a Function of Time in the Potentiostatic Experiment with Solid Copper at 940.4°C.

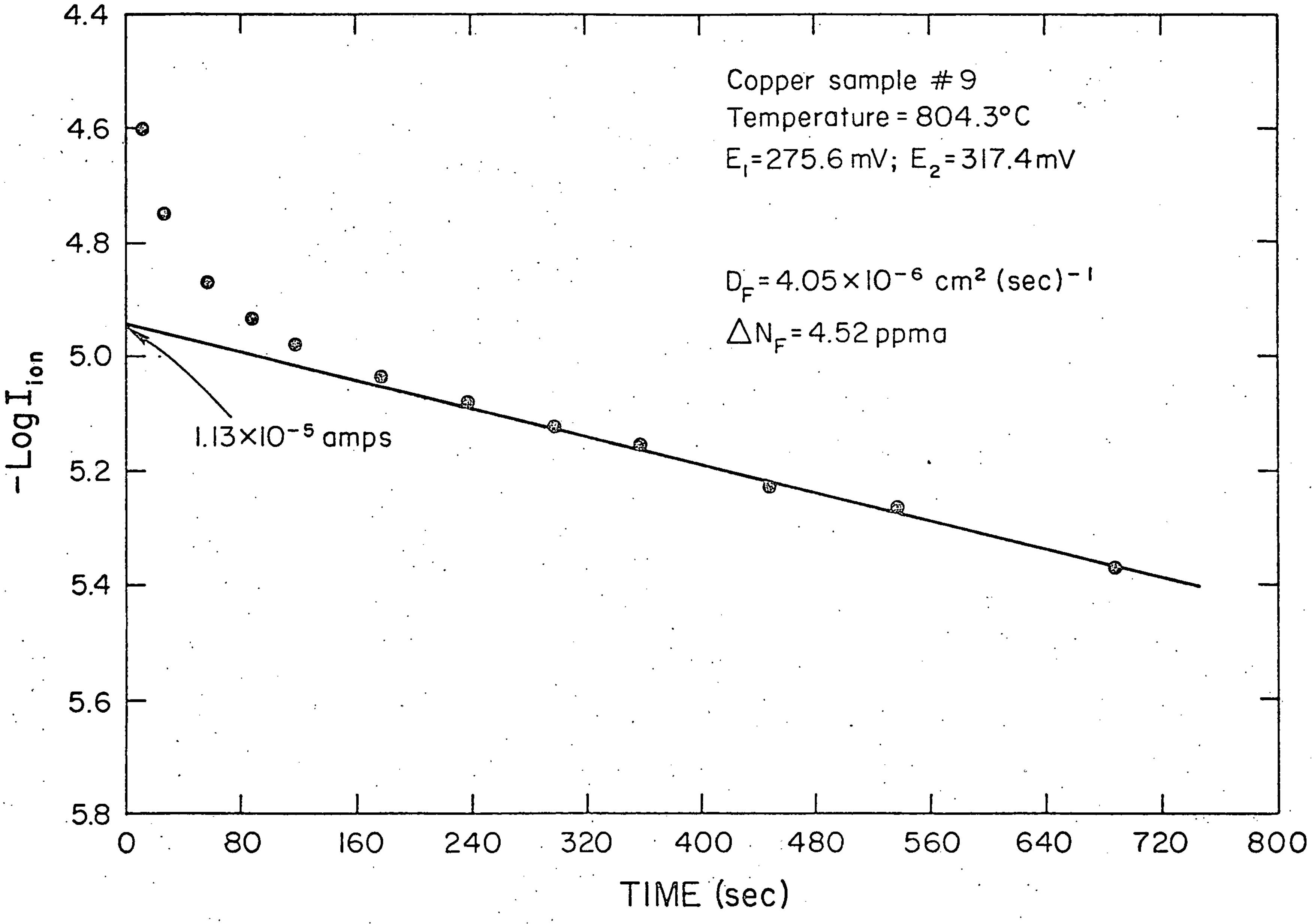

Figure 4 - Ionic Current as a Function of Time in the Potentiostatic Experiment with Solid Copper at 803.4°C.

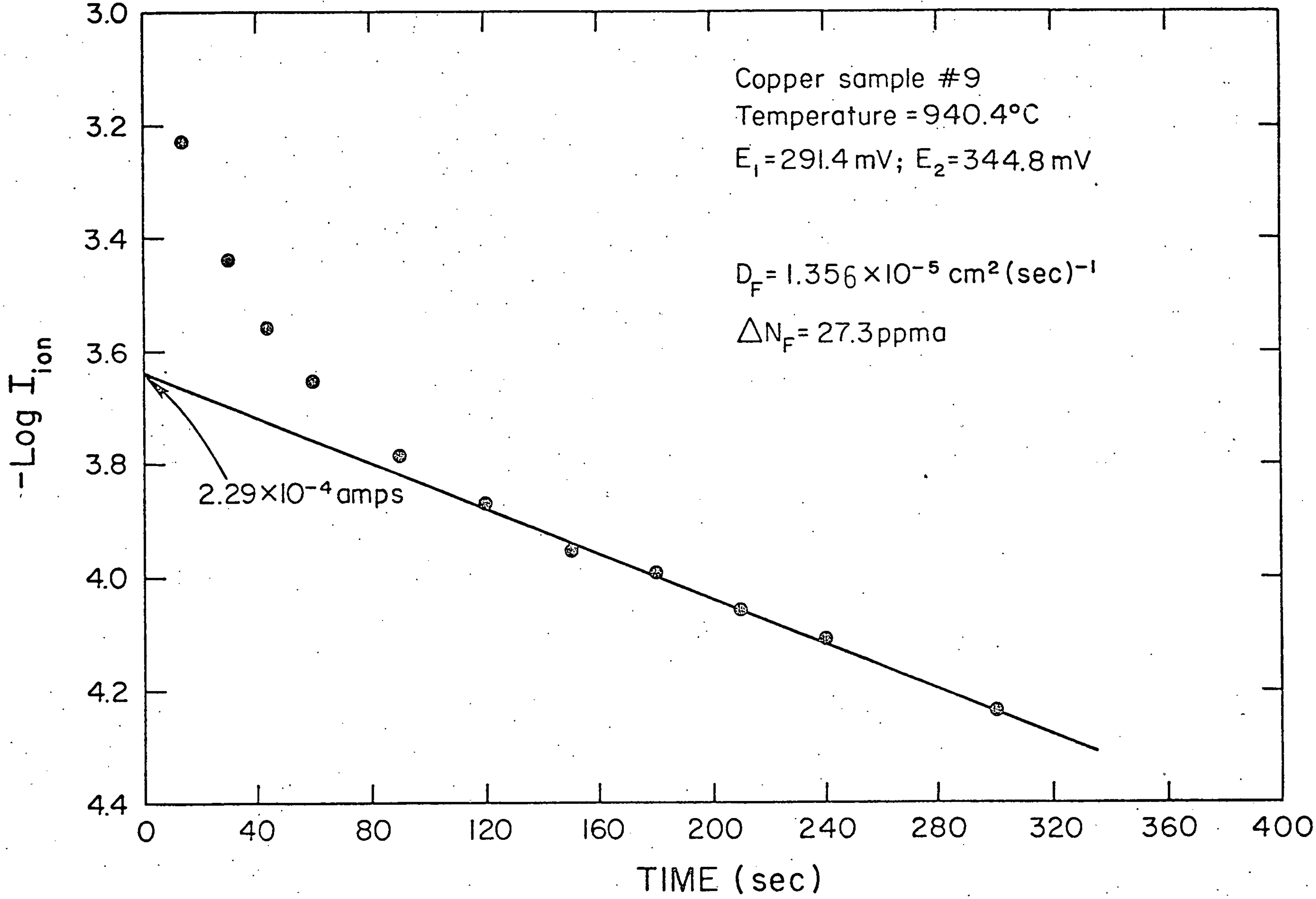

Fig. 5 - Ionic current as a function of time in the potentiostatic experiment with solid copper at 940.4 C.

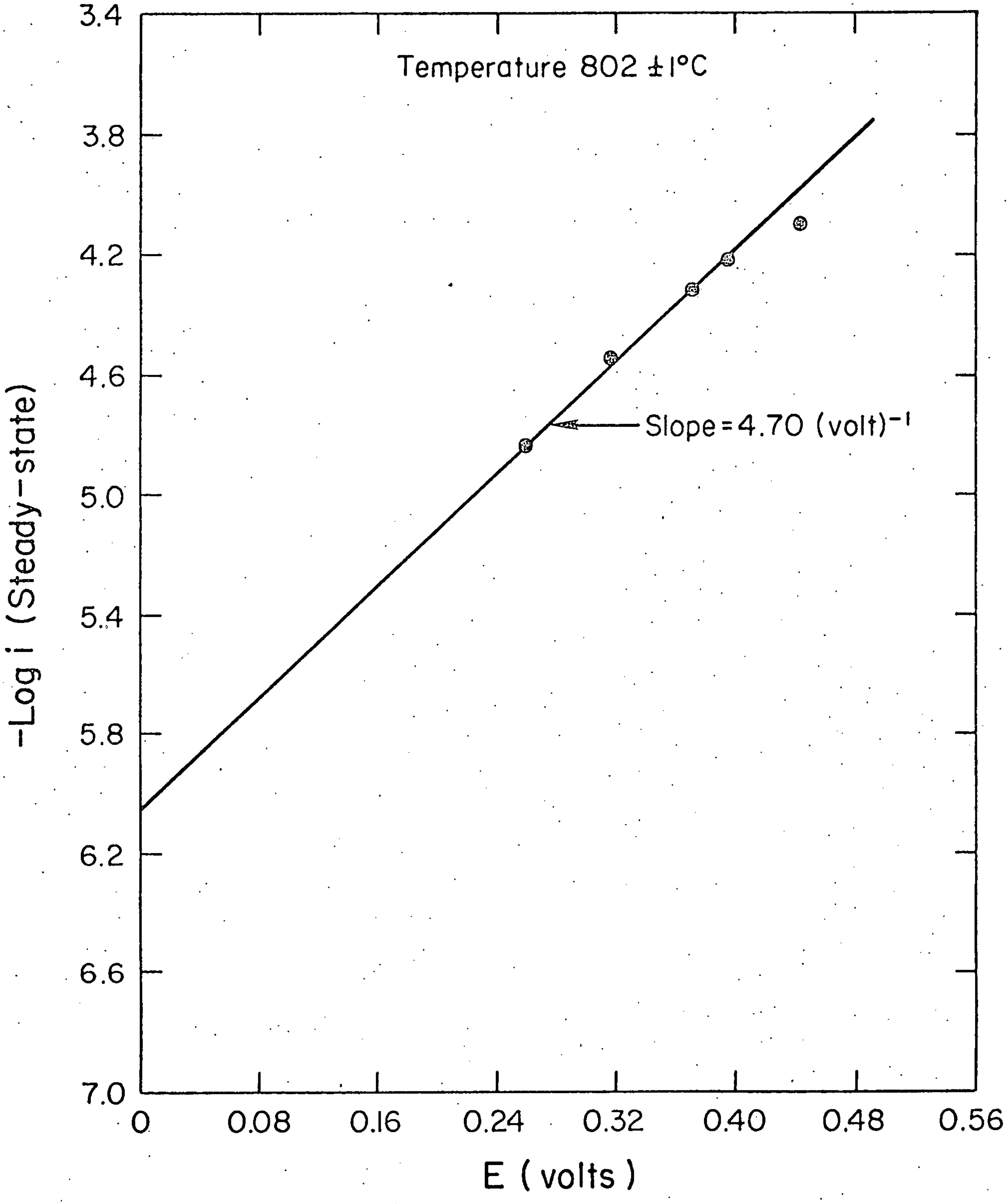

Figure 6 - Plot of log I vs E for the Cell Ni + $NiF_2|CaF_2|Cu$ at 802°C.

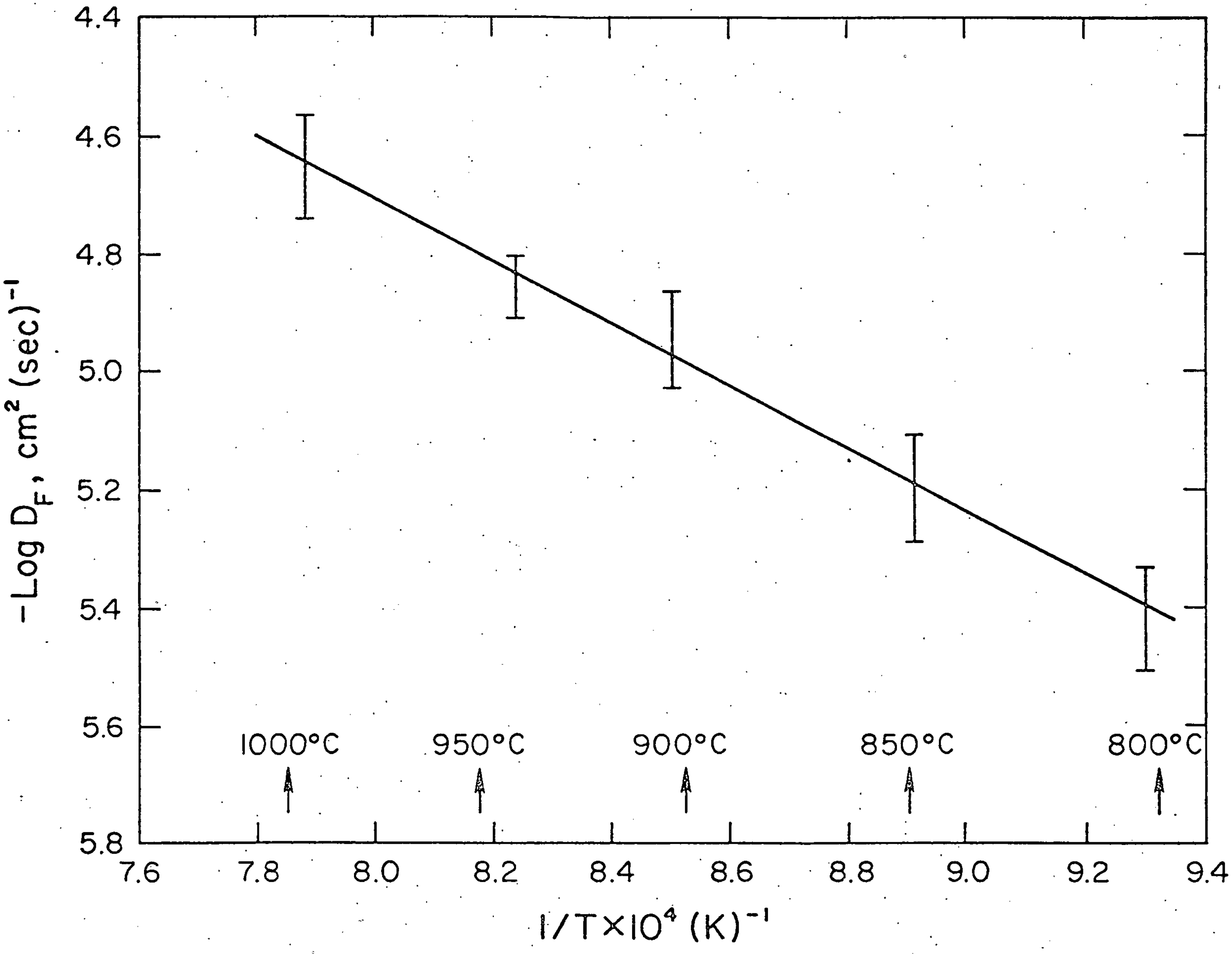

Fig. 7 - Diffusivity of fluorine in solid copper as a function of reciprocal temperature.

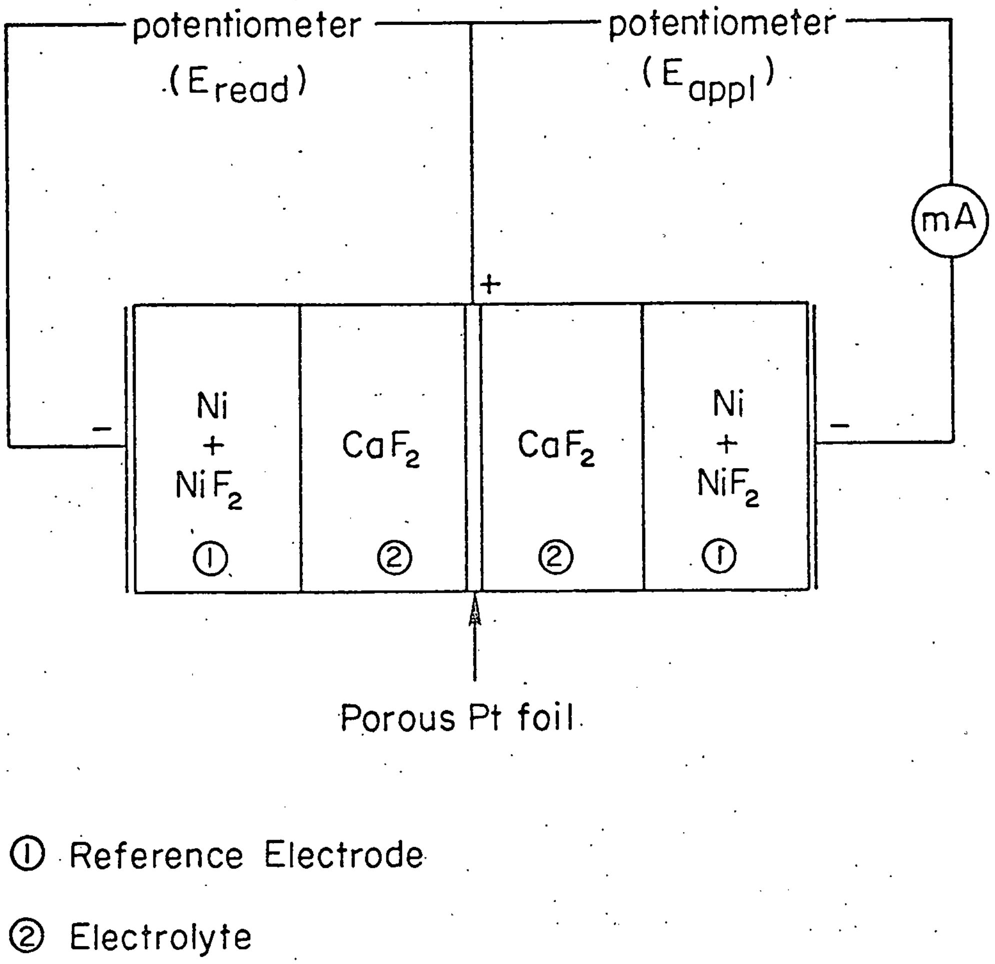

Figure 8 - Experimental Cell to Study the Fluorine Exchange Capacity of the Porous Platinum Electrode.

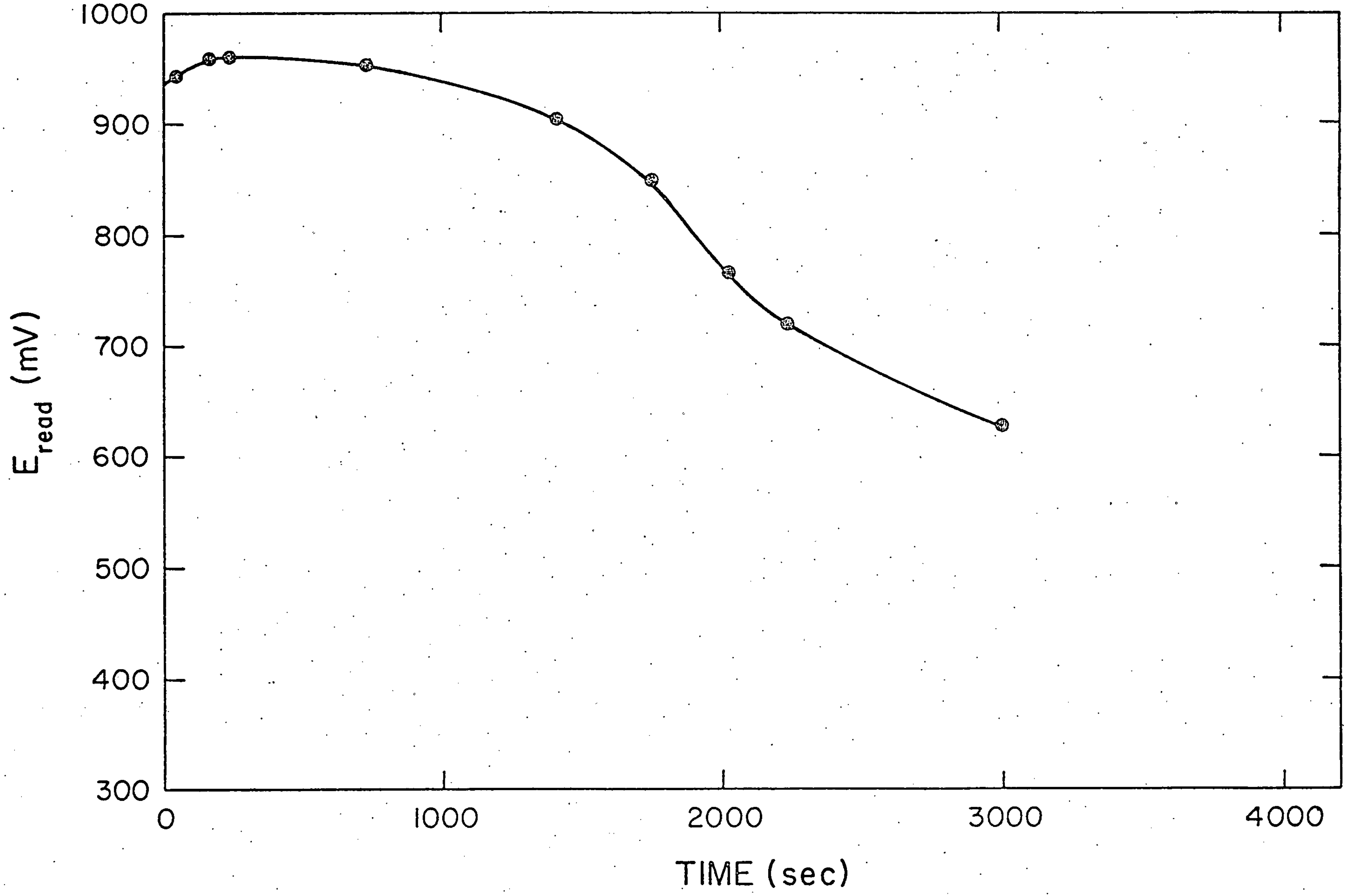

Fig. 9 - Open-circuit voltage as a function of time when reversible electrode is polarized. Applied voltage: 1000 mV. Temperature: 695 C.

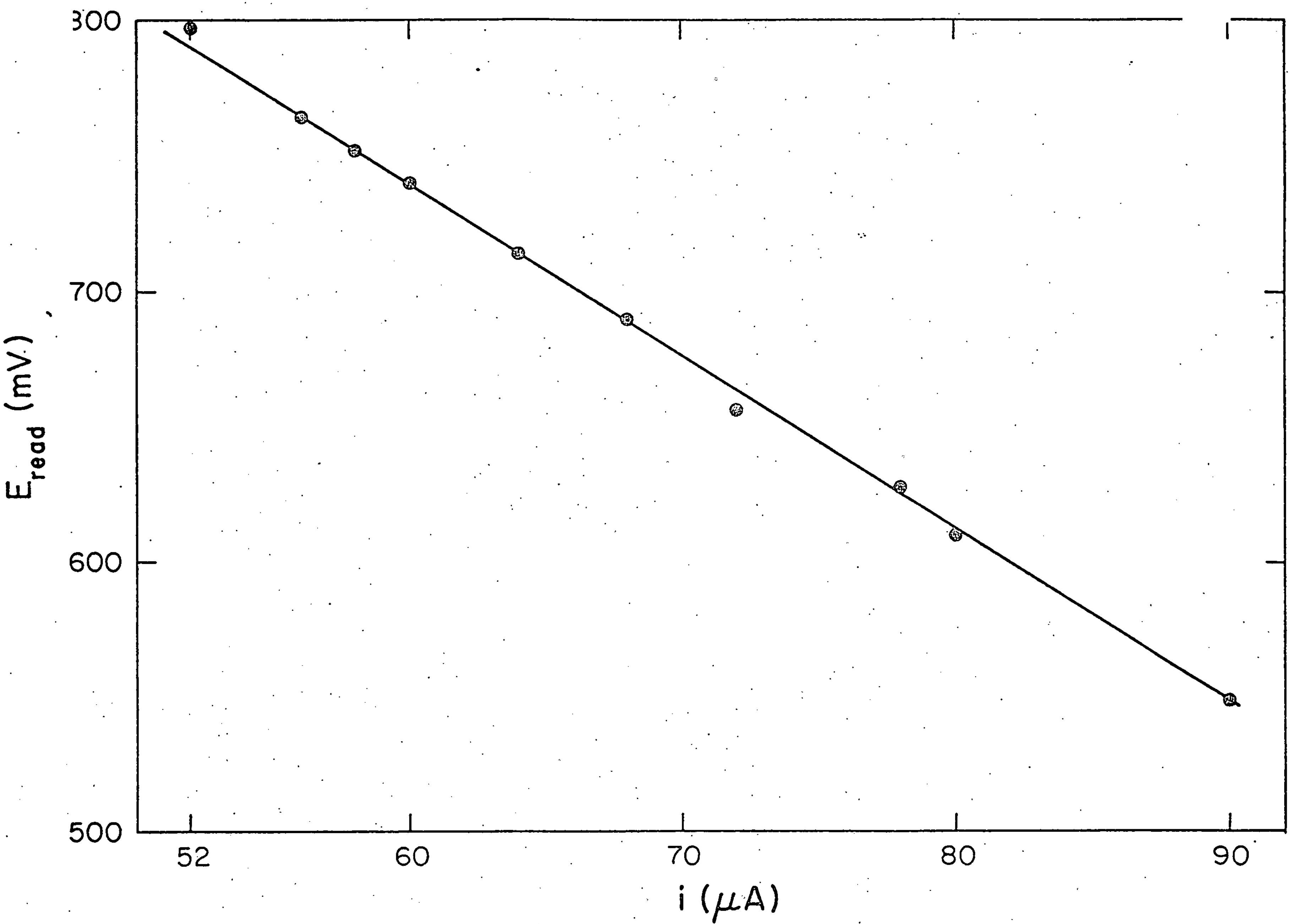

Fig. 10 - Open-circuit voltage as a function of current (i) at 800 C. Applied voltage: 1000mV.

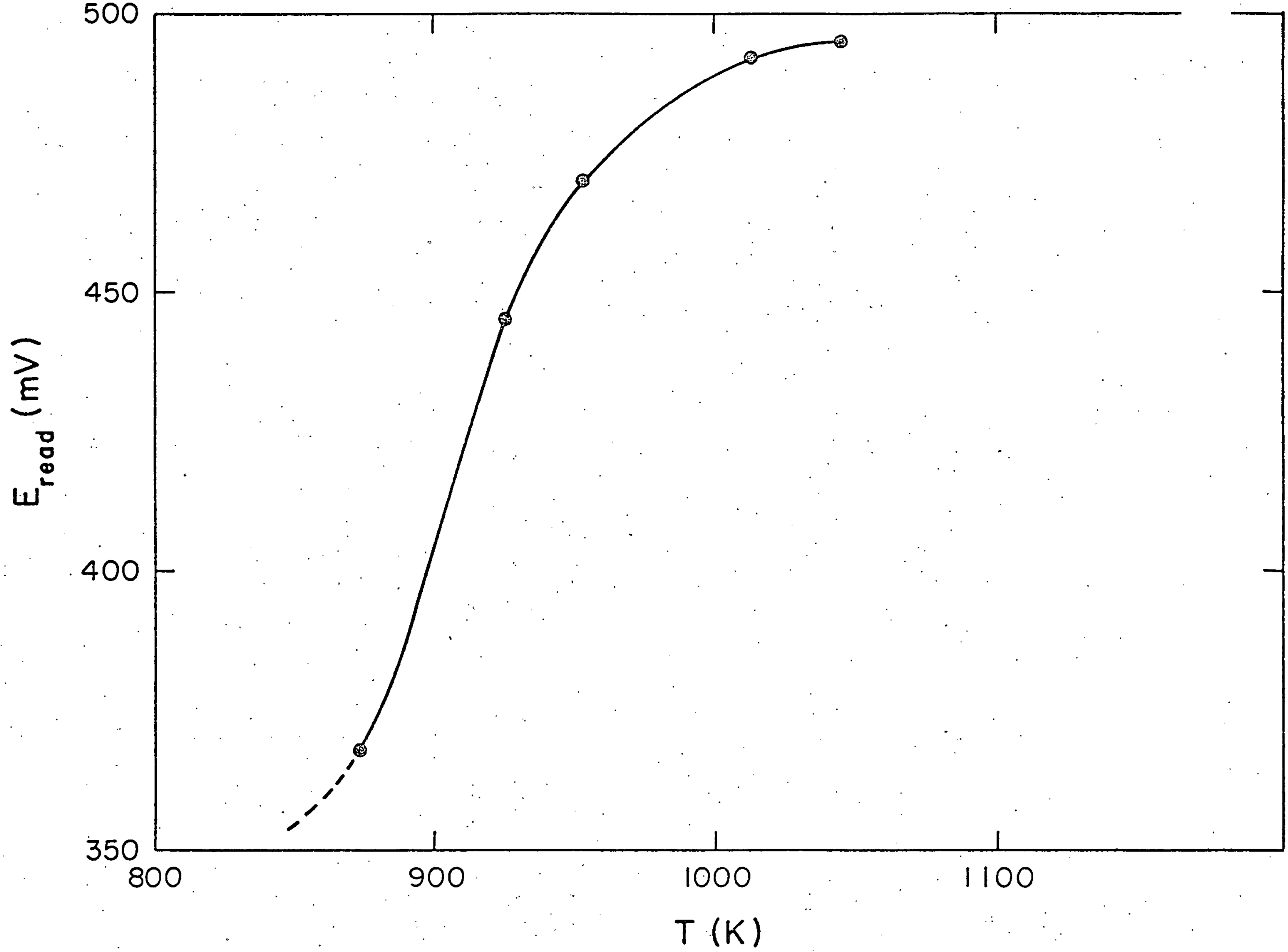

Figure 11 - Open-circuit voltage as a function of Temperature.
Applied voltage: 500mV

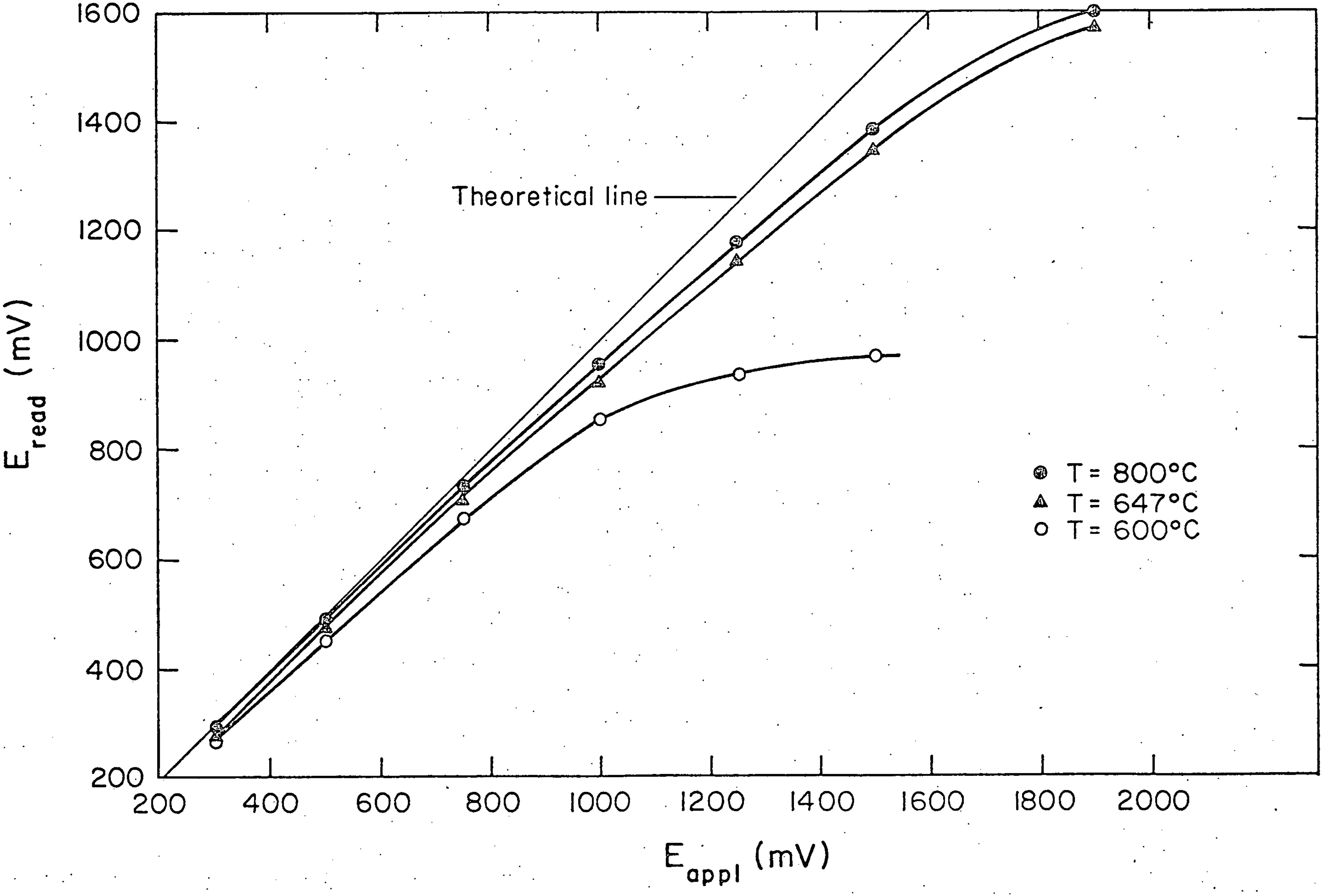

Figure 12 - Open-circuit voltage as a Function of Applied Voltage at Various Temperatures.

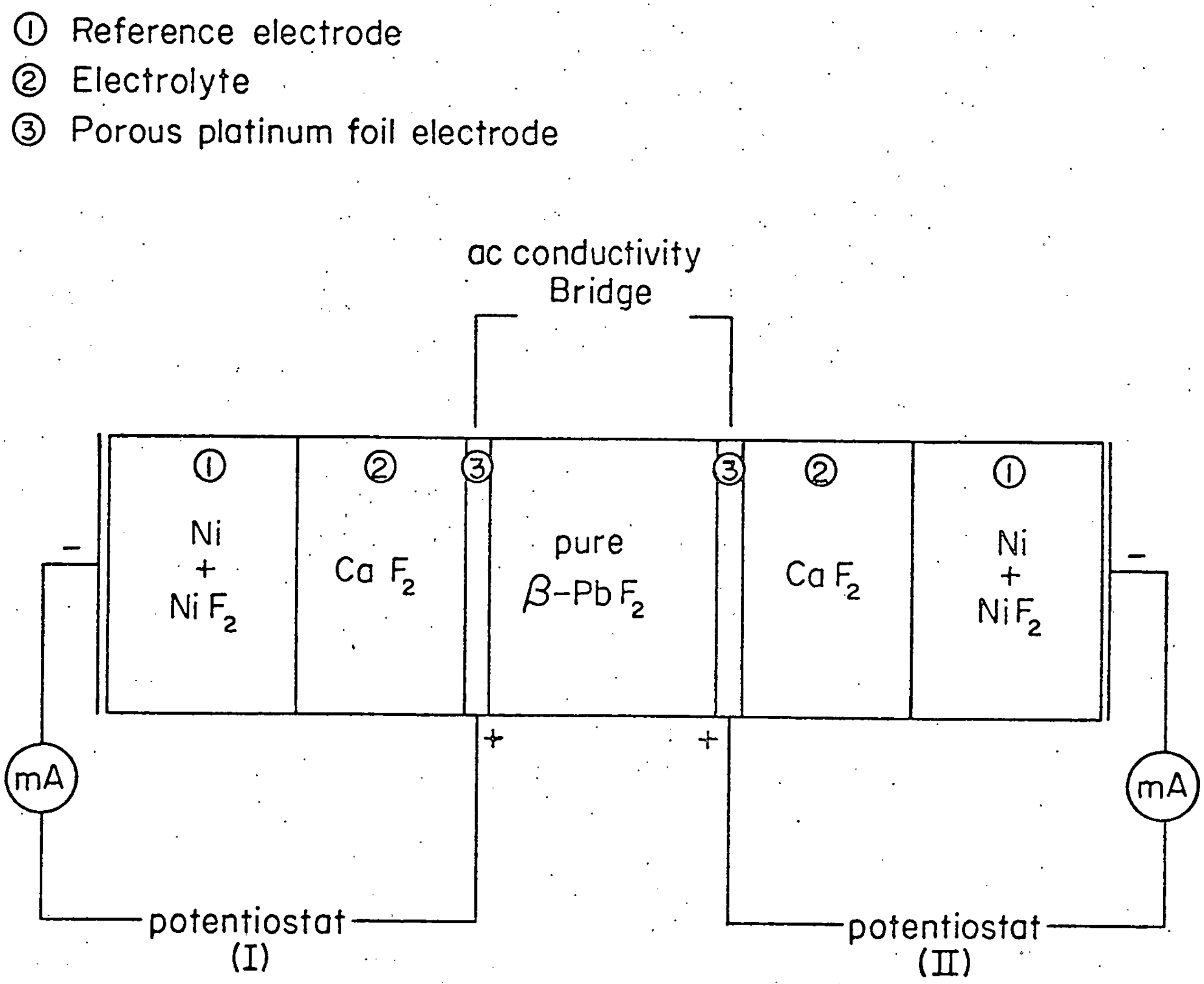

Figure 13 - Experimental cell to study the electrical conductivity of fluoride compounds.

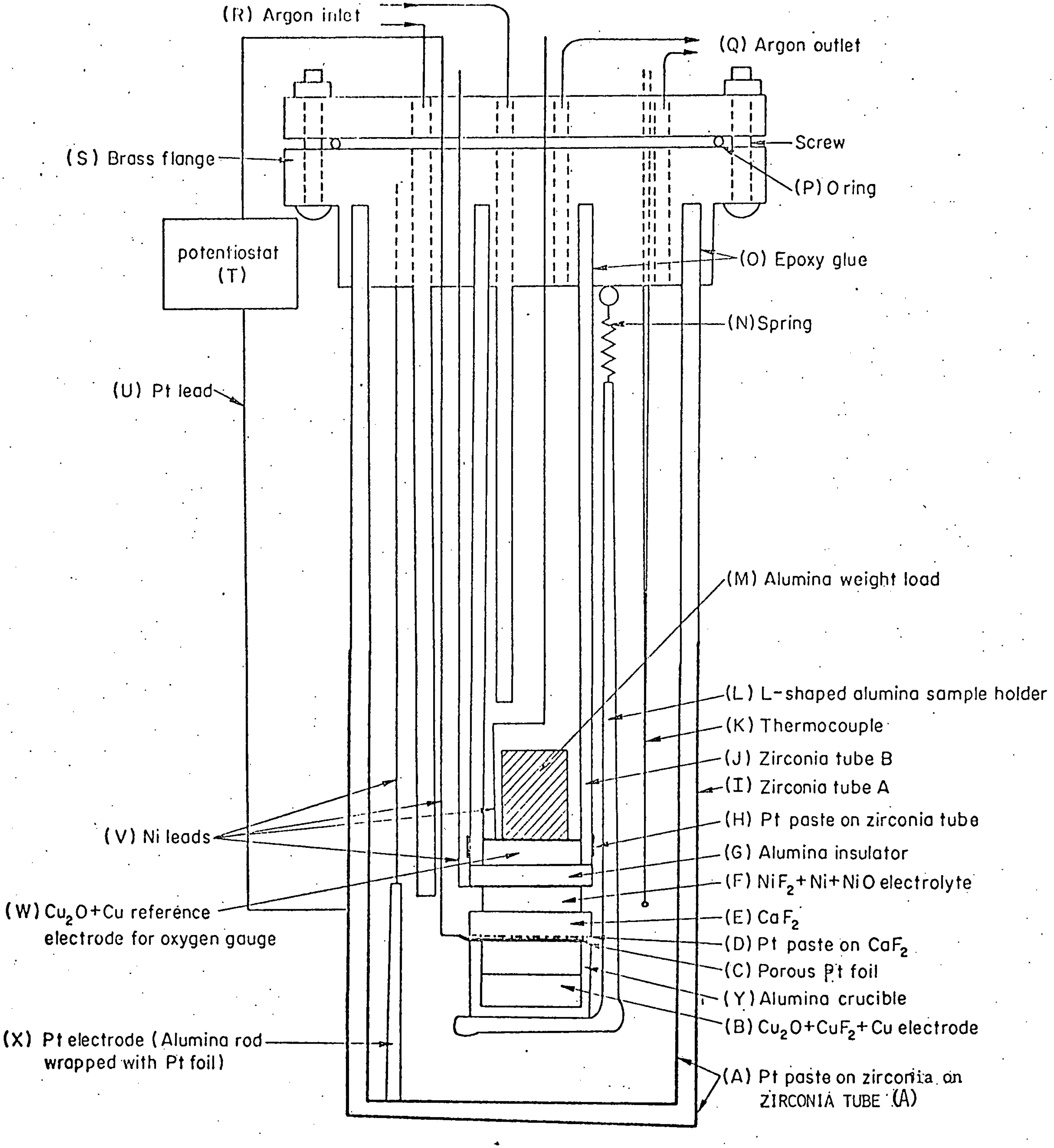

Fig. 17 - Experimental Arrangement for Fluorine Activity Probe.

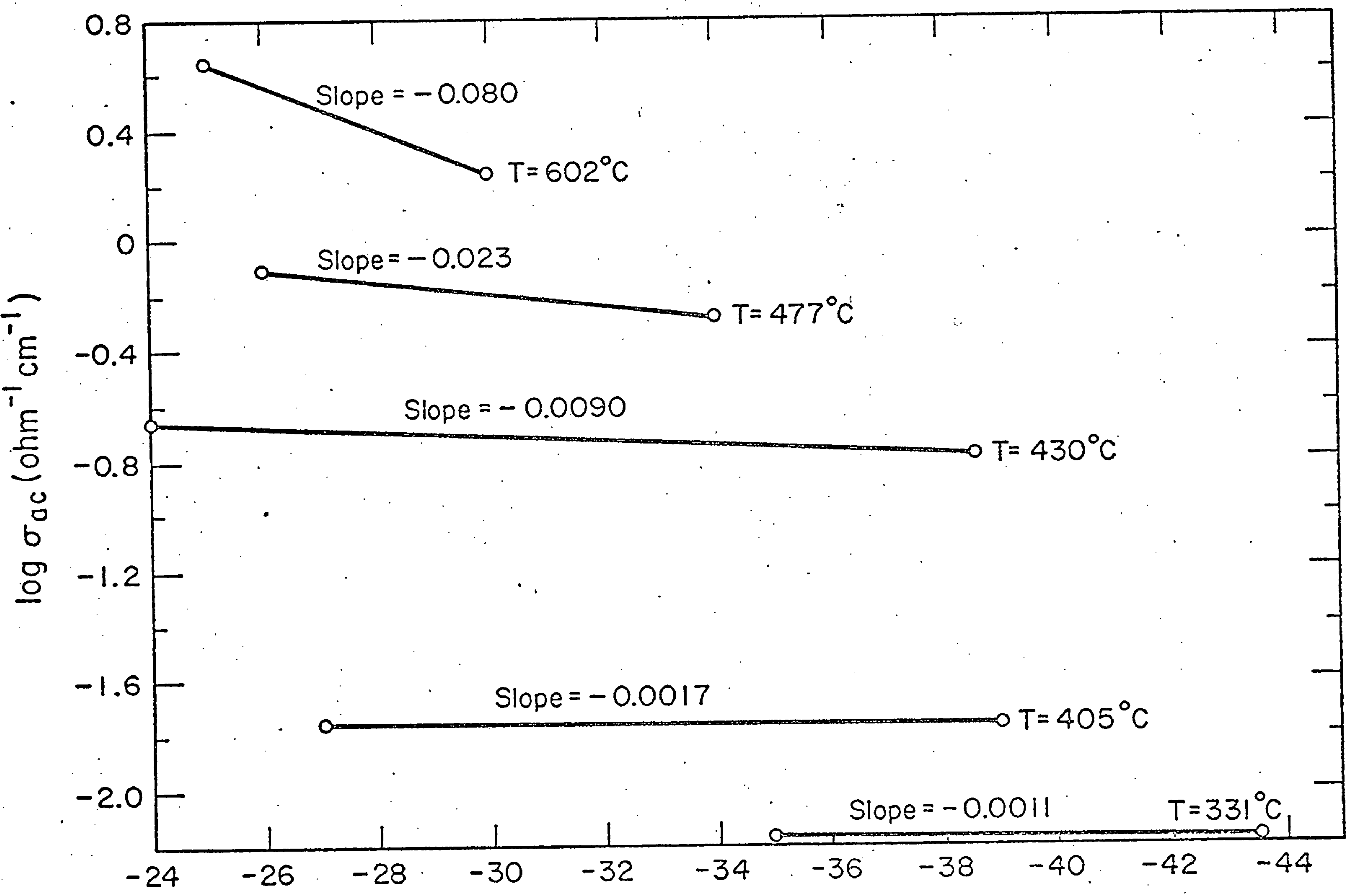

Figure 14 - Fluorine Pressure Dependence of Total Conductivity for PbF_2 at 330°C - 600°C.

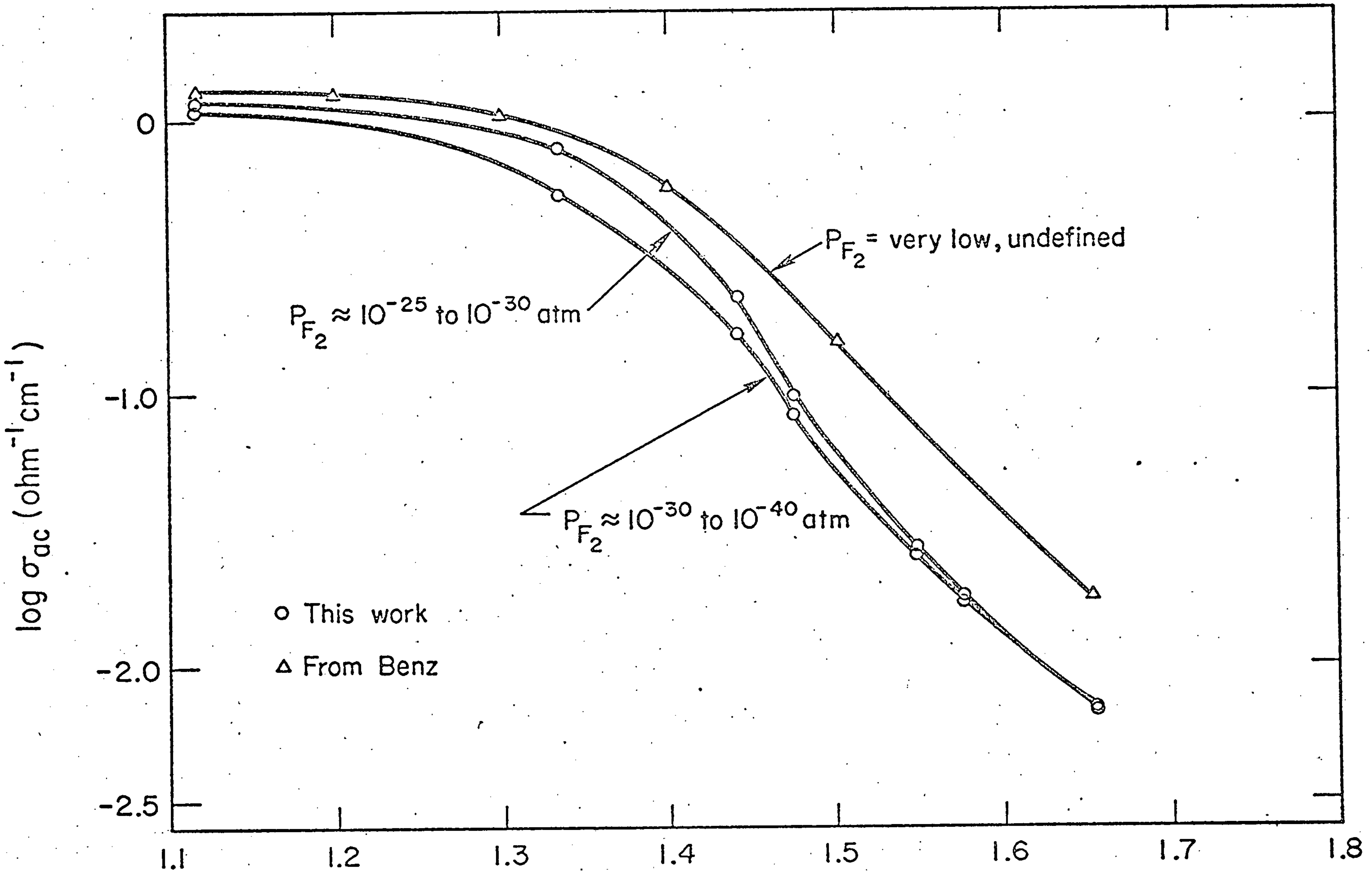

Figure 15 - AC Electrical Conductivity of β-PbF_2, as a Function of Temperature at Different Fluorine Pressures.

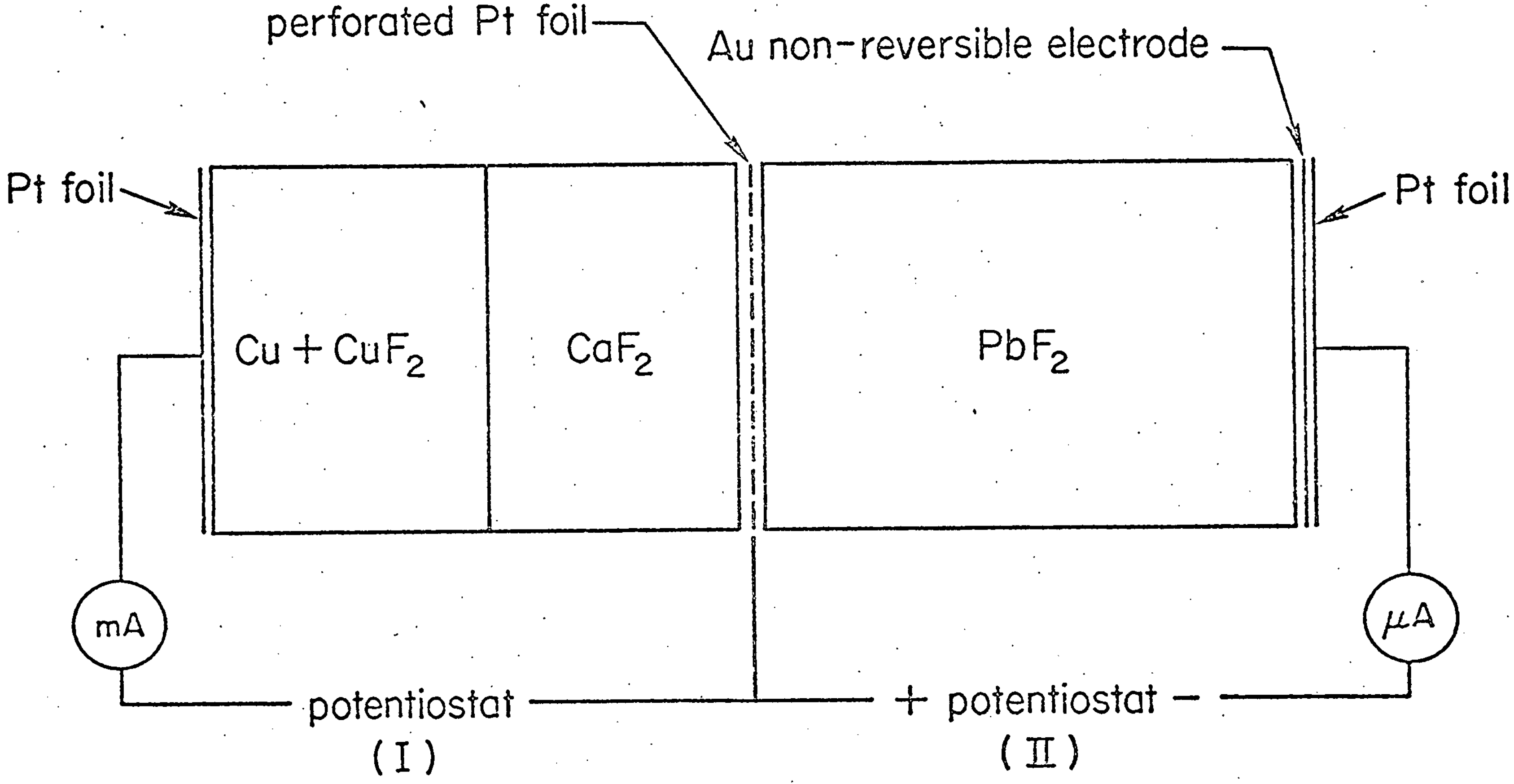

Figure 16 - Cell Arrangement for dc Polarization Studies of PbF_2.

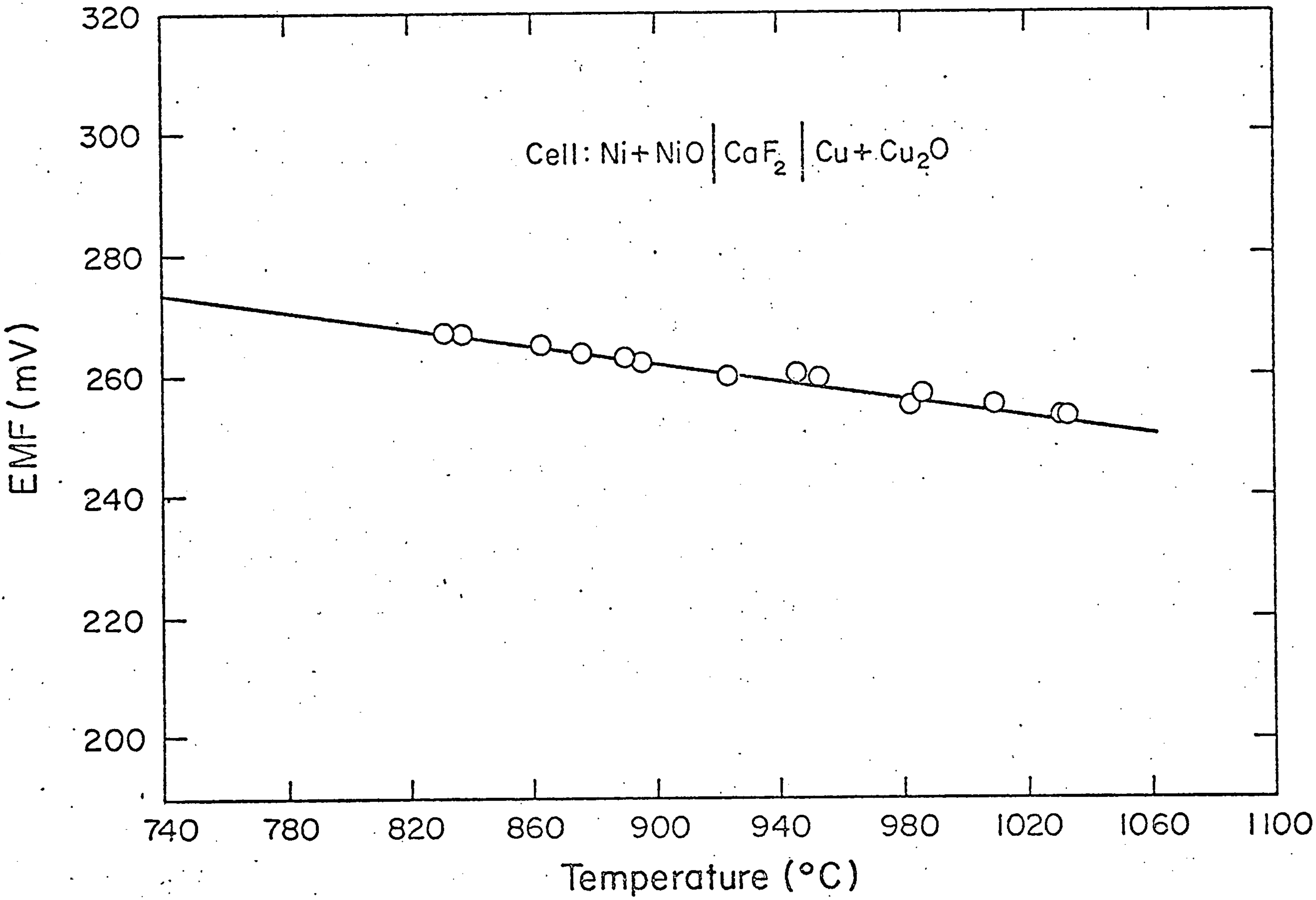

Figure 18 - e.m.f. Value of Cell 20 as a Function of Temperature.

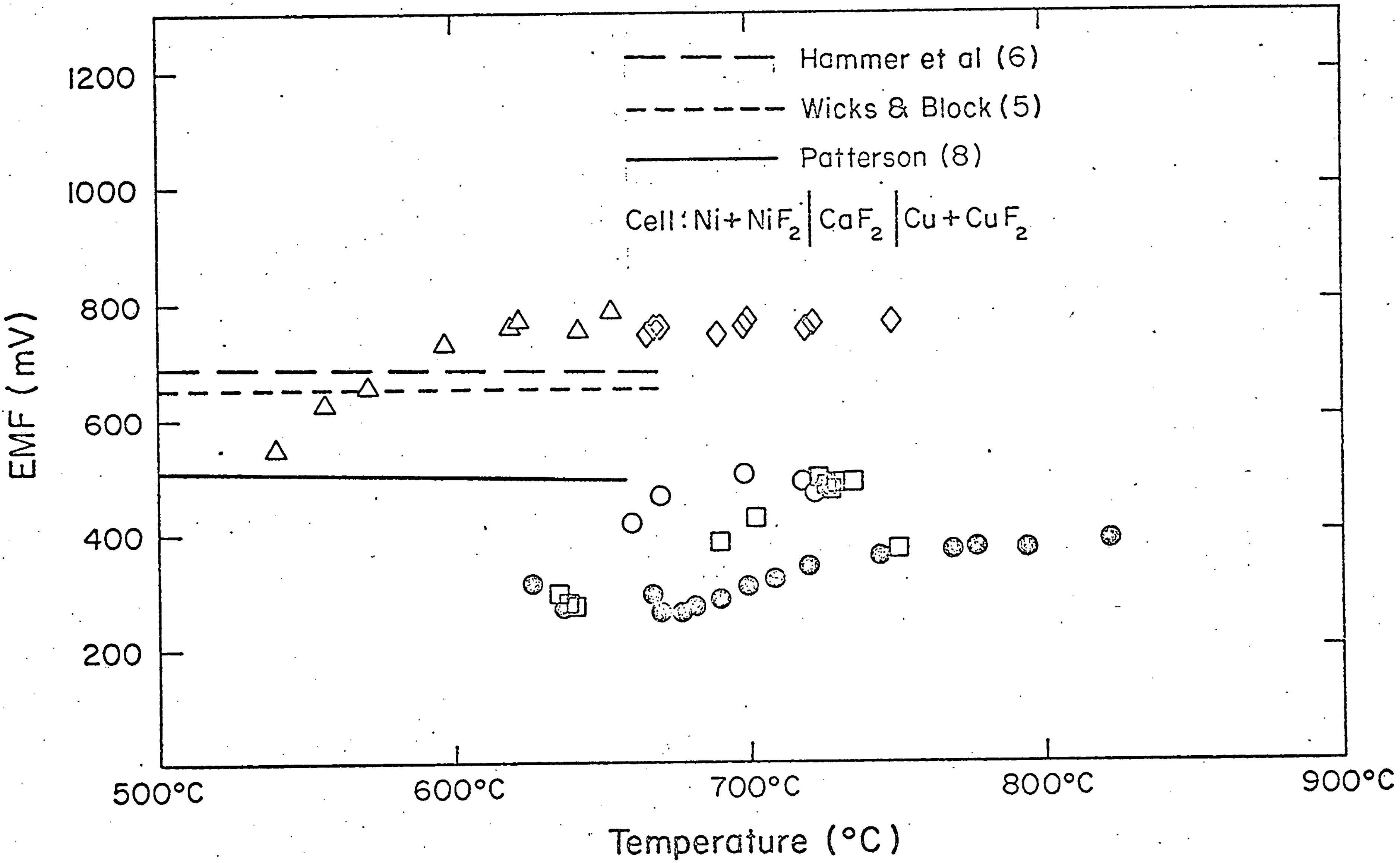

Figure 19 - e.m.f. Values of Cell 27 as a Function of Temperature.