A NEW EXPERIMENTAL APPROACH TO MEASURE ELECTRICAL CONDUCTIVITY OF MOLTEN FLUORIDE ELECTROLYTES

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Abstract

A method was developed for measuring the electrical conductivity of highly corrosive cryolite-based electrolytes and other molten fluoride systems. A pyrolitic boron nitride tube with a constant diameter was used to construct a conductivity cell, which in conjunction with a movable Pt-disc electrode constitutes a unique conductivity cell system. The electrical conductivity was determined from measuring a set of cell resistance versus a programmed linear variation of cell constant. The method, independent of the applied frequency and wiring contact resistance, was demonstrated to have distinct advantages over classic techniques in measuring the electrical resistance of highly corrosive fused fluoride electrolytes.
Introduction

Electrical conductivity of molten salts has been one of the fundamental research areas in molten salt physical chemistry. Because of its theoretical and technical importance, the electrical conductivity of molten fluoride systems has also received intensive attention in the past research. The molten fluoride system has several unique qualities, i.e., high melting temperature, high conductivity, and high corrosiveness to most commonly used materials which the conductivity cells are constructed with. These qualities require special experimental techniques to accurately determine the electrical conductivity of the fused fluoride systems. Measuring the electrical conductivity of a molten fluoride system can therefore be rephrased as a search for proper techniques and suitable materials to construct the conductivity cells.

A shortcoming associated with the traditional techniques in measuring electrical conductivity of molten salts is the dependence of the cell resistance on the applied frequency of the measuring current. Lack of proper materials also limited construction of a high cell-constant conductivity cell which could counter the highly corrosive nature and high conductivity of the melts. A number of articles have been published which have critically reviewed experimental techniques and electrical conductivity results. A comprehensive survey for the measurements of the electrical conductivity in the molten fluorides was published by Robins. Most measurements had been carried out either by using high cell-constant capillary-type cells which were made either from hot pressed boron nitride (BN) or from single-crystal magnesium oxide, or were made by using low cell-constant cells which made of platinum and Pt-Rh alloys. Due to either the limitation of the materials or experimental techniques, the reported results of the electrical conductivity bear a degree of uncertainty.

Significant progress has been seen both in the availability of advanced materials for conductivity cells and in experimental technique development for fused fluoride systems. A pyrolitic tube-type conductivity cell was reported for use in measuring electrical conductivity of cryolitic electrolytes. This material is immune to the molten fluoride attack and has a high thermal stability. The small inner diameter of the tube offers a greater cell constant. However, since a graphite crucible was used to hold a relatively small amount of fused electrolyte, it was difficult to hold the composition constant. Also, the technique did not overcome the applied frequency effect as in the conventional methods.

Investigation of the electrical conductivity is important to industries producing metals through electrolytic processes. More reliable data would help the aluminum industry by allowing us to predict with greater certainty those areas of the cryolitic system which may improve smelter efficiency. Consequently, old literature data has to be experimentally reviewed and new data generated. On the other hand, the availability of state-of-the-art engineering material which can resist the highly corrosive environment of the fused fluorides, make it possible to construct reliable conductivity cells. These aspects provided us an opportunity to develop new techniques for electrical conductivity measurements.
This paper presents an experimental approach designed for measuring electrical conductivity of fused fluoride salts. Unlike the traditional methods, the present technique uses the principle of linearly varying the cell constant and at the same time, continuously measuring the circuit resistance to determine the conductivity. The newest commercially-available material was used to construct the conductivity cell to counter the salt corrosion attack. The technique also employs a relatively large electrolyte pool to minimize variation in the electrolyte composition during measurements. The measured electrical conductivity is independent of the applied frequency and the effect of wire contact resistance.

**Theoretical Background**

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

\[ Z = R_m + X_L + X_C \]  

where \( Z \) is the impedance of the circuit, \( R_m \) is the real component (resistance) of the circuit, \( X_L \) is the inductive component of the impedance, and \( X_C \) is the capacitive component of the impedance. The real component of the impedance, \( R_m \), is of interest in this study and it may be expressed as follows:

\[ R_m = R_o + R_f + \Delta R \]  

where \( R_o \) is the ohmic resistivity of the electrolyte, \( R_f \) is the polarization resistance of the electrolyte, and \( \Delta R \) is the contact resistance between wires and electrodes. Equation (2) may be also expressed as:

\[ R_m = \gamma \cdot \frac{L}{S} + F(f) + \Delta R \]  

where \( \gamma \) is specific resistivity of electrolyte. \( L \) is the length of conductivity cell, \( S \) is the cross-sectional area of the conductivity cell, and \( f \) is the applied frequency. The specific resistivity, \( \gamma \), equals the reciprocal of the specific electrical conductivity, \( k \):

\[ \gamma = \frac{1}{k} \]  

The traditional methods (either high or low cell-constant conductivity cells) have been based on applying very high frequencies. At a sufficiently high frequency, the polarization resistance of the electrolyte, \( R_f \), which is usually a function of \( 1/f \), decreases to a minimal value and can be omitted when compared with the magnitude of \( R_o \).
\[ R_f = k \frac{1}{f} \rightarrow 0 \quad \text{as} \ f \rightarrow \infty \]  \hspace{1cm} (5)

The principle of the current technique is based on a continuously varying cell-constant, and at the same time measuring the real component of the circuit, \( R_m \), at a fixed frequency. Continuously varying the cell-constant is realized by linearly varying the length of the conductivity cell, \( L \), while keeping the cell cross-sectional area, \( S \), constant. Differentiation of equation (3) with respect to \( L \) and substituting in equation (4), will result in:

\[ \frac{dR_m}{dL} = \frac{1}{k} \frac{1}{S} \]  \hspace{1cm} (6)

The polarization resistance, \( R_p \), and the contact resistance, \( AR \), are constants and are independent of \( L \). Thus by measuring \( R_m \) while linearly varying \( L \), the electrical conductivity of the electrolyte, \( k \), can be obtained from:

\[ \kappa = 1/[S \frac{dR_m}{dL}] \]  \hspace{1cm} (7)

The electrical conductivity, derived from equation (7) through a set of precisely measured cell distance increments, is free of the effects of applied frequency and wire contact resistance.

**Experimental**

1. **Conductivity Cell Design**

The system assembly is shown in Figure 1. A graphite crucible was used as a molten electrolyte reservoir. It had 3.0 cm inner diameter (I.D.) and was able to hold over 100 grams of electrolyte sample. The graphite crucible was also used as a counter electrode which was connected to an LCR Impedance Meter via a thermocouple Inconel protection sheath. The thermocouple was screwed into the wall of the graphite crucible and was used to monitor the bath temperature. The graphite crucible also had a 3.8 cm I.D. concentric positioning hole at the open end for centering the pyrolytic BN tube-type conductivity-cell. The tube-type conductivity-cell was centered vertically in the graphite crucible by a BN disc which fit in the bigger diameter hole of the graphite crucible.

A schematic of the conductivity cells used in the tests is shown in Figure 2. The pyrolytic BN tube with a consistent I.D. was obtained from Union Carbide. The material was dense and electrically non-conductive. It was also able to resist the corrosion attack by the molten fluorides. One end of the tube was fixed on a BN disc holder through the center. A Inconel rod was connected to the BN disc via threads. At least 5.5 cm of the tube was immersed in the molten electrolyte during the measurement. A Pt disc electrode was connected to 0.16 cm Pt wire by threads. The other end of the Pt wire
was also threaded to connect with a 0.64 cm Inconel rod which was then connected to the arm of a positioner for the test. The Pt rod was covered with a BN insulating tube.

Figure 1 Schematic view of the electrical conductivity measurement system for the fused fluoride systems.

The electrode positioner used in this study was an Unidex Model XI from AeroTech, which was vertically mounted on a vibration-free stand. It could vertically move the Pt-disc electrode in the conductivity-cell with a positional accuracy of ± 0.001 cm via the extension arm. The positioner was controlled by a programmable position controller.

An Electro Scientific Industries SP2596 impedance Meter with a fixed frequency of 1 kHz was used in most of the tests. All three components of the measuring circuit, i.e., real component (resistance), capacity, and induction, could be measured. In the study of the frequency effect, a HP 4274A Multifrequency LCR meter was employed. The LCR meter had a frequency range from 100 Hz to 100 kHz with 11 intervals and measured resistance from milliohms to megohms with 5 significant digits.

2. Experimental Procedures

2.1 Calibration of Conductivity Cell: It was shown in equation (7) that to measure the electrical conductivity of an electrolyte, the inner cross-sectional area, S, of the tube-type cell has to be known. For the pyrolitic tube-type conductivity-cell, its cross-sectional area or I.D. is determined through measuring the conductivity of a 1.00 Molar KCl aqueous solution and back calculating the area from the published conductivity data.
at ambient temperatures.\cite{14} It is assumed that the thermal expansion of the tube I.D. due to an increase of the temperature can be neglected and was not taken into account. This was verified with molten KCl at 780°C.

![Figure 2 Schematic view of a pyrolitic BN electrical conductivity cell used for fused fluoride systems.](image)

Calibration or determination of the cell inner cross-sectional area was conducted in a 400 ml Beaker. An Inconel coil was placed on the bottom and used as the counter electrode. The fabricated tube-type cell was centrally suspended in the KCl solution via a clamp. The Pt electrode was centered in the cell through the positioner arm. Then the resistance versus the distance the Pt electrode moved was recorded. After completing the calibration, the conductivity cell and Pt electrode were fully rinsed with distilled water before being put into a 110°C oven for over-night drying.

2.2 Electrical Conductivity Measurement: A pre-treated graphite crucible loaded with about 100 grams of electrolyte sample was placed in a temperature stabilized furnace. Once the electrolyte sample was melted, the tube-type conductivity-cell with its support was positioned on the graphite crucible via the Inconel rod. About 5.5 cm of pyrolytic tube was immersed in the molten bath. Then the Pt-disc electrode was carefully loaded into the furnace and centered in the conductivity cell via the Inconel rod, which was then fixed on the positioner’s arm. The Pt-disc electrode was moved down and immersed in the molten bath by the position controller. The electrode position on the surface of the bath electrolyte was determined by the resistance reading suddenly becoming unmeasurable (Pt-disc electrode out of the electrolyte) when the electrode was moved up. Once the bath temperature was stabilized, the measurement began by moving down the Pt-disc electrode via the positioner one step at a time. The movement of the Pt-disc electrode in the conductivity cell was incremented by 0.2000 cm per each step. One set of measurements was made when the electrode was moved in the conductivity cell from the just below the surface of the bath to the lower open end of the conductivity cell and another set was made by moving back up. At least two sets of the measurements were conducted for each experimental condition, i.e., one bath...
composition at one desired temperature. The measured values were same when the electrode was moved either up or down. Electrolyte samples were taken from the crucible for compositional analysis after measurement of each experimental condition.

**Results and Discussion**

1. **KCl Aqueous Electrolyte**

   Two representative sets of resistance versus Pt-disc electrode moved distance in the 1.0 M KCl solution at ambient temperature are shown in Figure 3. The results were used to determine the conductivity-cell I.D. by referring to the literature data for KCl solutions\(^{[14]}\). The correlation coefficient, R-square, between the resistance and the distance moved had a value higher than 0.9999 for both sets of data. This high correlation coefficient means a high accuracy for the conductivity value of the electrolyte. The linear function verified the feasibility of the continuously-varying cell-constant method.

![Figure 3 Electrical resistance versus the distance moved by the Pt-disk electrode in the conductivity cell for 1.0M KCl electrolyte.](image)

2. **Molten NaCl and KCl**

   Molten NaCl and KCl systems were selected for the evaluation of the technique for higher temperature applications. Molten NaCl has a relatively high electrical conductivity (3.65 S·cm\(^{-1}\) at 815°C\(^{[15]}\)) and is ideal for use in evaluating this measurement technique. Molten KCl has an electrical conductivity value (2.25 S·cm\(^{-1}\)
at 800°C\(^{11}\) closer to most fused fluoride systems such as cryolitic electrolyte used in aluminum production.

Figure 4 shows two of four sets of measurements conducted in pure KCl. A close-to-perfect linear relationship was obtained between the circuit resistance and the distance moved by the electrode. The results of the electrical conductivity measurement for molten NaCl and KCl are presented in Table I.

![Figure 4](image)

**Table I.** Electrical Conductivity of Molten NaCl and KCl

| Test Set | Lin. Rgm. R\(^2\) | Slope (Ohm-cm\(^{-1}\)) | Electrical Conductivity Measured (S-cm\(^{-1}\)) | Conductivity Reference (S-cm\(^{-1}\)) | Temperature (°C) |
|----------|------------------|-------------------------|-----------------------------------------------|--------------------------------------|-----------------|
| NaCl     |                  |                         |                                               |                                      |                 |
| Down 1st | 0.9998           | 0.4214                  | 3.8162                                        | 3.6722                               | 821.4           |
| Down 2nd | 0.9999           | 0.4192                  | 3.8368                                        | 3.6714                               | 821.1           |
| Up 1st   | 0.9997           | 0.4232                  | 3.8003                                        | 3.6714                               | 821.1           |
| Up 2nd   | 0.9994           | 0.4223                  | 3.8081                                        | 3.6712                               | 821.0           |
| KCl      |                  |                         |                                               |                                      |                 |
| Down 1st | 0.9999           | 0.7248                  | 2.2188                                        | 2.2129                               | 790.7           |
| Down 2nd | 0.9997           | 0.7267                  | 2.1231                                        | 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           |

The measured electrical conductivity is higher by an average of 4.9% than the literature values for the pure NaCl at the temperatures measured, even though the correlation between the resistance recorded and the distance moved by the electrode is over 0.999. The error may be attributed to the possible impurities in the NaCl used. For the pure KCl, the average error is only 0.79% when compared with the literature values. The error is much lower than that for the molten NaCl. It should also be noted that the...
equation from the literature has ±1% uncertainty. From the high correlation coefficient 
($R^2 >0.999$), and close match to literature data, it can be concluded that this technique 
can be used with high accuracy for measuring electrical conductivity of molten salts.

Figure 5 shows the measured electrical conductivity of KCl as a function of 
temperature. Literature data are also provided for comparison. Again, less than 1.0% 
relative error was obtained for all of the data points in the temperature range. The 
literature data were calculated by a regression equation which has a ±1% uncertainty for 
quite a large temperature range. The system proved to be sensitive to the temperature 
changes of the KCl bath.

![Figure 5](image)

Figure 5  Electrical conductivity of KCl as a function of electrolyte temperature.

3. Frequency Effect

To examine the possible frequency effect, a series of frequencies from 100 Hz to 
100 kHz were applied and the corresponding resistance readings were recorded for each 
step of movement by the Pt-disc electrode. The tests were conducted in four types of 
electrolytes:

- Pure KCl at 818°C;
- Pure cryolite ($Na_3AlF_3$) at 1022°C;
- Cryolitic melt with a molar ratio (MCR=$N_{NaF}/N_{AlF_3}$) equal to 2.2 containing 3.0
  % $Al_2O_3$, and 5.0 % $CaF_2$ at 959°C;
- Cryolitic melt with MCR= 2.5 containing 3.0 % $Al_2O_3$, 3.0 % LiF, 4.0 % $CaF_2$
  and 2.0 % $MgF_2$ at 959°C.

Figure 6 shows the test results in a cryolitic melt with MCR equal to 2.5 
containing 3.0 % $Al_2O_3$, 3.0 % LiF, 4.0 % $CaF_2$, and 2.0 % $MgF_2$ at 945°C. At all the 
testing frequencies, the resistance of the measuring circuit responded linearly with the 
distance moved by the electrode. When the test frequency was increased, the resistance 
non-linearly decreased (shifted downward), but the slopes remained parallel. The 
changing resistance of the measuring electrolyte as a function of test frequency has been 
reported in the literature.$^{16,17}$ To overcome this resistance dependence on the applied
frequency, traditional techniques extrapolate the frequency to an infinite value or use a sufficiently high frequency in order to obtain an accurate electrical conductivity.

A very important aspect shown in Figures 6 is that the slopes of the resistance versus the distance moved by the electrode are same and independent of the applied frequencies. The same behavior was obtained for all four molten salts. Our experimental technique uses the slope to derive electrical conductivity rather than a single resistance reading at a high applied frequency. And the very same slope implies the same derived electrical conductivity value no matter what frequency is employed in the measurement.

Figure 7 shows the typical resistance responses for the four electrolytes at an 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 as the polarization resistance $R_f$ decreased to zero. It is also shown in Figure 7 that the resistance of the molten chloride salt KCl was the most frequency-dependent while the pure cryolite was the least dependent. For pure cryolite, its electrical conductivity at 100 kHz was measured to be 2.756 S·cm$^{-1}$, which agrees with the accepted literature value.$^{[3]}$ However, its apparent electrical conductivity value at 1.0 kHz was measured to be 2.305 S·cm$^{-1}$, only 83.6% of its accepted conductivity value.
Figure 7 Effect of applied frequency on the resistance readings for electrolytes with varied electrical conductivity. Cell constant $L=3.6$ cm.

Figure 8 shows the conductivity results as a function of the applied frequency. Lines in the graph represent the average electrical conductivity. No variations of the conductivity values were observed versus the applied frequencies from 100 Hz to 100 kHz. This proves that the technique is independent of the applied frequency unlike the conventional methods.

5. Applications

The present technique was specially designed for measuring electrical conductivity of cryolitic melts even though it can be used for other fused fluoride systems. It can be used for all types of electrolytes from aqueous at ambient
temperatures to molten salts at high temperatures. It has proved to be efficient and accurate in measuring electrical conductivity.

Figure 9 shows the results of the electrical conductivity measurements for analytically pure cryolite (99.5%) as a function of temperature in the range from 1020 to 1070°C. Some literature data are also presented in the Figure.

As seen from the Figure 9, the measured electrical conductivity increased from 2.82 S·cm⁻¹ at 1020°C to 2.98 S·cm⁻¹ at 1070°C, which agrees with that reported by Yim and Feinleib, Matiasovisky et al., and Edward. Other literature data for pure cryolite conductivity are quite scattered from very high values around 3.4 S·cm⁻¹ by Batashev to low values around 2.7 S·cm⁻¹ as reported by Abramov. The commonly accepted value for the pure cryolite conductivity is around 2.8 S·cm⁻¹ as reported by Yim and Feinleib.

![Graph showing electrical conductivity of cryolite as a function of temperature.](image)

Figure 9  Electrical conductivity of pure cryolite as a function of temperature.

Figure 10 presents an example of the LiF concentration effect on conductivity in cryolitic melts. The base electrolyte was started with weight cryolite ratio (WCR) and bath ratio (BR) equal to 1.44 in a melt containing 5.0% CaF₂ and 3.0% Al₂O₃. A discussion of WCR and BR as used in the aluminum industry can be found in Richards. The effect of the LiF addition on the conductivity was measured under both constant bath temperature and constant superheat.

The electrical conductivity of the base electrolyte was measured to be 2.5716 S·cm⁻¹ at 985°C and 2.5880 S·cm⁻¹ at 992.8°C. At WCR =1.44, when the LiF concentration increased up to 8.0%, the conductivity correspondingly increased up to 2.9458 S·cm⁻¹, a 14.6% of increase from the base electrolyte at an isothermal temperature of 985°C. For the same LiF concentration increase, only about 3.2% increase in the conductivity over the base electrolyte was observed at 15°C superheat above the solidus temperature. For the cryolitic electrolytes maintained at BR=1.44 (which was achieved by addition of AlF₃), no variation of the electrical conductivity values was observed at the isothermal temperature of 985°C while a 7.1% decrease in
electrical conductivity was measured at 15°C superheat when the LiF concentration increased from 0 to 8.0 %. These conductivity results helped us to understand and adjust bath chemistry of Hall cells for the purposes of maximizing current efficiency and minimizing energy consumption in conjunction with other physicochemical parameters.

![Figure 10 Measured electrical conductivity of cryolitic electrolytes as a function of LiF concentration.](image)

**Summary**

Development of the present technique takes advantage of pyrolitic BN material for the conductivity cells. In conjunction with a high-precision positioner which controls the Pt-disc electrode movement in the conductivity cell, the technique measures the electrical conductivity by determining the slope of the resistance of the measuring circuit versus the linear cell-constant variation. The technique was specially designed for conductivity measurements in fused fluoride systems which can cause difficulties when using conventional techniques. The technique was tested with aqueous electrolytes and high temperature molten chloride salts. It was then used for the high temperature cryolitic electrolytes. Important findings from this work include:

1. The electrical conductivity of high temperature electrolytes can be determined through the slope of a set of resistance versus a linear cell-constant variation.
2. The measured conductivity value is independent of the test frequency and measuring circuit contact resistance.
3. Pyrolitic BN material, which resists the corrosive attacks by high temperature fused fluoride salts, was employed to construct electrical conductivity cells.
4. A relatively large amount of electrolyte pool insures the electrolyte composition remains unchanged during the conductivity measurement.
5. The technique was successfully used for the measurement of electrical conductivity in cryolitic systems. The technique verified reported literature values and generated new data for modern bath chemistries used in Hall cells.

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