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ELECTRICAL CONDUCTIVITY OF CRYOLITIC MELTS

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Abstract

A laboratory study was conducted to determine electrical conductivity of cryolitic melts by using a novel moving electrode technique. The newly-developed method proved to have distinct advantages over previously-used, classical techniques in accurately measuring the electrical conductivity of highly corrosive cryolitic melts. Results were obtained for a comprehensive range of cryolite ratio, alumina, calcium fluoride, magnesium fluoride, and lithium fluoride concentrations at different bath temperatures. The results were compared with that predicted by the Choudhary model. Differences in the electrical conductivity of low cryolite ratio and high concentrations of additives at low bath temperatures were found and discussed.

Introduction

Although it has been one of the most intensively studied areas, the electrical conductivity of cryolitic melts continues to be an active research topic due to its importance for operation of modern bath chemistries for energy improvement in commercial aluminum cells. On the other hand, the availability of state-of-the-art engineering materials which can resist the highly corrosive environment of cryolitic melts, makes it possible to construct reliable conductivity cells for accurately determining the electrical conductivity of redundant cryolitic electrolytes.

Comprehensive literature reviews on the electrical conductivity of cryolitic melts and measurement techniques are available by Grojtheim et al (1), Edwards (2), and Robbins (3). The electrical conductivity research for cryolitic systems has a long history beginning early this century. However, there is still wide discrepancy in conductivity data of pure cryolite, and of multicomponent systems of cryolite-base melts due to the difficulties in measuring the electrical conductivity of fused fluorides.

The most widely accepted electrical conductivity model in the open literature was derived by Choudhary (4) twenty years ago. The model was based on the literature data available then and claimed to cover a wide range of cryolitic melt compositions and bath temperatures. Almost all of those data the model referred to was measured at temperatures at or higher than 1000°C, far higher than the operating temperatures in modern Hall cells.

Computer control and design of modern aluminum reduction cells require models which can accurately predict the electrical conductivity of industrial baths. Through years of both laboratory and industrial practice in applying the Choudhary model to predict conductivities of plant bath chemistries, experience has shown the need to improve the model especially for the low cryolite ratio melts containing high concentrations of additives at low bath temperatures.

A novel experimental technique was developed especially for determining electrical conductivity of molten cryolitic electrolytes. This paper presents the technique and the results of electrical conductivity determined for a cryolitic melt composition matrix containing varied concentrations of aluminum fluoride (AlF_3), alumina (Al_2O_3), calcium fluoride (CaF_2), magnesium fluoride (MgF_2), and lithium fluoride (LiF). The electrical conductivity results of the cryolitic melts matrix are presented and compared with that predicted by using the Choudhary model.

The Theory

Unlike traditional electrical conductivity methods, the present technique employs the principle of a Continuously Varying Cell Constant (CVCC) through a moving platinum (Pt) disc electrode in a relatively large diameter capillary (tube-type) conductivity cell. The equation used to calculate electrical conductivity basing on measurement data was formulated through classical electrical conduction theory.

In the measurement of electrical conductivity, the total impedance of a measuring circuit, Z, may be expressed by:

$$Z = R_m + X_L + X_C \tag{1}$$

where, R_m is the real resistance component of the measuring circuit.
X_L the inductive component of the impedance.
X_C the capacitive component of the impedance.

The real component of the impedance, R_m, may be expressed as follows:

$$R_m = R_0 + R_f + \Delta R \tag{2}$$

where, R_0 is the ohmic resistance of the electrolyte.
R_f the polarization resistance of the electrolyte due to frequency effects.
ΔR the contact resistance between wires and electrodes.

The classical methods (using either high or low cell-constant conductivity cells) have been based on applying very high frequency so that the polarization resistance of the electrolyte, R_f, is decreased to an infinitely small value and can therefore be omitted from R_m when compared with the magnitude of R_0.

$$R_f = 1/f(f) \text{ - } {>}0 \tag{3}$$

The principle of the present technique is based on the continuously varying cell constant, and at the same time measuring the real component of the circuit, R_m, at a fixed high frequency. Because of the linearity of R_m versus the cell constant, the electrical conductivity of the electrolyte, k, can be obtained by using:

$$k = 1/[\,A\,(\frac{dR_m}{dL})\,] \tag{4}$$

where, k is the conductivity of molten salts, in S/cm.

A is the inner cross-sectional area of conductivity cell, in cm^2, which is known through calibration.

$\frac{dR_m}{dL}$ is the slope of the resistance of the measuring circuit versus the programmed variation of the conductivity cell length, L.

A continuously varying cell constant was accomplished by linearly varying the length of the conductivity cell, L, by moving the Pt-disc electrode while keeping the cell cross area, A, unchanged. The slope is therefore derived through a series of circuit resistance measurements versus the programmed lengths of the conductivity cell.

The CVCC technique was verified initially by using aqueous electrolyte at ambient temperatures, and then molten chloride and fluoride systems at high temperatures. The electrical conductivity derived from the equation is free of the extraneous conductivity effects such as applied frequency and wire contact resistance.

Experimental Procedures

The equipment, cell design, and experimental procedures for the conductivity measurement in the cryolitic melts are described below.

CVCC Conductivity Cell Design

The CVCC theory and technique was first tested in aqueous solutions and then verified in molten chloride salts. It was then extended to molten fluoride systems for the conductivity measurements. The equipment and cell design are described for molten fluoride compositions even though it has also been used for other salt systems.

A schematic of the CVCC conductivity system assembly used in this study is shown in Figure 1. A graphite crucible which was used as molten bath sample holder, had a 3 cm inner diameter and was able to hold over 100 grams of molten bath. The graphite crucible was also used as the counter electrode which was connected to a LCR Impedance Meter via a thermocouple Inconel protection sheath. A type K thermocouple threaded into the wall of the graphite crucible was used to monitor the system temperature. The graphite crucible also has a 3.8 cm I.D. slot at the open end for centering a pyrolitic BN tube-type conductivity cell. The tube-type conductivity cell was centered vertically in the graphite crucible via connection through a BN disc which sits in a bigger diameter hole in the graphite crucible.

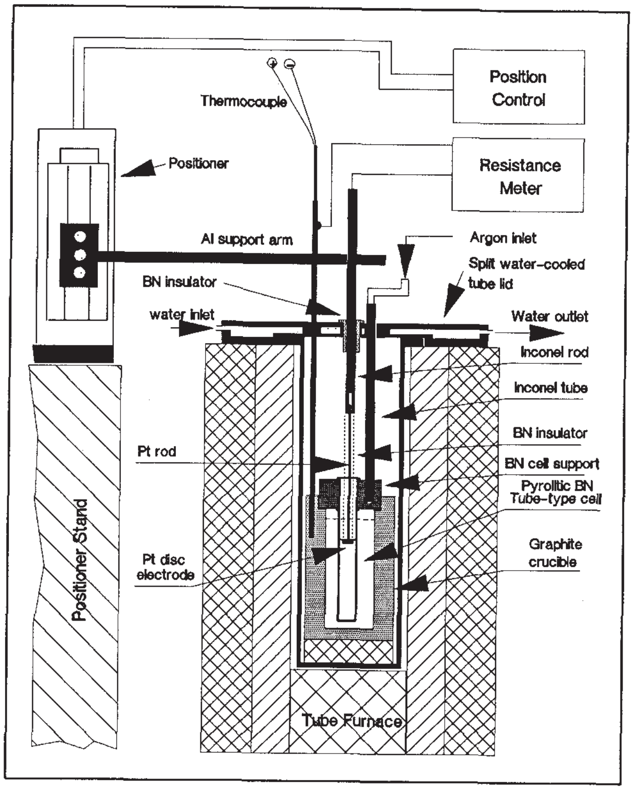

Figure 1: Schematic view of the electrical conductivity measurement using a moving Pt-disc electrode for the fused fluoride systems.

One of the CVCC conductivity cells constructed and used in the tests is shown schematically in Figure 2. The tube, which has a consistent I.D., purchased from Union Carbide (Cleveland, Ohio), was made of vapor deposited pyrolytic BN. The tube is dense, non-conductive, and able to resist corrosion by molten fluorides. One end of the tube was fixed on the BN centering disc. An Inconel rod was connected to the BN disc via threaded connection. The conductivity cell unit was centered on the top of the graphite crucible. About 5.5 cm of the pyrolytic BN tube was immersed in the molten bath. In conjunction with the Pt disc electrode, it formed a tube-type conductivity cell.

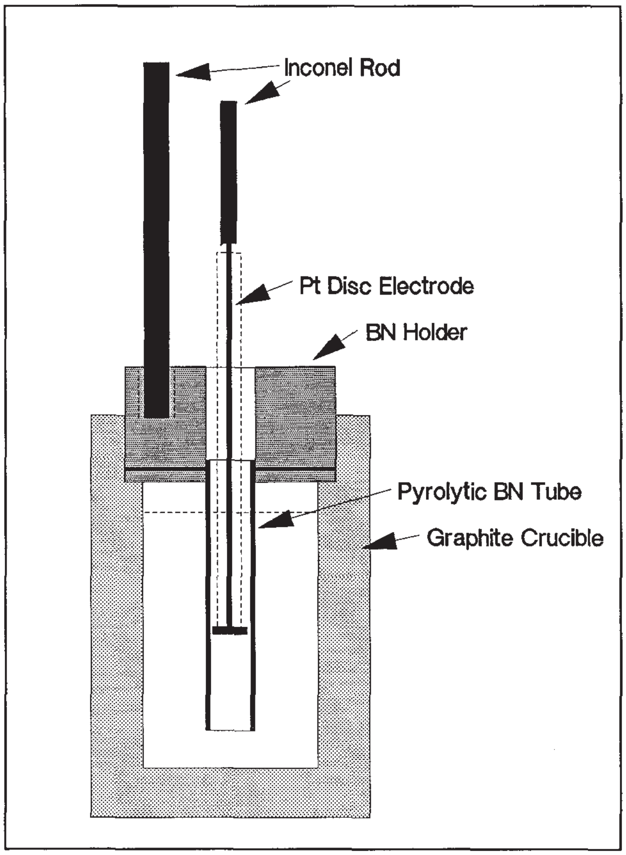

Figure 2: Schematic view of a pyrolytic BN conductivity cell system used for measuring electrical conductivity of fused fluoride salts.

A Pt disc electrode was connected to 0.16 cm Pt wire by threads. The Pt wire was insulated by a BN tube. The other end of the Pt wire was also threaded to connect with a 0.64 cm Inconel rod which was then vertically connected to the arm of a positioner for measurements.

The top end of the furnace tube was covered with a special split water-cooled lid. The furnace was purged with argon to prevent air burning the graphite crucible and to ensure the accuracy of the measurement.

The positioner used in this study was a Model Unidex XI from AeroTech (Pittsburgh, PA), which was vertically located on a vibration-free stand. It can move the Pt-disc electrode in the center of the pyrolitic tube-type conductivity-cell up and down to a known position with an accuracy of ± 0.001 cm via the extension arm. The positioner was controlled by a programmable position controller.

In most of the reported tests, electrical conductivity was measured using an Impedance Meter SP2596 from Electro Scientific Industries (Portland, OR) with a fixed frequency of 1 kHz. All three components of the measuring circuit, i.e., real component (resistance), capacity, and induction, could be measured by the meter. In a study of the frequency effect, an HP 4274A Multifrequency LCR meter from ElectroRent Corp. (Norcross, GA) was utilized, which has a frequency range from 100 Hz to 100 kHz with 11 intervals and measures resistance from milliohms to megohms with 5 significant digits.

Experimental Procedures

Calibration of Pyrolitic BN CVCC Conductivity Cell. It was shown in equation (4) that to measure the electrical conductivity of an electrolyte, the inner cross-sectional area, A, of the tube-type cell must first be known. The cross-sectional area or I.D. of the pyrolitic tube-type conductivity cell was determined by measuring the electrical conductivity of 1.00 M KCl aqueous solution according to the published data at ambient temperatures (5). It was assumed that the thermal expansion of the tube I.D. due to increased temperatures was insignificant and, therefore, was neglected.

Calibration or determination of the cell's inner cross-sectional area was conducted in a 400 ml beaker. An Inconel coil placed in the bottom of the beaker was used as counter electrode. The CVCC conductivity cell was centrally suspended in the KCl solution via a clamp, and the Pt-disc electrode was centered in the cell through the positioner arm. The resistance was recorded at each increment (or decrement) by the Pt electrode. Once the calibration procedure was completed, the conductivity cell and Pt electrode were fully rinsed with distilled water before being put into a 110 °C oven for over night prior to the high temperature measurements.

Measurement of Electrical Conductivity of Cryolitic Melts. The pretreated graphite crucible containing about 100 grams cryolitic bath sample of the desired composition was placed in the temperature stabilized furnace. When the bath sample melted, the tube-type CVCC conductivity cell with its support was positioned on the graphite crucible via the Inconel rod. About 5.5 cm of pyrolitic tube was immersed in the molten bath which formed the conductivity cell. Then the Pt-disc electrode was carefully loaded into the furnace and centered in the conductivity cell via the Inconel rod, and then fixed on the positioner's arm. The Pt-disc electrode was moved down and immersed in the molten bath through the control of the automatic positioner. The electrode position on the surface of the bath electrolyte was known from change in the resistance reading when it suddenly becoming unmeasurable as the Pt-disc electrode moved upward out of the electrolyte.

Once the temperature of the bath was stabilized at the target temperature, the electrical conductivity measurements began by incrementing down the disc electrode via the automatic positioner. The distance (increment or decrement) the Pt-disc electrode moved by the positioner for each step measurement was 0.2000 cm. One set of measurements was made when the electrode was moved downward in the conductivity cell from just below the surface of the bath to the lower open end of the conductivity cell. At least two sets of the measurements were conducted for each experimental condition, i.e., one bath composition at one desired temperature. It should be noted that the derived measurement results were the same when the electrode moved either upward or downward.

Only the resistance variations versus the electrode incremental (or decremental) distance are required to calculate the electrical conductivity. Bath samples were taken from the crucible for chemical composition analysis after measurement for each experimental condition.

Cryolite, 99.5% in purity, was purchased from CERAC, Inc.(Milwaukee, WS). All other chemicals used in this study (also CERAC) were analytical grade without further purifying treatment. They were pre-dried in a 110°C oven for at least 12 hours before use. Double distilled and deionized water was used to make KCl solution for the conductivity cell calibration.

Results and Discussion

Molten KCl Electrolyte

Molten KCl has a reported electrical conductivity value of 2.25 $S \cdot cm^{-1}$ at 800°C (6) which is close to the conductivity of cryolitic melts in which we are interested. It was used to evaluate the viability of the system and also as an example to demonstrate how to use the CVCC technique for the electrical conductivity measurement.

Figure 3 shows two of the four sets of measurements conducted in pure molten KCl. The resistance of the measuring circuit is a linear function of the disc electrode moving distance. As shown in Table I, the correlation between R_m and L is almost a perfect line, and the measured conductivity has a perfect agreement with the literature value. The average error, comparing the literature values, is only 0.79%. It should also be noted that the equation from the literature has ± 1% uncertainty. Also, since only analytical grade KCl was used in the measurement, this error cannot be completely eliminated.

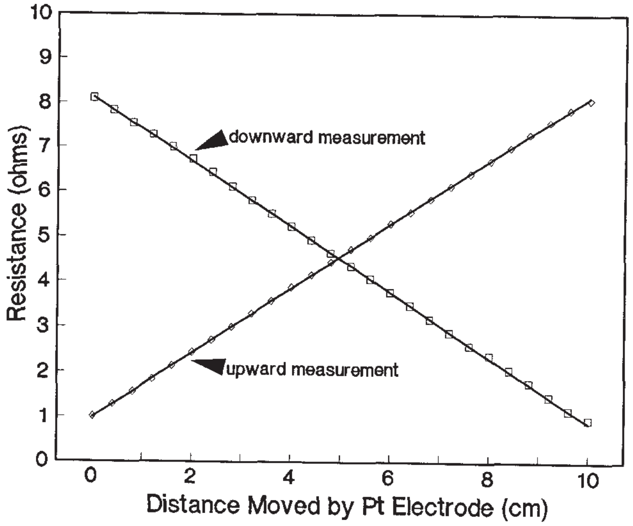

Figure 3: Resistance versus the distance moved by the Pt-disc electrode in the tube-type conductivity cell for pure molten KCl.

Table I. Results of KCl

Test Set No.	Lin. Rgrn R-Square	Slope Value (ohm/cm^{-1})	Elec. Cond. (S/cm) Msrd	Ref (6)	Temp. (°C)
Down 1st	0.9999	0.7248	2.2188	2.2129	790.7
Down 2nd	0.9997	0.7267	2.2131	2.2087	789.1
Up 1st	0.9999	0.7139	2.2528	2.2126	790.6
Up 2nd	0.9999	0.7225	2.2259	2.2065	788.3

It was concluded from the high correlation coefficient, R-square>0.999, and nearly perfect results, that this CVCC technique was a very successful method to obtain very high accuracy in measuring electrical conductivities of molten salts. And furthermore, it could be extended to provide improved accuracy of especially fused fluorides with about the same magnitude of the electrical conductivity values.

Frequency Effect

A series of frequencies from 100 Hz to 100 kHz was applied and responding resistance readings were recorded for each increment/decrement of movement by the disc electrode in order to examine the frequency effect.

Tests were conducted in four kinds of electrolytes: Pure KCl at 818°C; pure cryolite at 1020°C; cryolitic melts with molar ratio equal to 2.2 containing 3.0% Al_2O_3, and 5.0% CaF_2 at 959°C; and cryolite molar ratio equal to 2.5 containing 3.0% Al_2O_3, 3.0% LiF, 4.0% CaF_2, and 2.0% MgF_2 at 959°C.

Test results for pure KCl are shown in Figure 4. For each fixed frequency applied, the resistance reading, R_m, linearly increased with increasing the distance, L, as the disc electrode moved from the counter graphite-crucible electrode in the conductivity cell. For instance, the resistance of the measuring circuit increased from 1.621 to 8.608 ohms when the electrode was moved up from 0 (set-up start point) to 9.0 cm in the conductivity cell at 1.0 kHz.

The measured resistance was also a function of the frequency applied. Over the whole range of electrode movement, the resistance reading nonlinearly decreased (shift downward as shown in Figure 4) when the applied frequency was increased. For instance, at a fixed cell constant (e.g., a fixed distance moved by the electrode), L=2.0 cm, the resistance reading non-linearly decreased from 4.878 to 2.414 ohms when the applied frequency was increased from 100 Hz to 100 kHz. An identical behavior of resistance readings was also observed for other molten electrolyte tests as a function of the applied frequency.

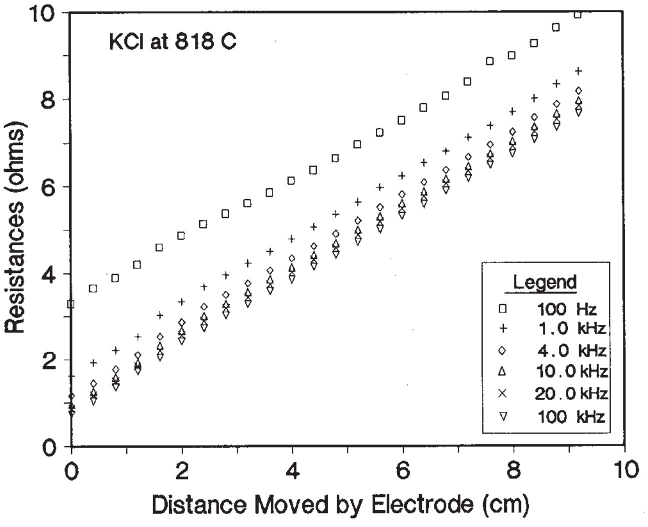

Figure 4: Resistance readings versus distance moved by the Pt-disc electrode in the tube-type conductivity cell at varying frequencies.

Figure 5 shows the test results in a cryolitic melt with molar ratio equal to 2.5 and containing 3.0 wt.% Al_2O_3, 3.0 wt.% LiF, 4.0 wt.% CaF_2, and 2.0 wt.% MgF_2 at 945°C. At all the fixed testing frequencies, the resistance of the measuring circuit linearly increased with the incremental increase of the electrode distance in the conductivity cell. When the test frequency was increased, the resistance nonlinearly decreased (shifted downward) when the cell constant was maintained unchanged. This was the same behavior observed for the molten KCl system. The dependence of the resistance of the measuring electrolyte on test frequency was also reported in the literature (7,8). These researchers all extrapolated the test frequencies to an infinite value or used a sufficiently high frequency in order to obtain the "polarization-free" electrical conductivity.

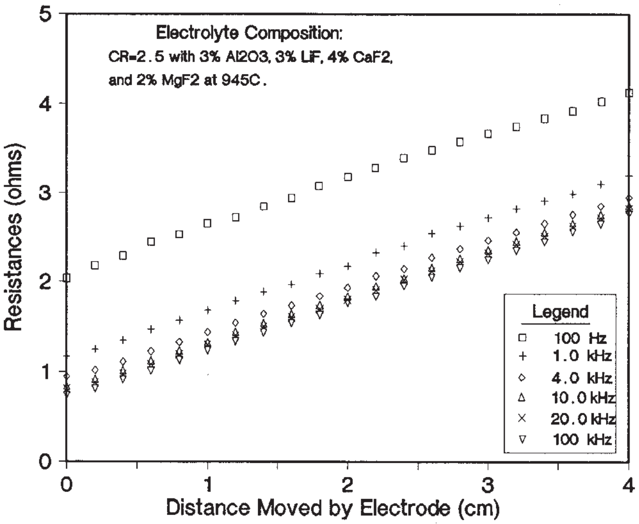

Figure 5: Resistance readings versus distance moved by the Pt-disc electrode in the tube-type conductivity cell at varying frequencies.

Figure 6 shows the typical responses of resistance readings recorded for the four electrolytes at the electrode distance of 3.6 cm when the applied frequency was increased from 100 Hz to 100 kHz. When the frequency increased, the resistance readings tended to decrease to constant values and the polarization resistance R_f decreased to zero, which agrees well with the literature (7,8). Figure 6 also shows that the resistance of the molten chloride salt, KCl, was the most frequency dependent while pure cryolite was the least frequency dependent electrolyte; the resistance of pure cryolite only decreased from 2.896 to 2.422 ohms when the frequency was increased from 100 Hz to 100 kHz. The electrical conductivity for the pure cryolite at 100 kHz was measured to be 2.756 S/cm, which agrees with the literature accepted value (1). However, the apparent electrical conductivity value for the cryolite at 1.0 kHz was measured at only 2.305 S/cm, which is 83.6% of the accepted conductivity value. This plot helps to explain why almost all the literature results were reported using at least 5 kHz in their conventional conductivity measurements.

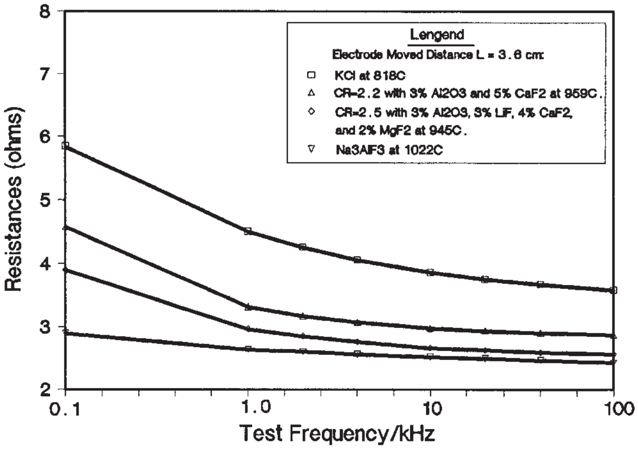

Figure 6: Test frequency effects on the resistance readings when the conductivity cell constant was maintained at L=3.6 cm.

Another important aspect of the CVCC technique shown in Figures 4 and 5 is that the slopes of the resistance readings versus the distances moved by the electrode are the same and are independent of the applied frequencies. The same behavior was obtained for all of the four tested molten salts. The CVCC experimental technique for this method is to use the slope to determine electrical conductivity rather than the commonly used method using a single resistance reading at a high applied frequency. The same slope yields the same derived electrical conductivity value no matter what frequency is employed in the measurement.

Table II lists the measured electrical conductivities of the four previously mentioned electrolytes at several tested frequencies. Statistical analysis indicated that the average electrical conductivity of each electrolyte was indeed independent of the applied frequency.

Table II. Electrical Conductivities at Different Test Frequencies for the Four Electrolytes

Test Frequency, kHz	Electrolytes No. 1	No. 2	No. 3	No. 4
0.1	2.2404	2.7694	2.3818	2.0469
1.0	2.2123	2.7446	2.3745	2.0434
2.0	2.2093	2.7442	2.3781	2.0473
4.0	2.2102	2.7337	2.3745	2.0651
10.0	2.2140	2.7319	2.3718	2.0499
20.0	2.2161	2.7822	2.3718	2.0344
40.0	2.2187	2.7759	2.3712	2.0318
100.0	2.2218	2.7661	2.3705	2.0226
Average	2.2179	2.7560	2.3743	2.0469

No.1: KCl at 818°C.
No.2: Cryolite at 1020°C.
No.3: MCR=2.5 containing 3.0 % Al_2O_3, 3.0 % LiF, 4.0 % CaF_2, and 2.0 % MgF_2 at 945°C.
No.4: MCR=2.2 containing 3.0 % Al_2O_3 and 5.0 % CaF_2 at 959°C.

Figure 7 shows the conductivity results as a function of the applied frequency. Lines in the graph represent the average electrical conductivities. No variations of the conductivity values were observed versus the applied frequencies from 100 Hz to 100 kHz. This verifies the principle on which this technique is based, i.e., the slope of resistance readings versus the distance moved by the disc electrode in the tube-type conductivity cell is independent of the applied frequency. The conventional methods which have been used to measure the electrical conductivity have to take the applied frequency into account. Many conductivity values were derived or extrapolated to an infinite frequency value. Because of complexity of the resistance function of the measuring circuit versus the applied frequency, the derived conductivity values are limited by the accuracy (3).

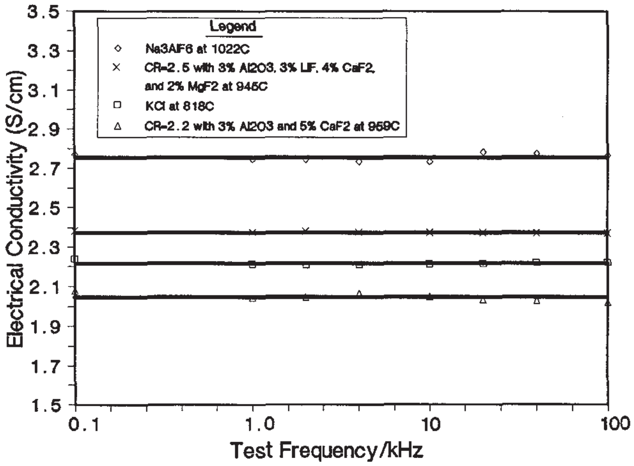

Figure 7: The measured electrical conductivity when varying test frequencies.

Electrical Conductivity of Pure Cryolite

Figure 8 shows the measured electrical conductivity of the pure cryolite as a function of bath temperature in a range from 1020 to 1070°C. Some literature data are also presented in the figure for comparison. The measured electrical conductivity increased from 2.81 S/cm at 1025°C to 2.98 S/cm at 1070°C, which agrees with the conductivity values by Yim and Feinleib (9), Matiasovisky et al. (10), and Edward (2). Some literature data for the conductivity of pure cryolite are quite diversified from very high values around 3.4 S/cm by Batashev (11) to low values around 2.7 S/cm as reported by Abramov (12). The most commonly accepted value for the pure cryolite conductivity is around 2.8 S/cm as reported by Yim and Feinleib (9). Hot pressed BN, which was the only available corrosion resistant material, and a classical method of employing a capillary-type conductivity cell were used in these studies. The measured electrical conductivity at temperature 1070°C was somewhat lower than those by Yim, et al. We cannot say for sure if this is real or the result of the compositional changes due to the vaporization of the cryolite melt during the course of measurement.

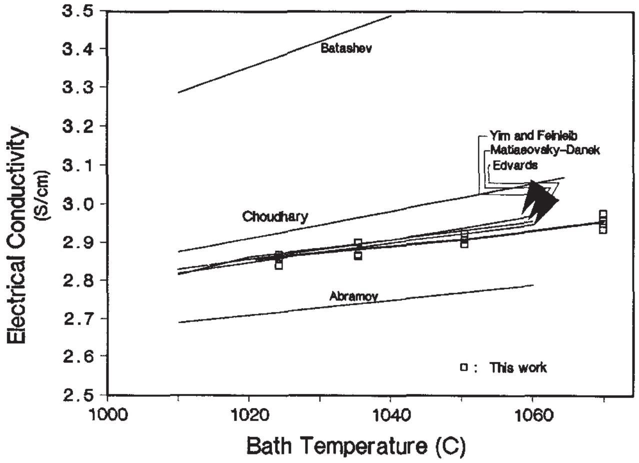

Figure 8: Electrical conductivity of pure cryolite as a function of bath temperature by this investigation and some literature references.

The electrical conductivity value as a function of bath temperature predicted by the Choudhary model is obviously consistently higher than the accepted value. It should be mentioned that the data by Yim and Feinleib and by Matiasovsky were also included when Choudhary derived his model.

Comparison of Measured Conductivity Results with the Choudhary Model

The electrical conductivity was determined for an array of electrolyte compositions covering molar cryolite ratio from 2.2 to 2.9 which, respectively, contained Al_2O_3 from 0 to 6 wt.%, MgF_2 from 0 to 8 wt.%, CaF_2 from 0 to 8 wt.%, and LiF from 0 to 8 wt.%. Measurements were conducted at bath temperatures with 15, 30 and 50°C of superheats, to ensure a comprehensive electrolyte composition range over a wide temperature range. The freezing points of the cryolitic electrolytes were calculated according to equations published by Tabereaux (13). Only the data obtained for the 30°C superheat are compared with that by the Choudhary model when considering the effects of bath ratio and additives. The cryolitic melt compositions were all reported as synthetic compositions.

The practical equation by Choudhary relating electrical conductivity to the composition and temperature of cryolitic melts was developed using a linear regression analysis of data computed from preferred, published, conductivity diagrams and a limited number of actual experimental values. The range of test conditions was also very limited.

Cryolite Ratio. The influence of cryolite ratio (NaF/AlF_3) on the electrical conductivity for two bath compositions is shown in Figure 9: cryolitic melt with 0 wt.% additives and one containing 3.0 wt.% Al_2O_3, 4.0 wt.% CaF_2, 4.0 wt.% MgF_2, and 4.0 wt.% LiF.

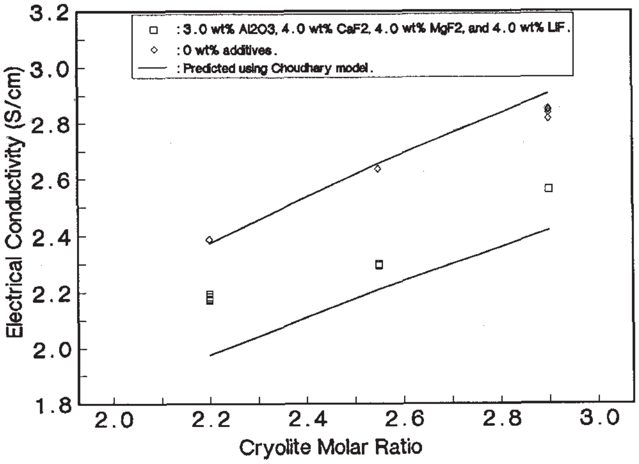

Figure 9: Electrical conductivity as a function of cryolite ratio at 30°C superheat.

The electrical conductivity increased as cryolite ratio increased. For the case where the melt did not contain any additives, the electrical conductivity increased from 2.3861 S/cm to 2.8361 S/cm when the cryolite ratio increased from 2.20 to 2.90. The Choudhary model agrees with the data well except for the case of cryolite ratio equal to 2.90. The value predicted by the model is higher than the measured value at MCR = 2.90. It has been mentioned in the previous section (shown in Figure 8) for the pure cryolite (MCR = 3.0), the model values are higher than the literature accepted conductivity values.

For the cryolitic melt containing additives, the predicted values are significantly lower than the measured data. The measured conductivity was increased from 2.1804 S/cm to 2.6070 S/cm when the cryolite ratio increased from 2.20 to 2.90. Every increase of 0.1 molar cryolite ratio corresponds to about 0.0609 S/cm in the electrical conductivity. It should be noted that the bath temperatures were 918.5°C at MCR = 2.20, and 954.0°C at MCR = 2.90, which are far lower than the normal temperature prediction range for the model.

Alumina Concentration. The impact of alumina content on the electrical conductivity of cryolitic melts was presented for two bath compositions and compared with the Choudhary model: Cryolite ratios equal to 2.20 and 2.50, both containing 4.0 wt.% CaF_2, 4.0 wt.% MgF_2, and 4.0 wt.% LiF. To maintain a constant 30°C superheat, the bath temperatures decreased from 926.8°C at 0 wt.% Al_2O_3 to 910.3°C at 6.0 wt.% Al_2O_3 for the MCR = 2.20, and bath temperatures decreased from 953.1°C to 934.8°C for the MCR = 2.55.

Figure 10 shows the results of the electrical conductivity obtained in this study and the predictions by the Choudhary model as a function of Al_2O_3 concentration. At MCR = 2.55, the measured conductivity values decreased from 2.6454 to 2.2133 S/cm while the predicted values by the model decreased from 2.3826 S/cm to 2.0512 S/cm when the alumina concentration increased to 6.0 wt.%. Every increase of 1 wt.% Al_2O_3 resulted in about 0.072 S/cm decrease in the electrical conductivity at the constant superheat. The predicted values are about 0.15 to 0.20 S/cm (about 6 to 8%) lower than the measured data. More difference exists for the MCR = 2.2 melts. The predicted values are about 0.20 S/cm (about 10 %) lower than the measured data. Figure 10 clearly shows that the model is no longer suitable for conductivity predictions at low cryolite ratio under conditions of low bath temperature and high concentrations of alumina.

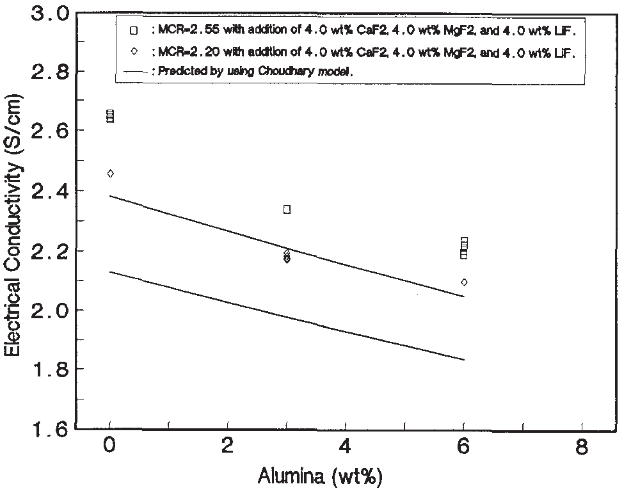

Figure 10: Electrical conductivity as a function of alumina concentration at 30°C superheat.

Calcium Fluoride Concentration. The impact of CaF_2 on the electrical conductivity of cryolitic melts is presented for bath compositions and compared with the Choudhary model: cryolite ratios equal to 2.20 and 2.50, both containing 3.0 wt.% Al_2O_3, 4.0 wt.% MgF_2, and 4.0 wt.% LiF. CaF_2 concentration varied from 0 to 8.0 wt.%. The bath temperatures decreased from 927.5 °C at 0 wt.% CaF_2 to 909.6°C at 8.0 wt.% CaF_2 for the MCR = 2.20, and 954.9°C to 933.1°C for the MCR = 2.55.

Figure 11 shows the electrical conductivity values measured in this study and the predictions by the Choudhary model as a function of CaF_2 concentration. Increasing CaF_2 concentration slightly decreased the conductivity of both cryolite ratios in both our study and the Choudhary model. For an example, the measured conductivity at MCR = 2.55 decreased from 2.4473 to 2.2512 S/cm when the CaF_2 increased from 0 to 8.0 wt.%, which corresponds to about 0.0245 S/cm decrease per 1.0 wt.% CaF_2 at the constant superheat. About the same decrease rate was also observed for the model predicted values.

The predicted values by the Choudhary model are about 0.15 to 0.20 S/cm (about 6 to 8%) lower for the MCR = 2.55 melts, and about 0.20 S/cm (over 10 %) lower for the MCR = 2.20 melts than the measured data.

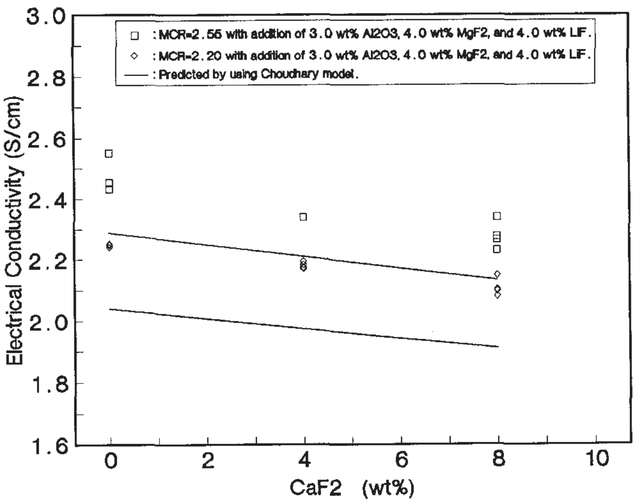

Figure 11: Electrical conductivity as a function of CaF_2 concentration at 30°C superheat.

Magnesium Fluoride Concentration. Increases in MgF_2 concentration decreased the electrical conductivity in a more pronounced way than CaF_2, as shown from Figure 12. The measured conductivity at MCR = 2.55 decreased from 2.5709 to 2.1976 S/cm when the MgF_2 content increased from 0 to 8.0 wt.%, which corresponds to about 0.0467 S/cm decrease per 1.0 wt.% MgF_2. This is almost twice the impact of CaF_2's influence, at 30°C constant superheat. The same decreasing rate was important. People have argued over it for some time (14). Addition of MgF_2 in the cryolitic bath causes greater decrease in the conductivity than CaF_2 due to the complex reaction:

$$2Na_3AlF_6 + 3MgF_2 <=> 3Na_2MgF_4 + 2AlF_3 \qquad (5)$$

The ion complex reaction forms MgF_4^{2-} and decreases the ion mobility and, therefore, reduces the conductivity.

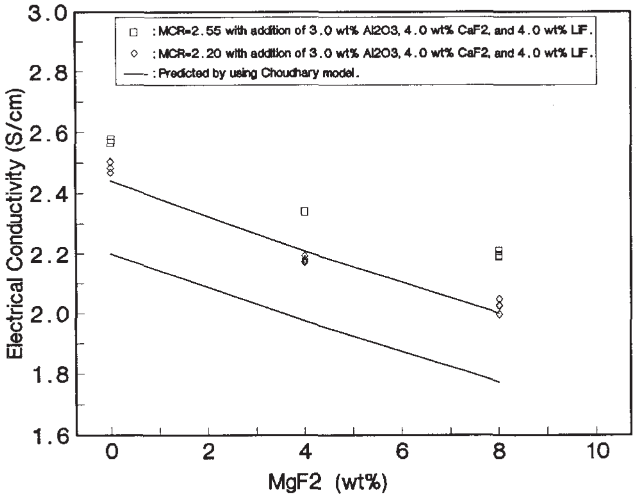

Figure 12: Electrical conductivity as a function of MgF_2 concentration at 30°C superheat.

To maintain the same bath superheat, the bath temperature was decreased from 947.6°C to 890.3°C for MCR = 2.20, and 967.5°C to 920.5°C for MCR = 2.55, when the MgF_2 concentration was increased from 0 to 8.0 wt.%.

The Choudhary model values were consistently lower than the measured data for various MgF_2 contents. Predicted conductivity values were about 0.15 to 0.20 S/cm (about 6 to 8%) lower for the MCR = 2.55 melts, and about 0.20 S/cm (over 10 %) lower for the MCR = 2.20 melts than the measured data.

Lithium Fluoride Concentration. The influence of LiF content in the bath on the electrical conductivity of cryolitic melts was also presented for two cases: cryolite ratios equal to 2.20 and 2.50, both containing 3.0 wt.% Al_2O_3, 4.0 wt.% CaF_2, and 4.0 wt.% MgF_2 at 30°C superheat. The bath temperatures decreased from 947.3°C at 0 wt.% LiF to 890.6°C at 8.0 wt.% LiF for the MCR = 2.20, and 977.9°C to 911.1°C for the MCR = 2.55.

890.6°C at 8.0 wt.% LiF for the MCR = 2.20, and 977.9°C to 911.1°C for the MCR = 2.55.

Figure 13 shows the electrical conductivity values of cryolitic melts as a function of LiF concentration. Increase in LiF concentration resulted in increases in the electrical conductivity. For the MCR = 2.55 melts, the conductivity increased to 2.5067 S/cm from 2.2369 S/cm when the LiF addition was increased up to 8.0 wt.%. An increase of every 1 wt.% LiF in the bath resulted in about 0.0337 S/cm increase in the electrical conductivity.

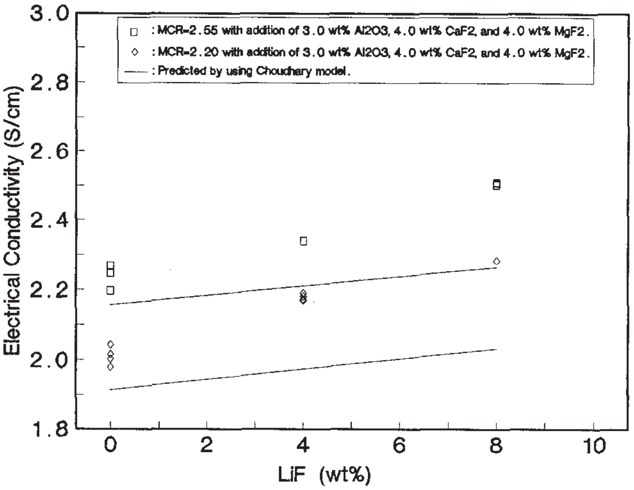

Figure 13: Electrical conductivity as a function of LiF concentration at 30°C superheat.

Also shown in Figure 13 is that the Choudhary model not only predicted lower conductivity, but also had a smaller increase rate when the LiF concentration was increased. Again, the model is no longer suitable for the conductivity prediction in the studied range.

Electrolyte Temperature. The impact of bath temperature influence on the electrical conductivity is shown in Figure 14 for three different compositions: MCR = 2.55 melts containing 3.0 wt.% Al_2O_3 and 4.0 wt.% of three different additives.

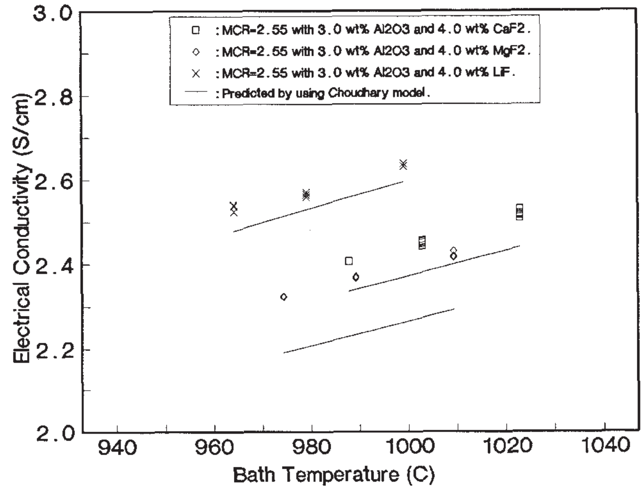

Figure 14: Electrical conductivity as a function of bath temperature.

The electrical conductivity of cryolitic melts increased with increasing bath temperature. The increasing rate conductivity for the three electrolytes appeared to be about the same as predicted by the model: 0.0034 S/cm per degree. However, all the test data were consistently higher than that predicted by the Choudhary model. The greatest 4.0 wt.% MgF_2 where the predicted value was about 7% lower than our test data.

Summary. For all cases studied, the electrical conductivity values predicted by the Choudhary model were up to 10% lower than the experimentally measured data except for one case where the electrolyte contained no additives. The comparison of the test data with the model values is presented in Table III.

Table III. Electrical Conductivity Comparison of the Choudhary Model with Test Data

Cryolite Ratio	
No Additive	No Difference
With 3.0% Al_2O_3, 4.0% CaF_2, 4.0% MgF_2 and 4.0% LiF	6% lower than test data
Alumina Concentration	
MCR = 2.20 with additives	8% lower
MCR = 2.55 with additives	6% lower
CaF_2 Concentration	
MCR = 2.20 with additives	10% lower
MCR = 2.55 with additives	6 to 8% lower
MgF_2 Concentration	
MCR = 2.20 with additives	10% lower
MCR = 2.55 with additives	6 to 8% lower
LiF Concentration	
MCR = 2.20 with additives	8% lower, smaller rate
MCR = 2.55 with additives	6% lower, smaller rate
Bath Temperature	
MCR = 2.55 with 3.0% Al_2O_3 and 4.0 CaF_2	4% lower
With 3.0% Al_2O_3 and 4.0% MgF_2	8% lower
With 3.0% Al_2O_3 and 4.0% LiF	2% lower

As can be seen from the table, there is up to 10% difference in the electrical conductivity between the measured data and that obtained by the Choudhary model. The differences were more pronounced when the cryolite ratio and temperature were low and when the concentrations of additives were high. Difference between our measured data and that predicted by the Choudhary model in these extreme ranges is not surprising, considering that almost all the literature data referred to by Choudhary are at 1000 °C and higher. This presentation shows that the model cannot be used to accurately predict the electrical conductivity of modern bath chemistries. A new regression model is needed and will be developed to replace the current Choudhary model.

Conclusions

Development of the CVCC technique makes it possible to accurately determine the electrical conductivity of cryolitic melts. In conjunction with a high-precision automatic positioner which controls the Pt-disc electrode movement in the conductivity cell made of pyrolytic BN, the technique measures the electrical conductivity through determining the slope of the resistances of the measuring circuit versus the programmed linear cell-constant changes.

Using the new technique, measurement of electrical conductivity of cryolitic melts was conducted which emphasized low bath ratio, and high additives at low bath temperatures. The regression model developed by Choudhary was tested through comparison with the measured results. Important conclusions are summarized as follows:

1. The electrical conductivity of molten cryolitic melts was determined from the slope of a set of resistances versus the programmed linear cell-constant changes rather than a single measurement of resistance.

2. The measured conductivity value is independent of the test frequency. It is also free of the effect of the wire contact resistance and cell constant. The relatively large size of the conductivity cell minimized electrolyte concentration changes during measurements.
3. A good agreement was obtained between the experimentally measured electrical conductivity of pure cryolite and commonly accepted values. Values of electrical conductivity for pure cryolite predicted by the Choudhary model were consistently higher.
4. The electrical conductivity regression model by Choudhary does not accurately predict the conductivity of the cryolitic melts when the cryolite ratio is low (excess AlF_3) and/or additive concentrations are high.
5. A new regression model is being developed based on the systematic determinations of electrical conductivities of cryolitic melts containing additives with varied concentrations.

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