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SUBJECT: MEASUREMENTS OF THE ELECTRICAL CONDUCTIVITY OF MOLTEN FLUORIDES

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MEASUREMENTS OF THE ELECTRICAL CONDUCTIVITY OF MOLTEN FLUORIDES

Introduction

This report concerns itself with electrical conductivity measurements of some of the molten fluoride mixtures encountered in the A.N.P. Project. Conductivity data are required generally to describe more completely the physical properties of these new liquids, and specifically for design purposes when electrical circuits are being considered; such data may perhaps also be used to help interpret the behavior of mass transfer in fluoride systems. These measurements are now being carried out by the A.N.P. Physical Property Laboratory for the purpose of supplying the conductivities of the pertinent, molten fluorides.

Preliminary measurements of the conductivities of several fluoride compositions in the range 1000°F to 1700°F, together with a brief description of the attendant measuring apparati appear in the following paragraphs.

Since it was possible to redetermine the conductivities of known melts to within approximately ± 10% of the values reported in the literature, it is felt that the fluoride measurements possess about the same deviation from the correct values.

Literature Survey

Few workers are known to have dealt with the problem of measuring the electrical properties of those molten salts, which are not compatible with any

[redacted]

known insulators. Those[1,2] who have recently carried out such measurements utilized some form of low resistance cell, which was composed entirely of platinum. Platinum was found to be one of the few, known, compatible substances.

A considerable amount of work has been done in the study of molten salts using cells composed of quartz and ceramics, but their use, here, is precluded because of the corrosive nature of some fluoride compositions.

Experimental Work

1. Materials

All pure salts used in this work were supplied by the S. T. Baker Company, and constituted their best grade of chemical reagents.

The fluoride compositions were supplied by the ORNL Materials Chemistry Division.

The compositions in mole percentages of the proposed reactor fuels and coolants appear below:

Mixture No.	12(Flinak)	30	31	34	44
Chemical Composition	NaF-11.5 M%	NaF-50 M%	NaF-50 M%	NaF-57 M%	NaF-53.5 M%
	KF-42.0 M%	ZrF_4-46 M%	ZrF_4-50 M%	ZrF_4-43 M%	ZrF_4-40 M%
	LiF-46.5 M%	UF_4-4 M%			UF_4-6.5 M%

[1] J. D. Edwards, C. S. Taylor, A. S. Russell, and L. F. Maranville, Trans. Electro-Chemical Soc.; 99, 12, 1952

[2] M. D. Thompson, and A. L. Kaye; Trans. Electro-Chemical Soc.; LXVII, 177, 1935

Chemically pure platinum, graphite, and hot-pressed beryllium oxide were those materials with which the molten salts were in contact.

2. Apparatus

An electric furnace of the crucible type, having a throat capacity of 3 inches, with a 9 inch depth was used in this work. The heat input was regulated by a varistor, which controlled the primary voltage of a step-down transformer supplying the heating elements.

A Leeds and Northrup type K potentiometer was used in conjunction with a platinum-platinum/10% Rhodium thermocouple, which was calibrated at three points from Bureau of Standards samples of tin (449.4°F), lead (621.3°F), zinc (787°F); and the boiling point of water from an isothermal bath. From the uniformity of the above points, it was felt safe to extrapolate to the somewhat higher temperatures encountered.

Since it was necessary to make accurate measurements in the vicinity of 0.2 ohm, a Wheatstone bridge was modified so that corrections for the lead resistances, which were of the same magnitude as the resistance of the cell was possible. Reference to Figure 1 will show a Wheatstone bridge assembly with a low resistance slide-wire inserted between the standard resistance arm, and that of the unknown.

Upon shorting the low resistance cell (Figure 9) electrodes with a copper block, and zeroing the standard resistances, the lead resistance to the cell was so adjusted that the slide-wire could be balanced at its mid-point. The short resistance was then measured with a special Kelvin bridge. The usual ratio

between the arms then obtains, and the fine adjustment is afforded by the slide-wire, the resistance of which is accurately known. Condenser C_1 corrected the quadrature resulting from polarization within the cell.

A vacuum tube amplifier with a gain of 10,000, and an oscillograph together with earphones comprised the detection circuit components.

The high frequency power supply was a Packard-Hewlett Model 200 AB variable frequency audio oscillator.

Three distinct types of conductivity cells (Figures 1, 2, 3) were employed in this investigation. Figure 2 shows the beryllia dip cell, which employs a highly resistant ceramic, beryllium oxide, which was found to be compatible with only certain types of salts, e.g., sodium, zirconium, and potassium based fluorides. The end of this tube is inserted into a cylindrical, platinum crucible containing a melt, and the resistance of the material contained within the narrow, cylindrical annulus, bounded on both ends by a platinum surface is then measured.

The low resistance conductivity cell (Figure 1) was similar to that used by Thompson and Kaye.[2] This consisted of a spherical electrode projecting below the surface of a melt, which was contained within a cylindrical, platinum crucible. A vernier is used to adjust the central electrode until contact is made with the surface of the melt as evidenced by the change in wave form on the oscillograph screen. The liquid depth is thus determined. The central electrode is then farther immersed a fixed distance below the surface of the melt by the vernier. Resistance measurements between this electrode and the outer platinum crucible are made with the bridge. Appearing in Figure 1 is the associated bridge circuit.

The current-potential conductivity cell (Figure 3) possesses the advantage that since the current and potential measurements are taken separately, the effects of polarization are greatly diminished. A cylindrical, potential probe measures the voltage drop between the current-carrying electrodes by means of a high resistance, vacuum tube voltmeter. This electrode contacts the surface of the melt, and is in series with the outer electrode and the vacuum tube millivolt meter. A central, spherical electrode, and a hemispherical, outer crucible constitute the current-carrying electrodes.

Since polarization is primarily dependent upon the current density at the electrode, the effect of polarization at the large electrode, which is approximately 100 times the area of the smaller, may be considered negligible. It is, therefore, a reasonable assumption that, little, or no interface resistance is present at the large electrode. The high frequency current further mitigates these effects.

That the above assumptions are substantially correct is verified by the results of the measurements in Figures 4 and 5, where satisfactory agreement of the data with the literature values can be noted.

Some further advantages of this type of cell lie in its invariability of cell constant regardless of possible electrode-contamination by the salt being measured, and relative insensibility of cell constant with liquid level.

3. Procedure

The Beryllia Dip Cell

Resistance measurements in conjunction with the beryllia dip cell (Figure 2) were of a reasonable magnitude, thereby permitting the use of a conventional Wheatstone bridge assembly. However, correction for the lead resistances was also made. Measurements were taken with decreasing temperature, allowing sufficient time for a uniform temperature distribution at each determination. Several adjustments of the central electrode, and determinations of the resistance were made for each temperature, and the lowest values were recorded.

That no penetration of, and subsequent conduction through the ceramic occurred was evidenced by the coincidence of measurements taken with both increasing and decreasing temperatures.

The Low Resistance Cell

In the case of the low resistance conductivity cell (Figure 1), resistance measurements were made with the Wheatstone bridge modification in the range 0.1 to 0.5 ohms. During a typical run, the depth of the salt was determined by adjusting the electrode vernier until contact was made with the surface. It was possible to repeat this setting to within $\pm$ .002 inches. The electrode is then dropped to that depth to which a particular cell constant corresponds. Measurements are then quickly taken on the decreasing temperature scale. The system was held at a constant temperature for approximately a half hour before a determination was made. At high temperatures, not more than a few reliable

determinations could be made before dismantling the cell and recoating the electrodes with platinum black was necessary. It is known that platinum black rapidly deteriorates in the presence of molten fluorides, and soon becomes ineffective in reducing polarization. It has been observed that as this platinum layer is reduced, the lowest frequency at which the bridge can be balanced rapidly increases. This effectually alters the cell constant.

A considerable degree of polarization, which appeared in the exterior circuit as a series capacitance was compensated for by means of a parallel capacitance in the opposite arm of the bridge.

All measurements were made with a power source at a frequency of 1000 cycles per second.

Following a lengthy run, the cell resistance was observed to increase sharply above the requisite value for that temperature. Dismantling of the cell, revealed the central electrode to be coated with a dense, grey, non-electrically conducting film. This film appeared to form quite rapidly following the reduction of the platinum black.

The disparity in the relative areas of the electrodes further intensified the normal interface polarization effect as a result of a high current density gradient in the vicinity of the central electrode.

The Current-potential Cell

In making a measurement with the current-potential cell, (Figure 3) the central electrodes, which move vertically are adjusted by a vernier to a depth at which the central electrode is half submerged, and the potential electrode

is just in contact with the surface. Voltage and current measurements are then taken with decreasing temperature, allowing sufficient time for the system to become isothermal at each determination. A power supply of 500 cycles per second was used with this cell.

Cell Constant Calculation

From Ohm's law, the resistance of the passage of a current through a conductor of uniform cross section may be represented:

$$R = \frac{\ell}{\sigma A}$$

where: ℓ = length of conductor

A = area of conductor

σ = conductivity

If the lines of current flow are always perpendicular to cross sections, the resistance of a conductor of variable section may be obtained by applying Equation (1) to each infinitesimal segment:

$$R = \frac{1}{\sigma} \int_{\ell} \frac{d\ell}{A} \tag{2}$$

Consider the case of a hemispherical electrode system:

$$R = \frac{1}{\sigma} \int_{\ell} \frac{d\ell}{A} = \frac{1}{\sigma} \int_{\ell} \frac{d\ell}{2\pi \ell^2} = \frac{1}{2\pi\sigma} \int_{\ell} \ell^{-2} d\ell$$

$$= \frac{1}{2\pi\sigma} \left[\frac{1}{\ell}\right]_b^a = \frac{1}{2\pi\sigma} \left[\frac{1}{a} - \frac{1}{b}\right]$$

$$= \frac{1}{2\pi\sigma} \left(\frac{b-a}{ab}\right) = \frac{C}{\sigma} \tag{3}$$

where C is defined as the cell constant for the hemispherical system and is equal to

$$C = \frac{b-a}{2\pi ab} \tag{4}$$

Upon measuring the voltage and current in such a cell system one can then determine the conductivity from the following equation:

$$\sigma = \frac{C}{R} = \frac{CI}{E} = \frac{(b-a)}{2\pi ab}\frac{I}{E} \tag{5}$$

The Cell Constants

The cell constant for the beryllia dip cell (Figure 2) was determined both from its geometry, and by means of a standard potassium chloride solution, the conductivity[3] of which is accurately known. Using Equation (1), the constant was determined from the cell geometry to be simply the ratio of ℓ by A. This value agreed to within 1/2 of 1 percent of that value obtained by means of the standard solution, and was about 24.0 cm^{-1}.

A calculation of the thermal expansion of the tube at the highest temperature achieved, showed an insignificant change of approximately .1 percent in the cell constant above that at room temperature.

The cell constant of the low resistance cell (Figure 1) could only be obtained accurately by means of a standard solution, since its cross section is

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[3] G. Jones, and M. J. Prendergast; J. Am. Chem. Soc., 59, 731 (1937)

not uniform. This constant was about .493 cm^{-1}, but varied slightly with the depth of liquid within the crucible. The liquid level versus cell constant was then plotted, and preceding each measurement, a determination of the liquid level was made thereby permitting a suitable correction.

Molten potassium chloride was also used to determine the constant at high temperatures, but the value obtained in this manner did not agree with the constant obtained at room temperature better than 7 percent.

The current-potential cell constant (Figure 3) was determined both by direct calculation from its geometry, and by means of a standard conductivity solution. From Equation 4 the constant was determined to be .162 cm^{-1}. Using the standard solution, a cell constant of .165 cm^{-1} was obtained, or, within 1.8% agreement.

Results and Discussion

Figures 4, 5 and 6 show mean distributions well within $\pm$ 10% of the values in the literature[4]. The low resistance cell, and the current-potential cell were used in making these measurements.

Appearing also in Figure 5, is an extension of the conductivity of molten NaOH to 1500°F. This is approximately 650°F higher than the values reported in the literature. These data tend to follow the usual pattern of other molten salts at elevated temperatures.

In Figure 7, it is noted that while the data obtained by the two different methods did not agree too well at high temperatures, reasonable agreement was nevertheless evident in the lower temperature range. The lower values recorded

[4] International Critical Tables; 6, 149, 1929

here can be explained by the formation of a partially conducting film observed upon the central electrode. The greater confidence, therefore, is expressed in those values obtained by means of the dip cell method.

The results of several best runs for the compositions 12, 34, 30 and 44 appear in Figures 8, 9 and 10.

The lithium containing salt, No. 12 possesses somewhat greater conductivity than the straight sodium-zirconium fluoride compositions; a similar behavior has been observed in regards to thermal conductivity measurements of these salts.

Referring to Figure 7, it is seen that for a given composition, the conductivity appears to vary inversely with its mole percentage of UF_4. This also coincides with the fact that the thermal conductivity of this salt decreases with UF_4 content.

A further refinement of the current-potential cell (Figure 3) is now under development, and it is felt that this new cell will greatly mitigate the effects of:

1. Dependence of cell constant upon liquid level (which is, in turn, dependent upon temperature).
2. Dependence of cell constant upon formation of partially conducting film upon electrode surfaces.
3. Dependence of cell constant upon frequency.

The usual sources of error, among which are the following: thermal gradients, inaccuracy in cell constant determination, high temperature measurements, and inaccuracies of equipment can only be alleviated through refinement of associated apparati.

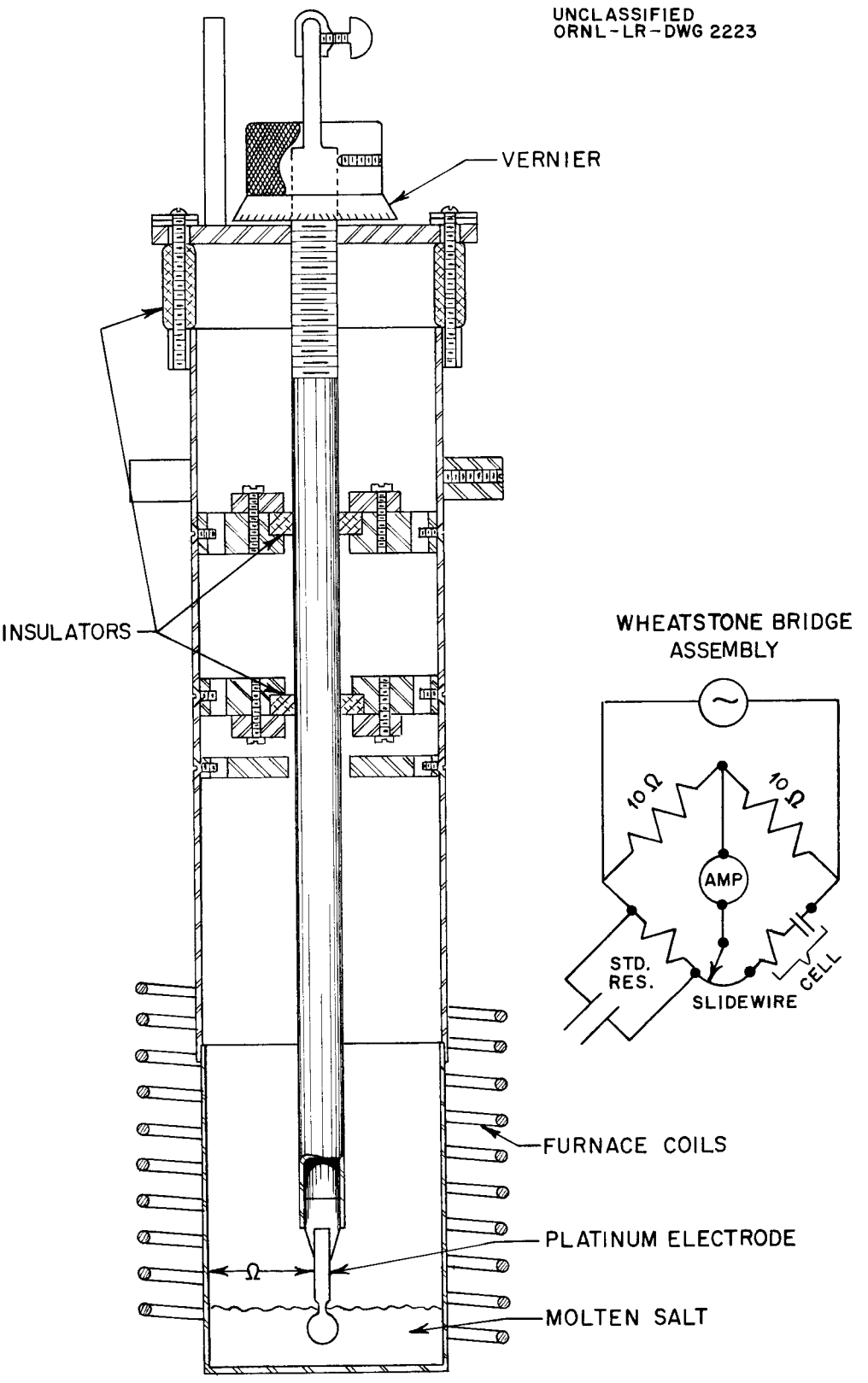

Fig. 1. Low Resistance Conductivity Cell Assembly.

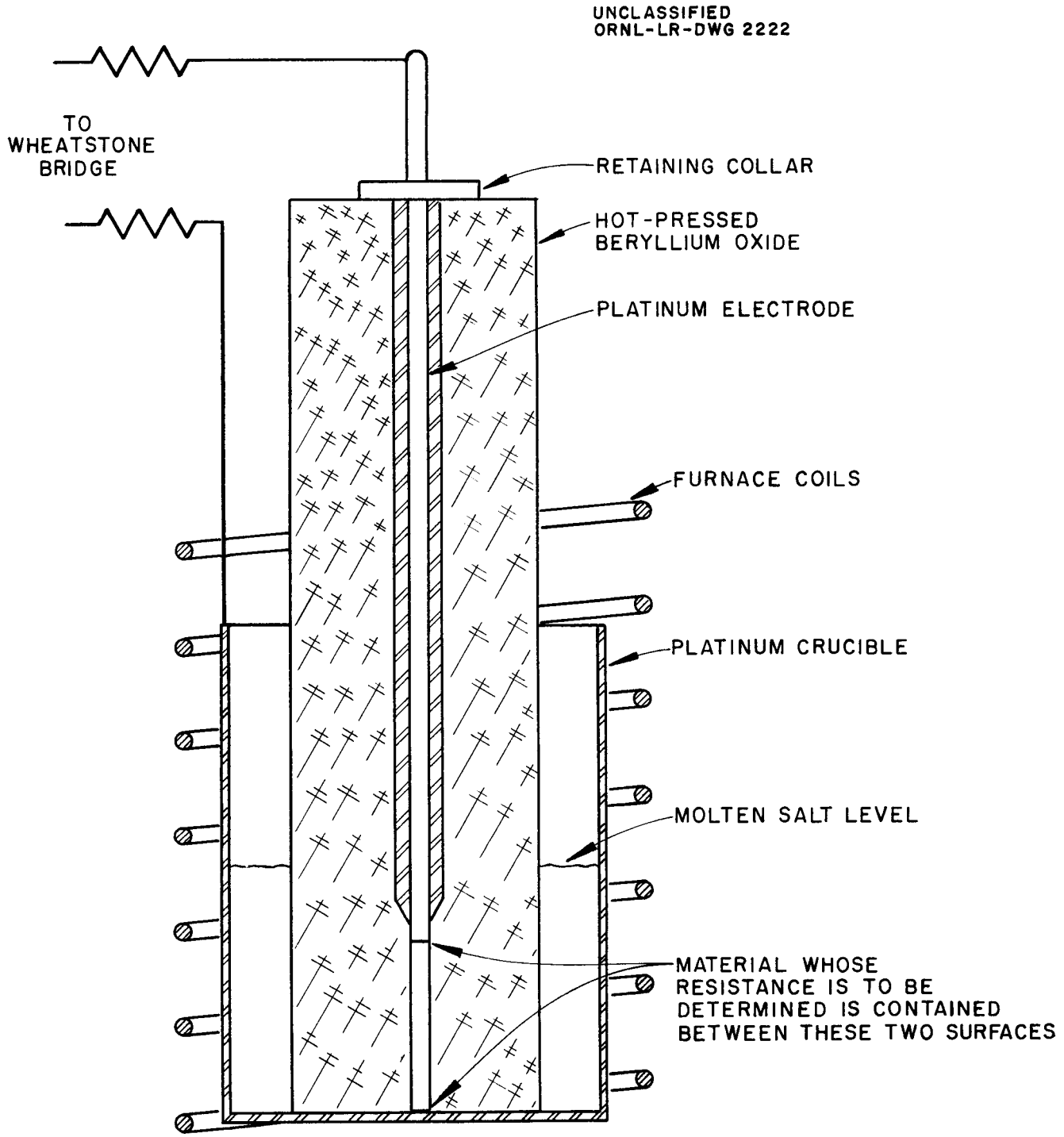

Fig. 2. High Resistance Beryllia Dip Cell for Measuring Conductivity of Molten Salts

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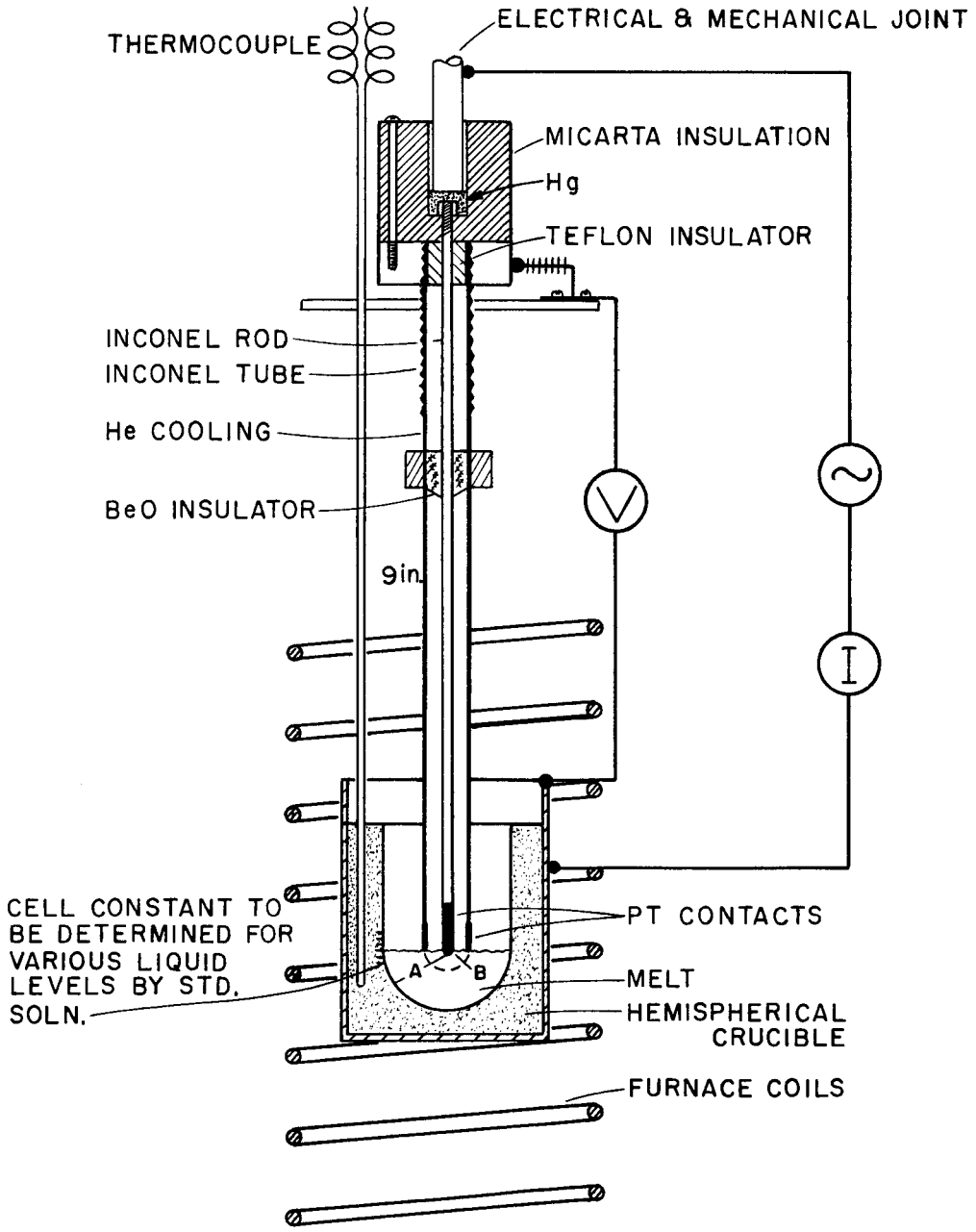

Fig. 3. Apparatus to Determine Conductivity of Molten Salts Through Potential and Current Measurements

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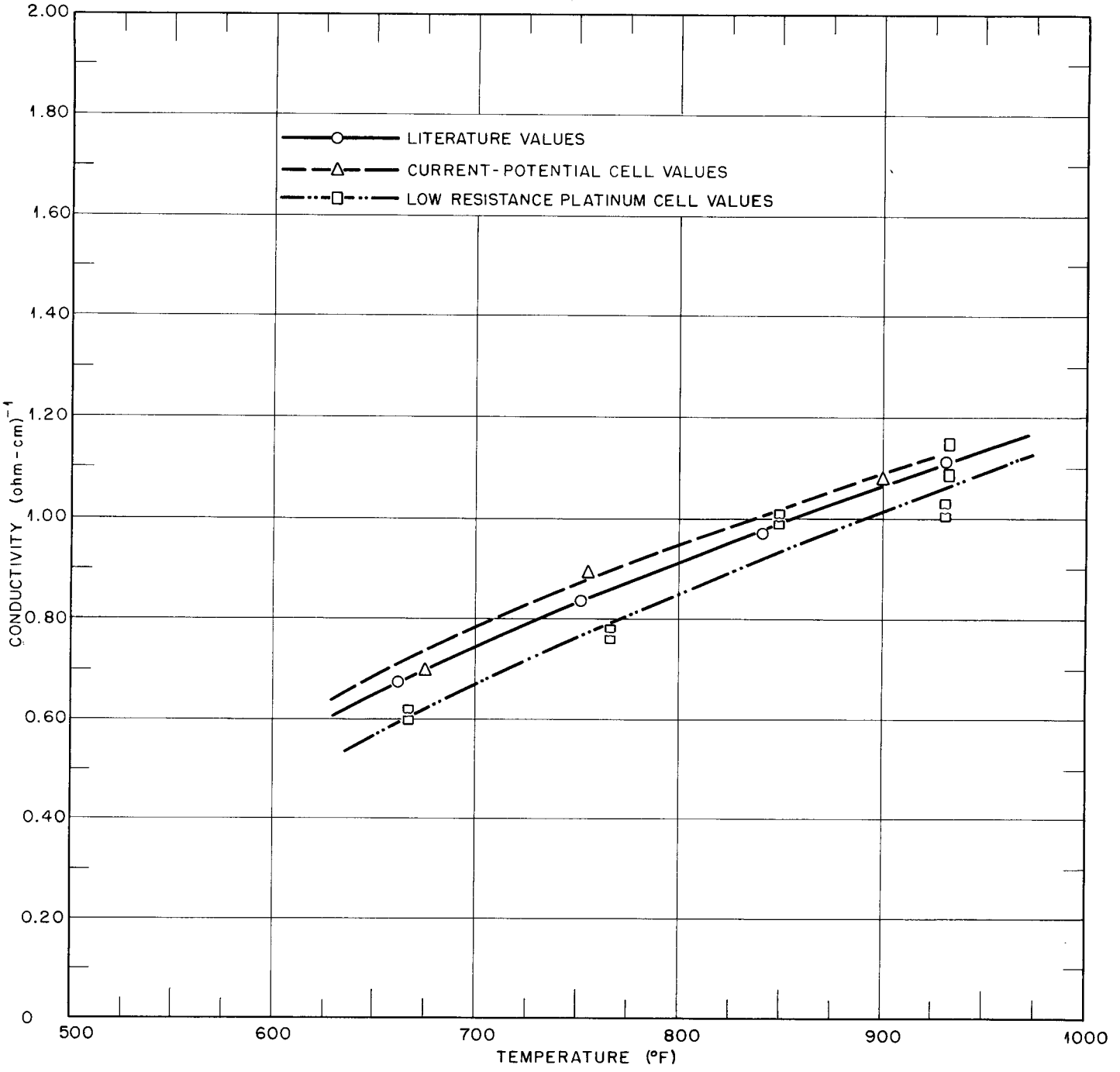

Fig. 4. Electrical Conductivity of KNO_3 vs. Temperature

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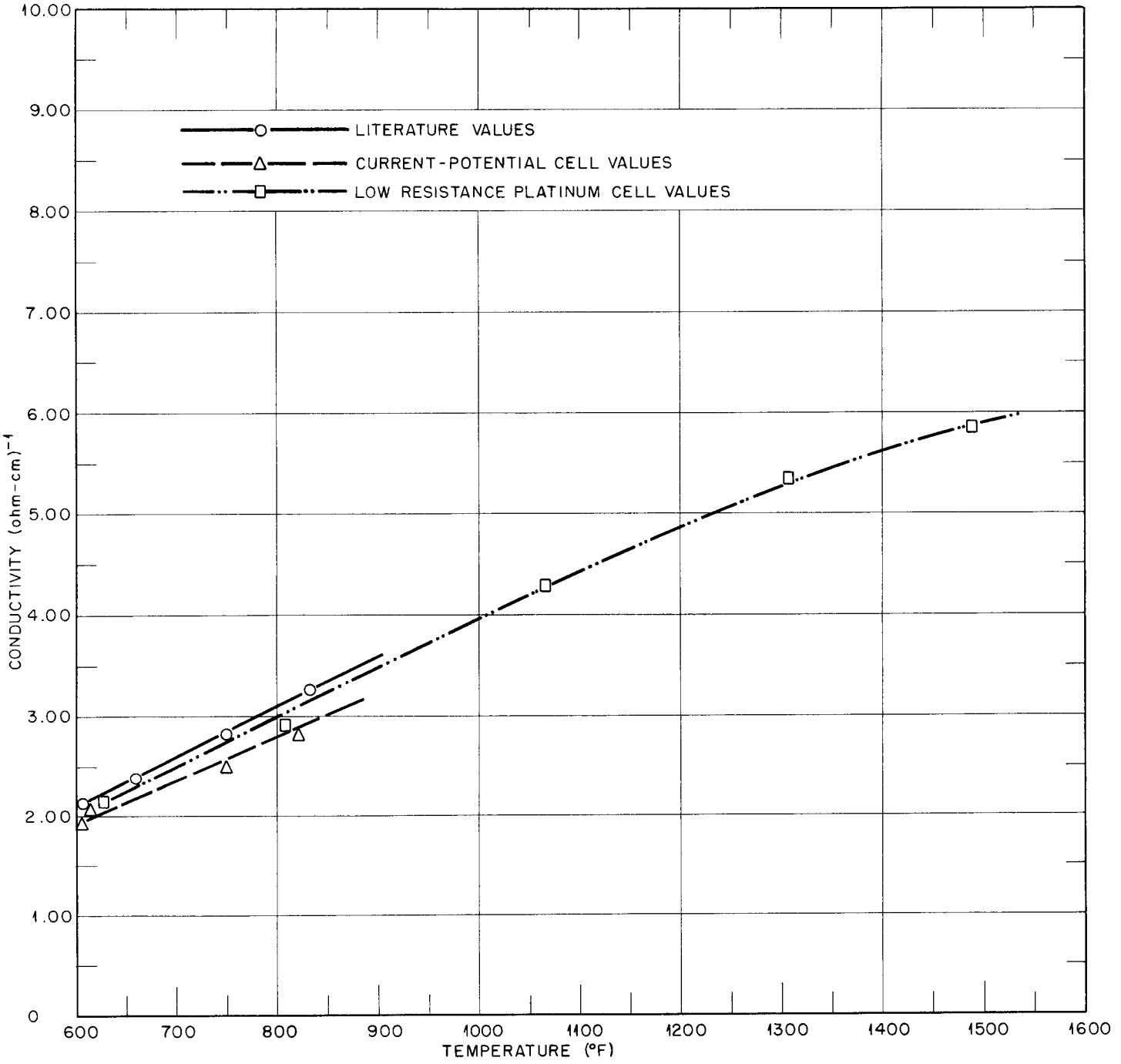

Fig. 5. Electrical Conductivity of NaOH vs. Temperature

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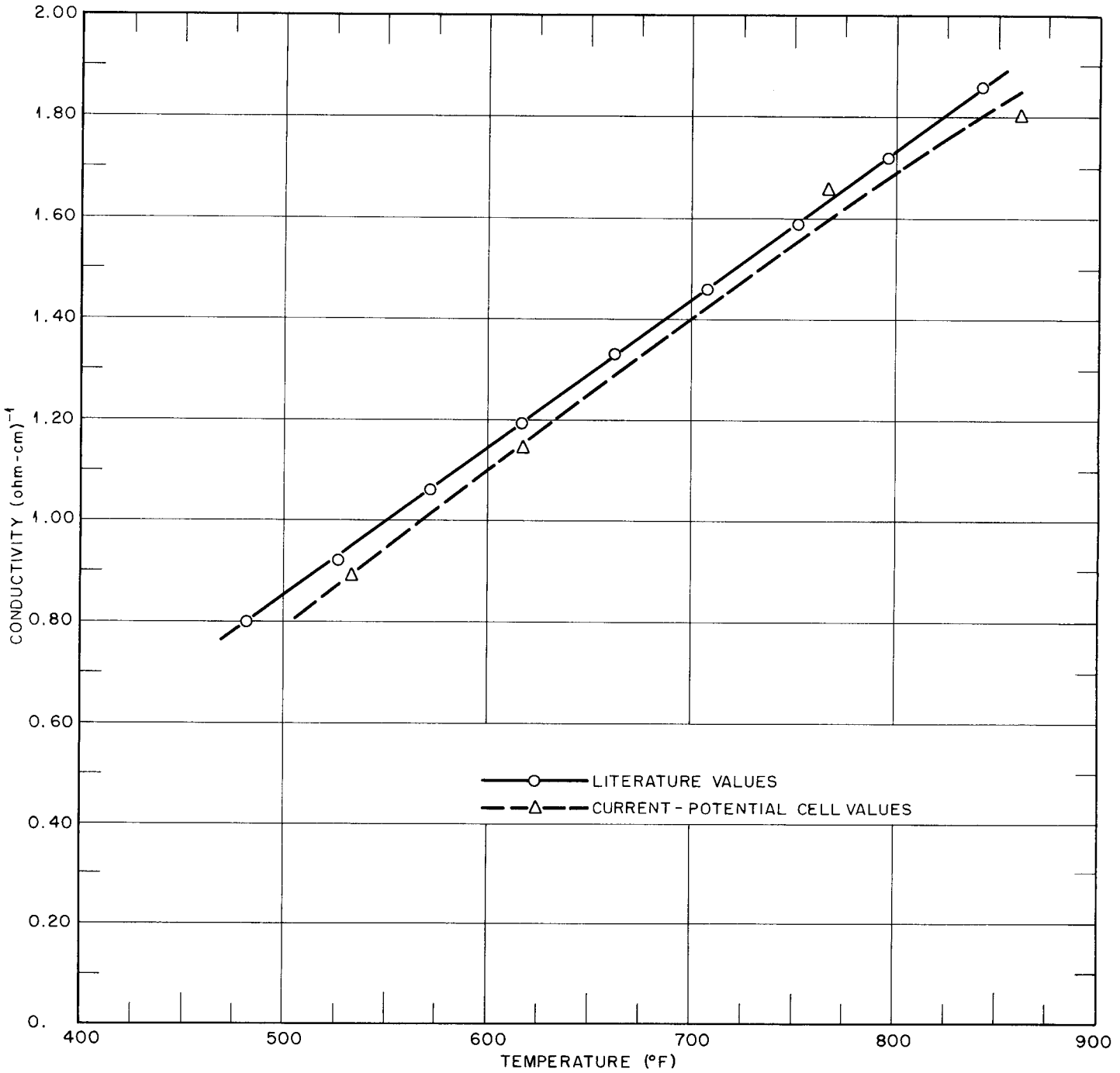

Fig. 6. Conductivity of $LiNO_3$ vs. Temperature Showing Comparison of Experimental Values

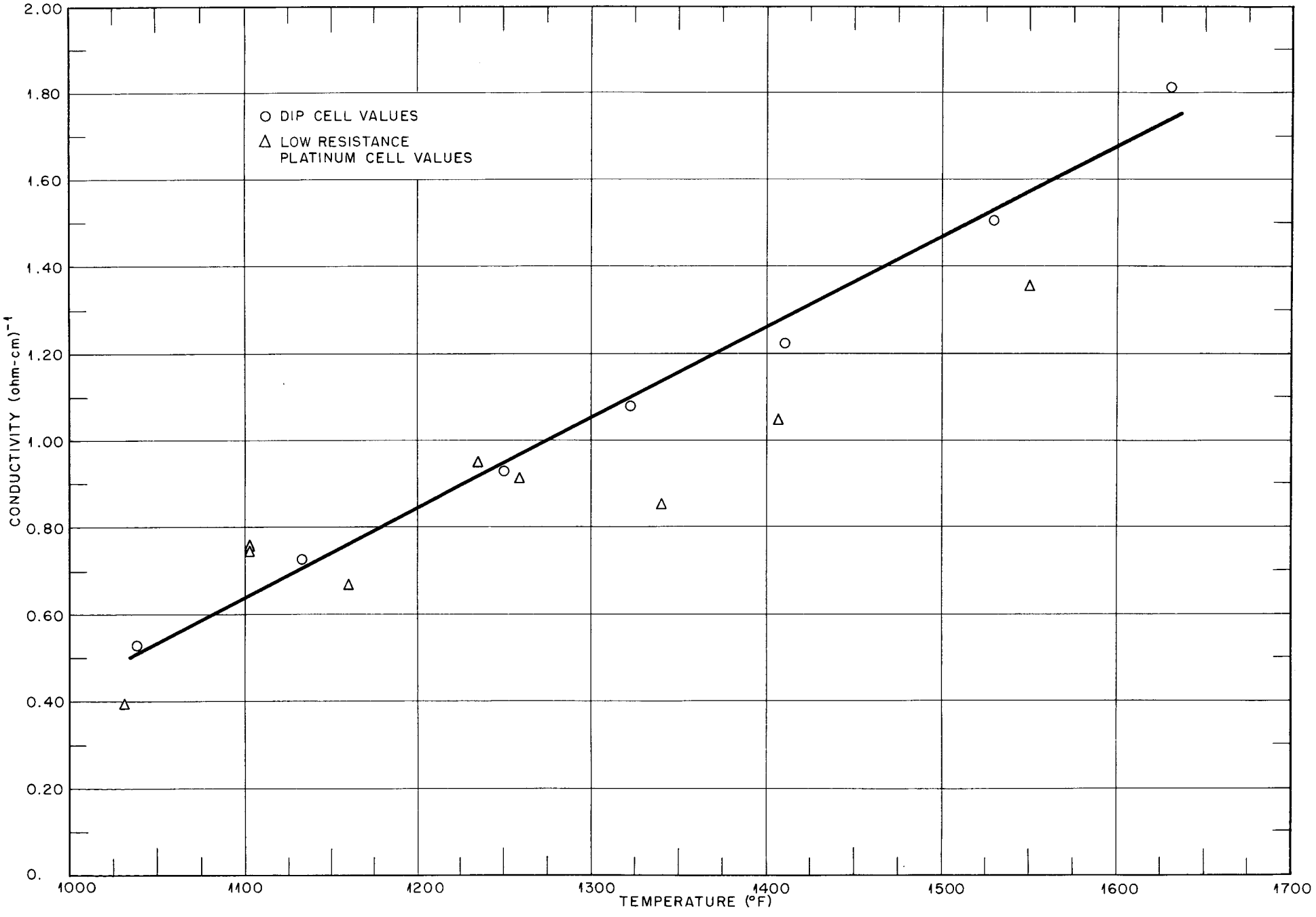

Fig. 7. Electrical Conductivity of Composition No. 31 vs. Temperature

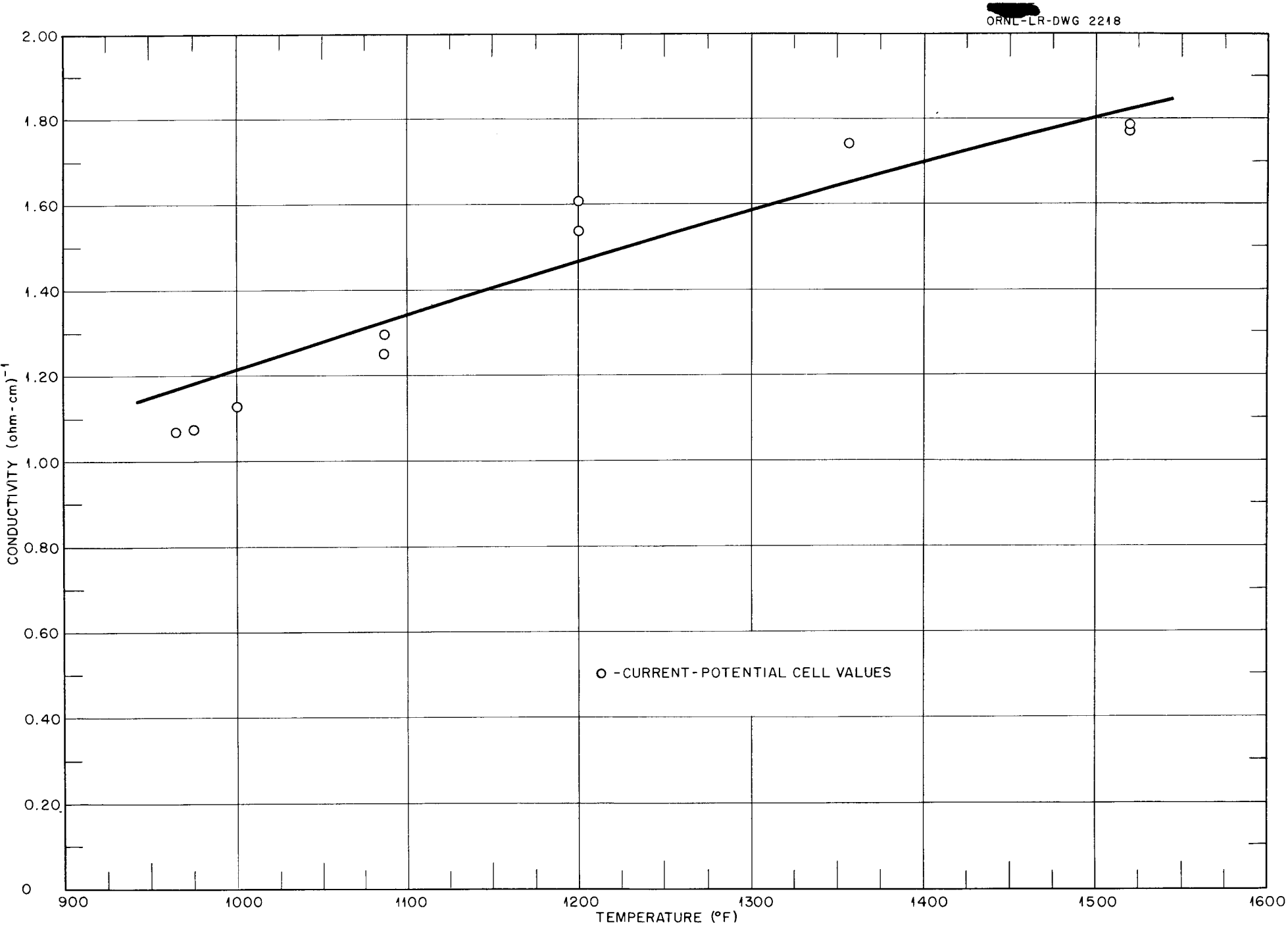

Fig. 8. Conductivity of Composition No. 12 vs. Temperature

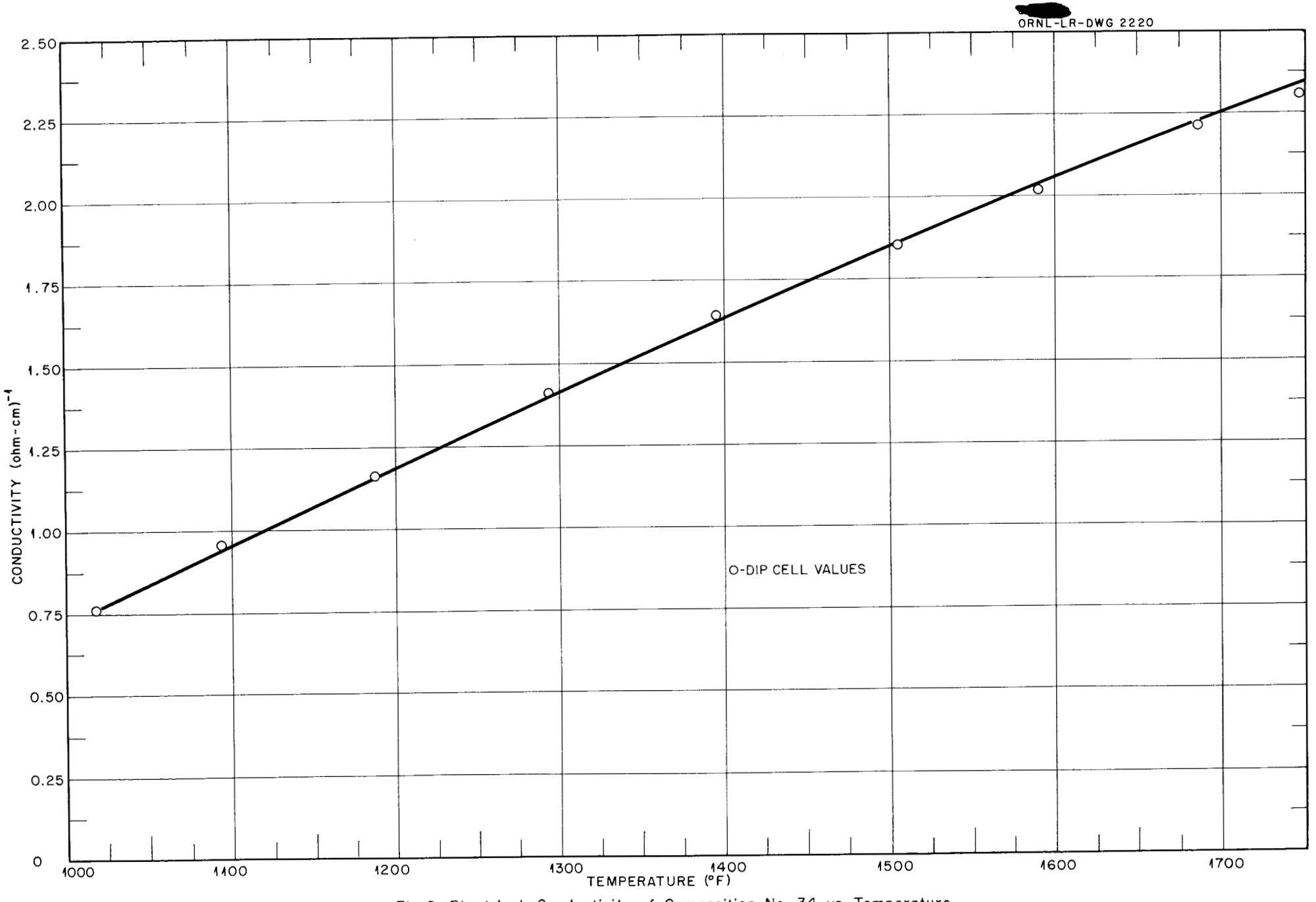

Fig. 9. Electrical Conductivity of Composition No. 34 vs. Temperature

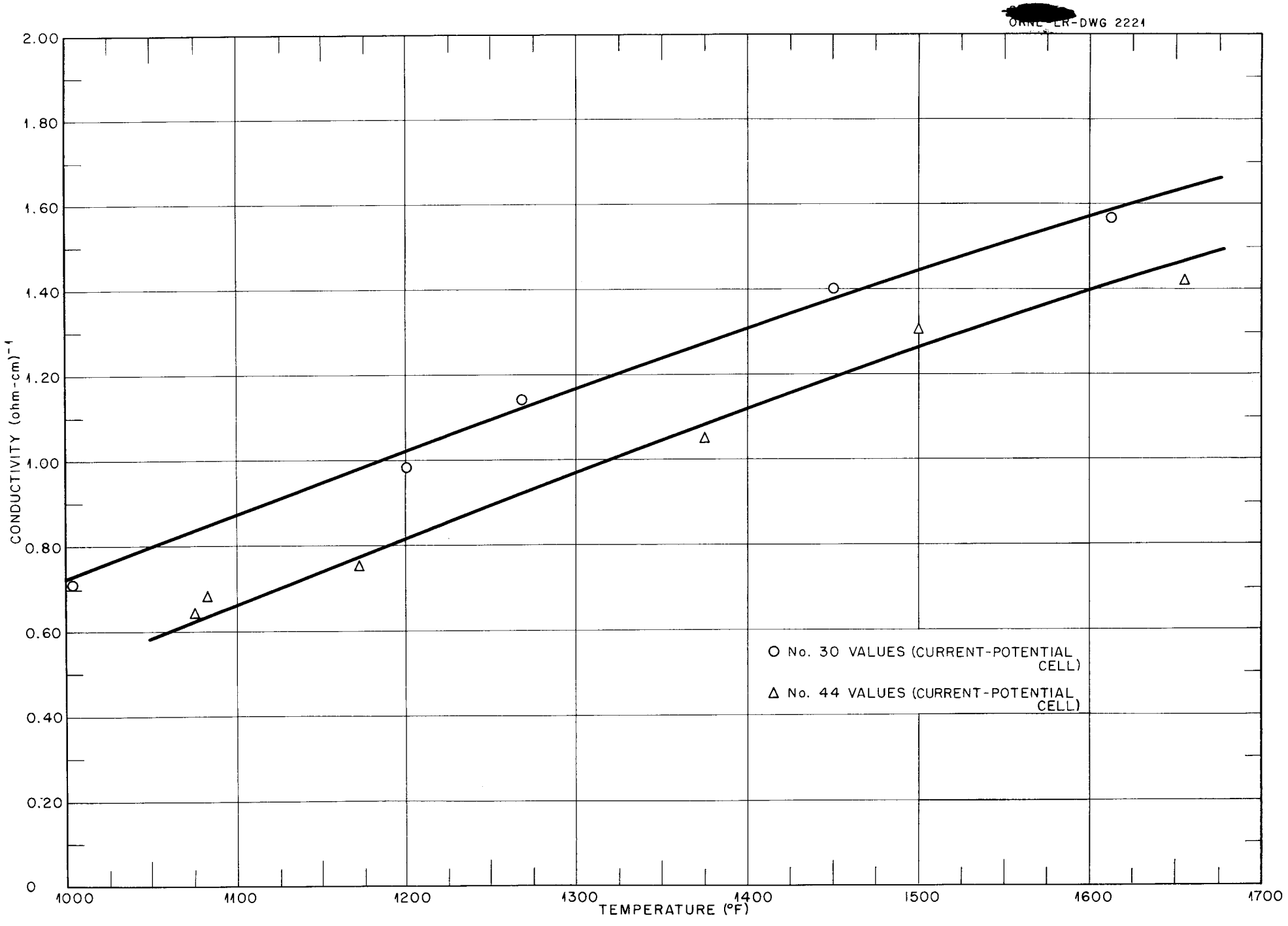

Fig.10. Electrical Conductivities of Compositions No. 30 and No. 44 vs. Temperature