

A NEW TECHNIQUE FOR ELECTRICAL CONDUCTIVITY MEASUREMENTS IN MOLTEN SALTS

Naomi A. Fried, Susan L. Schiefelbein,
Kevin G. Rhoads, and Donald R. Sadoway

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139-4307

ABSTRACT

A new technique has been developed for making highly accurate electrical conductivity measurements in molten salts. The success of this technique derives from a new cell design along with an appropriately specified experimental procedure and methods of data reduction and analysis. At the heart of the conductance cell is a **moveable pair** of coaxial, cylindrical electrodes. No dielectric contacts the melt. The cell does not require calibration. This paper reports the results of certification experiments performed on standard solutions of $\text{KCl}_{(\text{aq})}$.

INTRODUCTION

As part of a study of the physical chemistry of molten oxides considered to be candidate electrolytes in new high-temperature electrochemical processes, the electrical conductivities of multicomponent solutions will be measured. Laboratory tests have shown that no dielectric material is capable of resisting chemical attack by these oxide melts. Thus, it is not possible to employ any of the classical cell designs (for example, capillary-type conductance cells (1)) capable of giving highly accurate results. The need to make accurate electrical conductivity measurements of highly corrosive melts provided the motivation to invent the new technique presented here. This technique, which has now been tested and certified, involves the use of a new cell design along with an appropriately specified experimental procedure and methods of data reduction and analysis. At the heart of the conductance cell is a **moveable pair** of coaxial, cylindrical electrodes. Although Nichol and Fuoss (2) had made conductance measurements with an apparently similar cell geometry, their electrodes were stationary and totally submerged; these conditions fail to exploit the full potential of this electrode configuration. This article describes a new technique and reports the results of certification experiments performed on standard

solutions of $\text{KCl}_{(\text{aq})}$. The complete description of the theoretical underpinnings of the technique will be given in a forthcoming publication (3).

CELL DESIGN

Figure 1 shows the electrodes and their fixture as constructed for the certification study in aqueous solutions. Made of platinum, the outer electrode measured 18 mm o.d. \times 52 mm long; the inner electrode 3 mm o.d. \times 104 mm long. The outer electrode was formed by spot welding a piece of platinum foil, 0.0381 mm thick, around a tubular glass mandril which became its permanent support. Rubber o-rings secured the outer electrode to the glass tube and formed a pressure contact between the platinum lead wire and the outer electrode. The glass tube was held by a clamp attached to a height gage which allowed accurate determination of relative electrode immersion in the solution. A more robust variation of this model has been built for use with molten salts at temperatures up to 1000°C.

EXPERIMENTAL PROCEDURE

Certification of the cell design consisted of measuring the impedance of the cell containing three standard solutions: 1.0, 0.1, and 0.01 D KCl. These were prepared in conformity with the Janz and Tomkins demal standards (4). For each solution an appropriate amount of KCl (99.999%, Cerac) was weighed out in a glove box and dissolved in high purity water. Appropriate corrections were made for buoyancy of air, temperature, pressure, and humidity.

Conductance measurements were carried out in a glove bag. The glove bag was filled with ultra-high purity argon (99.999%) which had been bubbled through a KCl solution identical to that under investigation. This bubbling was done to minimize evaporation of water from the specimen and the attendant shift in composition. After two hours of purging the bag, the solution under investigation was deaerated in a 100 ml tall-form beaker with this same gas for ten minutes and then left to stand for two hours to reach thermal equilibrium with the glove bag atmosphere. After the temperature of the solution had stabilized, the electrodes were immersed in the solution. At each depth of immersion, the impedance was measured with an impedance/gain-phase analyzer (Solartron 1260, Schlumberger Instruments, Burlington, MA) over a wide range of frequency: 5kHz - 5MHz for 1.0D KCl; 4kHz - 4MHz for 0.1D KCl; 2kHz - 2MHz for 0.01D KCl. Data acquisition, storage, and analysis were controlled by a personal computer using the Z60 impedance program (Scribner Associates, Charlottesville, VA). For each solution at

least six impedance spectra were taken, each at successively deeper immersions. The a.c. excitation voltage was set at a value between 30 and 50 mV. At the end of the experiment, the temperature of the KCl solution was again measured to confirm that the data were free from variation caused by temperature drift.

DATA ANALYSIS

To extract the value of the specific electrical conductivity of the solution, κ , from the measured impedance, $Z_{\text{measurement}}$, it is necessary to know the equivalent circuit of the test cell. Shown in Figure 2, the equivalent circuit for the present cell design consists of three elements in series: the impedance of the lead wires, $Z_{\text{leadwires}}$, the impedance of the electrodes, $Z_{\text{electrodes}}$, and the impedance of the solution under investigation, $Z_{\text{sol'n}}$. Thus,

$$Z_{\text{measurement}} = Z_{\text{leadwires}} + Z_{\text{electrodes}} + Z_{\text{sol'n}} \quad [1]$$

The value of solution impedance can be isolated from $Z_{\text{measurement}}$ with the aid of a nulling procedure consisting of measuring the open and short circuit impedances of the electrodes and lead wires. This information is combined with $Z_{\text{measurement}}$ in the following manner:

$$Z_{\text{sol'n}} = \{(Z_{\text{measurement}} - Z_{\text{short}})^{-1} - (Z_{\text{measurement}} - Z_{\text{open}})^{-1}\}^{-1} \quad [2]$$

The lead wires from the impedance/gain-phase analyzer should be secured so that their inductive contribution to the measured impedance remains constant. Furthermore, the connections between the lead wires and the electrodes should be durable and stable in order to minimize variation in contact resistance.

Also shown in Figure 2 are the components of the solution impedance: 1) radial contributions, $R_{\text{sol'n, radial}}$ and $C_{\text{sol'n, radial}}$, 2) fringe contributions, $R_{\text{sol'n, fringe}}$ and $C_{\text{sol'n, fringe}}$, and 3) contributions from the double-layer capacitance, C_d , at each electrode. From first principles the relationship between $R_{\text{sol'n, radial}}$ and κ can be expressed as

$$R_{\text{sol'n, radial}} = (1/\kappa) [\ln(b/a)] (2\pi z)^{-1} = (1/\kappa) G \quad [3]$$

where b is the inner radius of the outer electrode, a is the outer radius of the inner electrode, and z is the depth of immersion of the electrodes. The ratio, $[\ln(b/a)] (2\pi z)^{-1}$, is the cell constant, G .

Clearly, use of equation 3 requires knowledge of the absolute depth of immersion of the electrodes, a quantity that generally cannot be measured with sufficient accuracy

when the solution under study is a melt at elevated temperatures. To circumvent this problem and to eliminate the complication presented by the effect of the fringe field at the lower extreme of the electrodes, impedance measurements are made at different depths of electrode immersion. The mathematical expression of the effect of the variation in electrode immersion on solution conductance is given by equation 3 written in differential form:

$$\kappa = \{d(1/R_{\text{sol'n, radial}})/d\xi\} / \{d(1/G)/d\xi\} \quad [4]$$

where ξ is defined as the relative immersion, i.e., $\xi = z + \text{constant}$, and hence, $d\xi = dz$. It is evident from equation 4 that it is necessary to know only the relative, not the absolute, position of the electrodes. In equation 4, the term $d(1/G)/d\xi$, which is equal to $2\pi/\{\ln(b/a)\}$, is the constant of proportionality between the specific conductivity of the solution and $d(1/R_{\text{sol'n, radial}})/d\xi$, and is called the effective cell constant.

Figure 3 shows measured values of $Z_{\text{sol'n}}$ for 0.01 D KCl plotted in the complex plane. ω^* is the frequency at which the contribution of the reactive elements of the equivalent circuit to the solution impedance is least significant, i.e., the magnitude of the imaginary part of $Z_{\text{sol'n}}$, denoted $|Z''_{\text{sol'n}}|$, is at a minimum. Therefore, at frequency ω^* , the real part of $Z_{\text{sol'n}}$, denoted $(Z'_{\text{sol'n}})^*$, is related to $R_{\text{sol'n}}$ by

$$1/(Z'_{\text{sol'n}})^* = 1/R_{\text{sol'n, radial}} + 1/R_{\text{sol'n, fringe}} \quad [5]$$

In differential form equation 5 is simply

$$d[1/(Z'_{\text{sol'n}})^*]/d\xi = d[1/(R_{\text{sol'n, radial}})]/d\xi \quad [6]$$

In equation 6 there is no term associated with the fringe contribution: it does not vary with electrode position. The evidence to support this claim is given in Figure 4 which shows the linear relationship between the measured value of $1/(Z'_{\text{sol'n}})^*$ and relative electrode immersion for 0.01 D KCl. When the electrodes at their lower extreme are too close to either the floor of the container or the free surface of the solution, this linear relationship breaks down.

Thus, the combination of equations 4 and 6 gives the relationship between the measured solution impedance at ω^* and the specific conductivity

$$\kappa = \{d[1/(Z'_{\text{sol'n}})^*]/d\xi\} / \{d(1/G)/d\xi\}. \quad [7]$$

RESULTS

Certification of the new cell proceeded as follows. The value of $d[1/(Z'_{sol'n})^*]/d\xi$ was obtained from measurements made on 1.0 D KCl and was used in equation 7 with the accepted value of κ reported by Wu et al. (5) to determine the value of the effective cell constant, $d(1/G)/d\xi$. Next, this value of the effective cell constant and $d[1/(Z'_{sol'n})^*]/d\xi$ obtained from measurements made on 0.1 D KCl were used in equation 7 to calculate κ . This value was within 0.5% of that reported by Wu for 0.1 D KCl. In addition, $d[1/(Z'_{sol'n})^*]/d\xi$ obtained from measurements made on 0.01 D KCl and the effective cell constant determined with 1.0 D KCl were used in equation 7 to calculate κ . Again, this value was within 0.5% of that reported by Wu for 0.01 D KCl. Finally, values of the effective cell constant calculated independently for all three solutions, using measured $d[1/(Z'_{sol'n})^*]/d\xi$ and the accepted value of κ , differed by less than 1.0% and were within 0.5% of the theoretical value, 3.515, calculated on the basis of the geometry of this electrode configuration.

CONCLUSIONS

These results are unambiguous in their certification of the new cell design. There are two important attributes of this new cell which make it especially well suited for studies of molten salts. The first is that no dielectric material contacts the melt under investigation. Therefore, this cell can be used in chemically aggressive melts, such as fluorides and oxides. The second is that the effective cell constant is calculable from first principles. This obviates the need to calibrate the cell in a standard solution.

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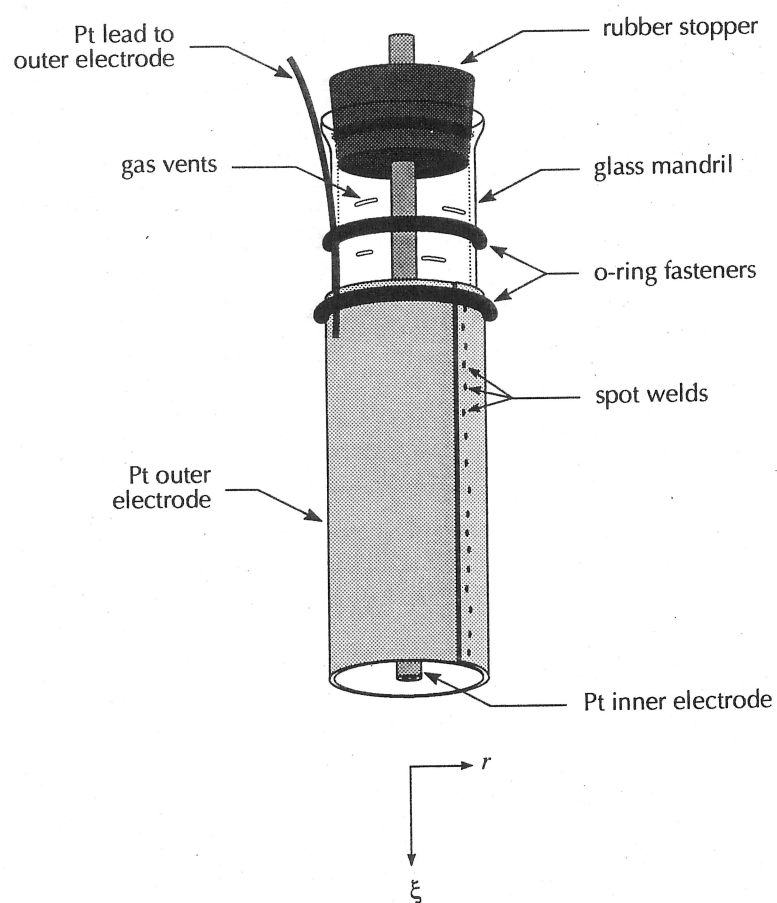


Figure 1. Moveable pair of coaxial cylindrical electrodes.

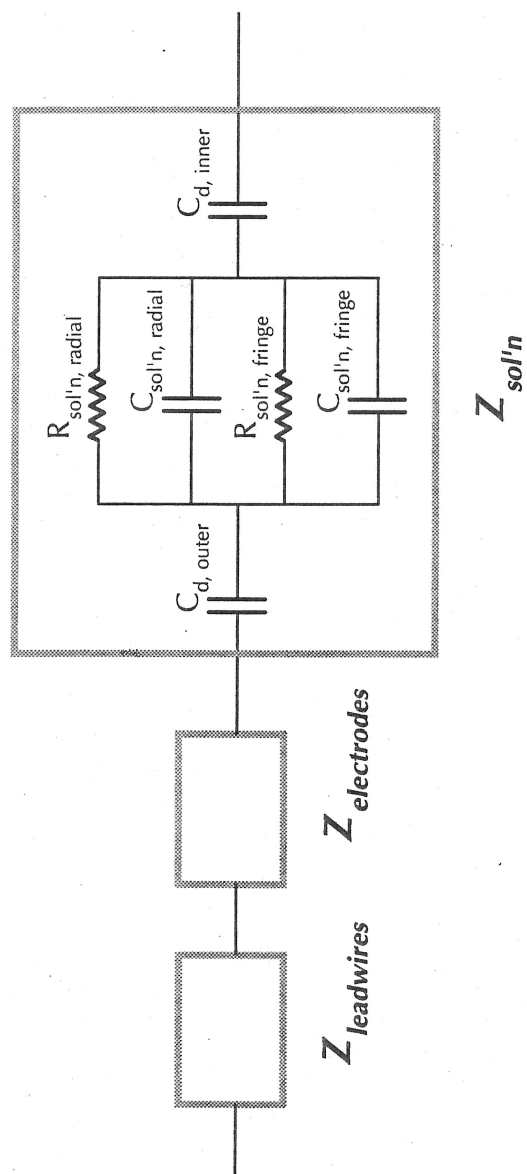


Figure 2. The equivalent circuit of the conductance cell.

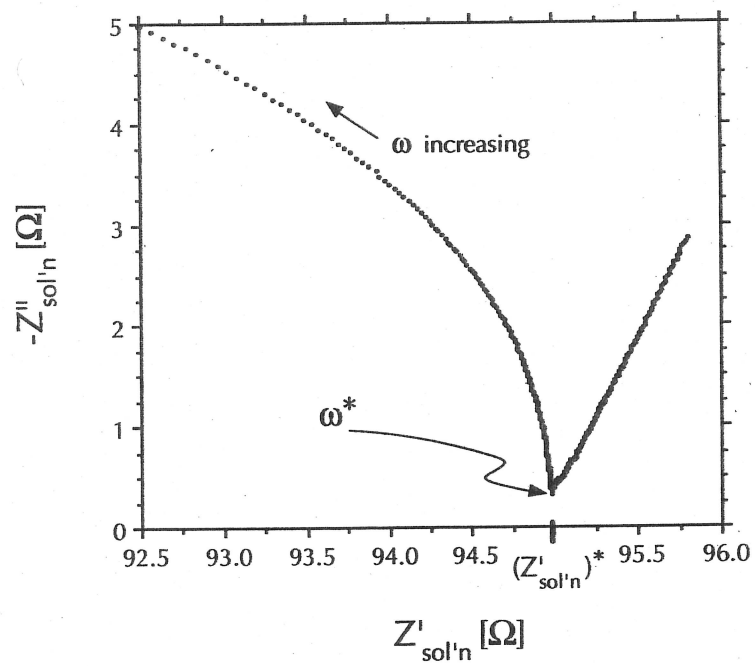


Figure 3. Measured values of the solution impedance of 0.01 D KCl plotted in the complex plane.

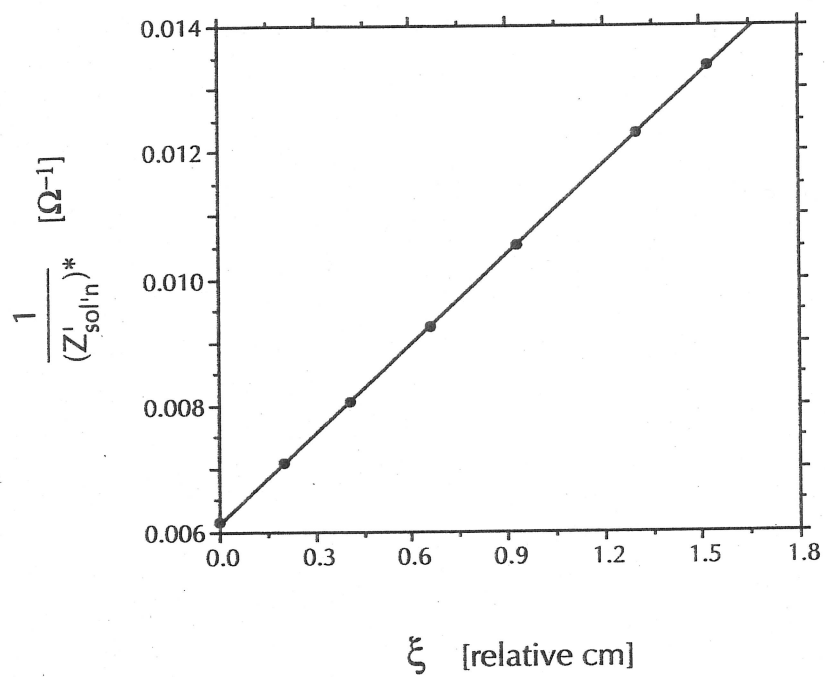


Figure 4. The variation of $1/(Z'_{sol'n})^*$ with relative immersion for 0.01 D KCl.