High-Accuracy Electrical Conductivity Measurements of Corrosive Melts Using the Coaxial Cylinders Technique

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ABSTRACT

The coaxial cylinders technique was developed in response to the need for high-accuracy electrical conductivity measurements of relatively conductive, corrosive liquids. It has been applied successfully to molten salts and glass melts, and has two important advantages over other techniques – it does not require calibration in a standard reference liquid, and it permits measurement of previously inaccessible corrosive liquids. In this technique, coaxial cylindrical electrodes are positioned at successive immersions in the liquid, a.c. impedance is measured at each immersion, and the electrical conductivity is calculated from the change in measured conductance with immersion.

I. INTRODUCTION

Electrical conductivity is an intensive property and cannot be measured directly; it must be calculated from a measurement of the corresponding extensive property, resistance:

$$R=\rho\left(\frac{l}{A}\right)=\left(\frac{1}{\kappa}\right)\left(\frac{l}{A}\right)=\frac{G}{\kappa}$$

where R is resistance, ρ is electrical resistivity, κ is the electrical conductivity, l is the effective length of the current path, A is the effective cross-sectional area of the current path, and G is the cell factor (the current path length-to-area ratio). Nearly all published techniques for measuring the electrical conductivity of liquids are comparative techniques; they rely on calibration in a standard liquid. Calibration[1] is accomplished by measuring the resistance of a standard liquid, R_{std}, and calculating the cell factor, G, by the relationship, $G = \kappa_{std}R_{std}$. The conductivity of the liquid of interest, κ_{liq}, is then calculated by measuring its resistance, R_{liq}, and using the previously determined cell factor, $\kappa_{liq} = G/R_{liq}$..

This comparative procedure of calibration works well only when the cell factor is constant, *i.e.*, when the current path is independent of the electrical properties of: (i) the liquid under investigation, (ii) the electrodes, and (iii) the container. High-accuracy techniques satisfy these conditions; low-accuracy techniques do not.

Factors to consider in choosing a technique for a specific application include (i) desired accuracy, (ii) chemical compatibility between the liquid and the materials of construction of the cell, (iii) the conductance of the liquid under investigation (*i.e.*, the conductivity as seen through the cell factor of the particular electrode configuration), and (iv) the range limits of the available impedance measuring instrument. None of the eleven techniques found in the literature is suitable for high-accuracy measurements in relatively conductive, corrosive liquids. All published techniques suitable for use in corrosive liquids (*i.e.* techniques employing all-metal cells) are either low-accuracy (*e.g.*

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[1] Janz and Tomkins /1/ give a thorough review of calibration conventions. KCl (aq) solutions, as determined by Jones and Bradshaw /2/, are often used as conductivity standards.

the crucible technique), or limited to resistive liquids (*e.g.* the interdigitated technique).

Seven low-accuracy techniques based on five electrode designs were found in the literature. The five electrode designs are shown in Figure 1. Consider what makes each of these techniques low-accuracy and therefore unsuitable for the present application. The main problem with the two-wire /3-9/, four-wire /10/, four-wire with double immersion /11, 12/, ring /13-15/, and two toroid /16/ techniques, is that the current path is not confined, and is, therefore, a function of κ and ε of the liquid. And when the current path is a function of the electrical properties of the liquid, calibration is unreliable. Current spreads out in all directions in the two-wire, four-wire, and two toroid techniques. The four-wire with double immersion technique accounts for and eliminates the current that strays below the electrodes, but not the current that spreads out radially beyond the electrodes. The ring technique does not account for current that strays above and below the cylindrical electrodes. The main problem with the crucible /17-19/ and the differential crucible /20/ techniques is that the current distribution is a function of κ and ε of both the liquid and the electrodes.

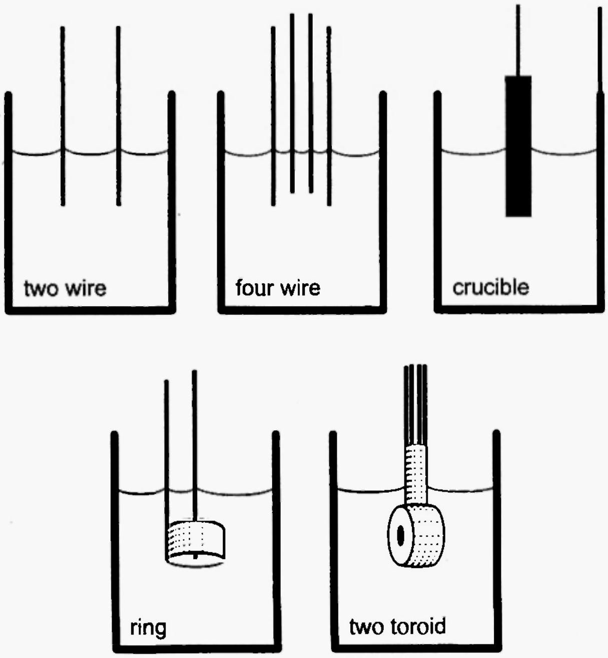

Fig. 1: Five electrode designs for the seven low-accuracy techniques.

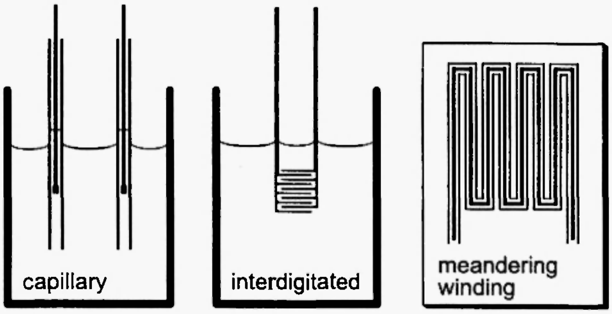

Fig. 2: Three electrode designs for the four high-accuracy techniques.

Four high-accuracy techniques based on three electrode designs were found in the literature. The electrode designs are shown in Figure 2. Consider what makes each of these high-accuracy techniques unsuitable for the present application. The interdigitated electrode design /21/, featuring relatively short and wide current paths, is best suited for use in resistive liquids (*e.g.*, transformer oil), while the capillary design /2, 22-29/, featuring relatively long and narrow current paths, is best suited for use in conductive liquids (*e.g.*, molten NaCl). The meandering winding technique /30/, which has been used for measuring the electrical conductivity of solid metals, is, in principle, suitable for use with conductive liquids. As for the molten salts and glasses of interest, their relatively high conductivity excludes the interdigitated design, while their chemical incompatibility with dielectric materials excludes the capillary techniques and the meandering winding technique.

The coaxial cylinders technique was developed so that high-accuracy electrical conductivity measurements could be made in relatively conductive, corrosive liquids like molten oxides /31-33/. Besides enabling the measurement of liquids inaccessible by other high-accuracy techniques, the coaxial cylinders technique has two unique advantages: (i) it does not require calibration in a standard reference liquid; and (ii) only the *relative* (not *absolute*) depth of immersion of the electrodes need be known.

II. THE COAXIAL CYLINDERS TECHNIQUE

The coaxial cylinders technique employs cylindrical

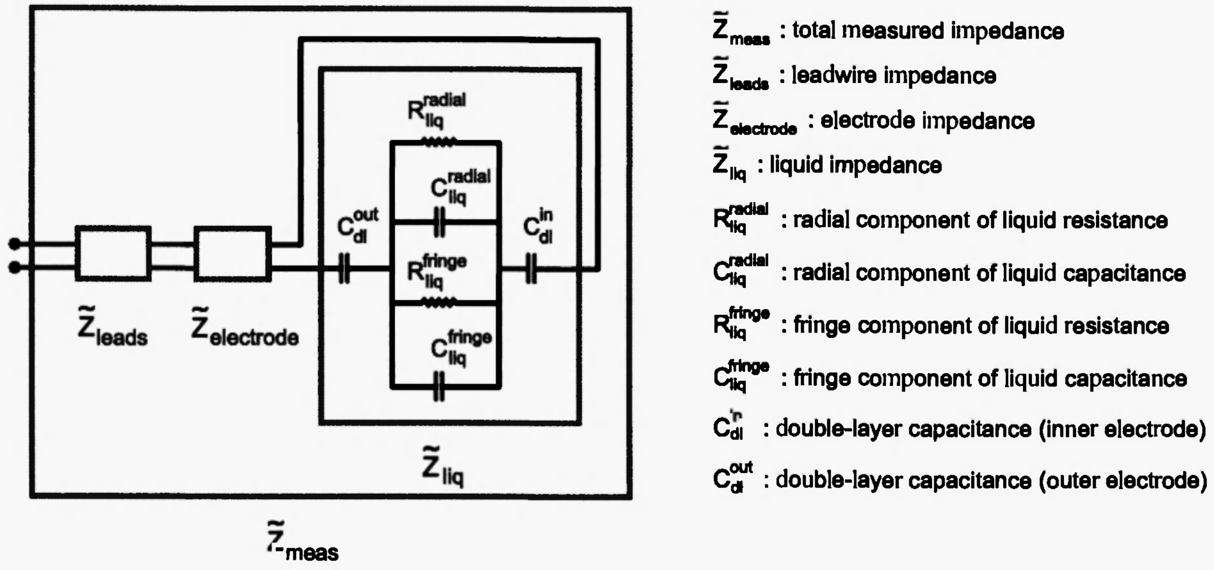

Fig. 3: Equivalent circuit for impedance measurement.

electrodes: the inner electrode is a rod coaxially positioned inside the outer tube electrode. At the top the two are positioned by a dielectric separator that never contacts the liquid under investigation. Briefly, the technique is deployed as follows: the electrodes are immersed in the liquid to an arbitrary initial depth, and a.c. impedance is measured over a wide frequency range. The electrodes are then immersed deeper, and a.c. impedance is again measured over the same frequency range. This process is repeated at several immersions. The electrical conductivity is calculated from the change in measured conductance with immersion.

The electrical conductivity of the liquid, κ, is derived from its impedance, $\tilde{Z}_{liq}$, (the tilde denotes a complex number), but an impedance measurement,[2] $\tilde{Z}_{meas}$, necessarily contains contributions from other sources, *e.g.*, electrodes, leadwires, *etc.*, so that $\tilde{Z}_{meas} \neq \tilde{Z}_{liq}$. The primary goal of the technique presented below is extraction of κ from $\tilde{Z}_{meas}$.

The equivalent circuit for the measurement is shown in Figure 3.[3] Summing series impedances gives: $\tilde{Z}_{meas} = \tilde{Z}_{leads} + \tilde{Z}_{electrode} + \tilde{Z}_{liq}$, where $\tilde{Z}_{leads}$ is the impedance of the leadwires from the impedance measuring instrument, $\tilde{Z}_{electrode}$ is the impedance of the electrodes, and $\tilde{Z}_{liq}$ is the impedance of the liquid under investigation.

Since κ derives solely from $\tilde{Z}_{liq}$, $\tilde{Z}_{leads}$ and $\tilde{Z}_{electrode}$ must be eliminated from $\tilde{Z}_{meas}$. This is done by measuring the impedance of the system with the electrodes shorted, then subtracting this from $\tilde{Z}_{meas}$.[4] And as κ influences only resistance (not capacitance or inductance), it is necessary to isolate the *purely resistive* part of $\tilde{Z}_{liq}$, denoted here as $\left(Z_{liq}^{real}\right)^*$. $\left(Z_{liq}^{real}\right)^*$ contains radial and fringe resistances related as follows:

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[2] Impedance can be measured by a variety of techniques. In this presentation it is assumed that impedance is measured by electrochemical impedance spectroscopy /34-36/.

[3] It is assumed that the resistance of the electrode is invariant with depth of immersion, *i.e.* the electrode is ideal or nearly ideal as described in section V. When this simplifying assumption does not apply, *e.g.* in the case of highly conductive liquids, a more complex equivalent circuit and procedure must be employed /44, 45/.

[4] Most generally, and especially for poorly conductive liquids, an open-circuit impedance measurement should be included in the analysis /31/.

$$\frac{1}{\left(Z_{liq}^{real}\right)^*} = \frac{1}{R_{liq}^{radial}} + \frac{1}{R_{liq}^{fringe}} \tag{3}$$

where $1/R_{liq}^{radial}$ is the radial contribution to the liquid conductance, and $1/R_{liq}^{fringe}$ is the fringe contribution to the liquid conductance. Figure 4 schematically illustrates the fringe and radial current paths. Because it is *purely* radial, the length and area of the radial current path is independent of the electrical properties of the liquid. In the fringe sections the current paths are *not* purely radial, and consequently their length and area are influenced by the electrical properties of the liquid. Fortunately, over a wide range of electrode immersion, the extent of the length and area of the fringe current paths are constant.

$\left(Z_{liq}^{real}\right)^*$ was isolated from $\tilde{Z}_{liq}$ by electrochemical impedance spectroscopy. The value of Z_{liq}^{real}, corresponding to the minimum in $\left(-Z_{liq}^{im}\right)$, is taken as the purely resistive part of $\tilde{Z}_{liq}$ and denoted $\left(Z_{liq}^{real}\right)^*$ (mathematical justification of this assignment can be found in /31/).

For the coaxial electrode geometry, κ is related to R_{liq}^{radial} as follows /37, 38/:

$$\frac{1}{R_{liq}^{radial}} = \kappa\left(\frac{2\pi z}{\ln(b/a)}\right) = \kappa\left(\frac{1}{G}\right) \tag{4}$$

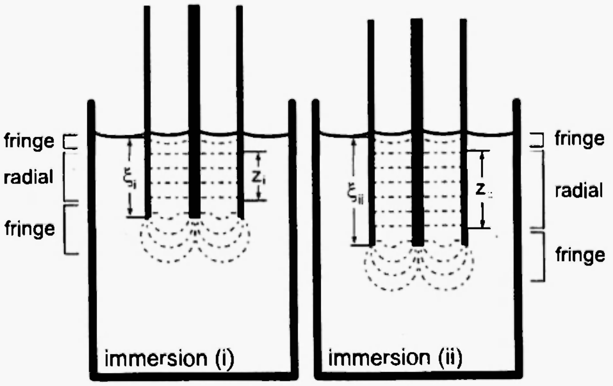

Fig. 4: Definition of fringe and radial current paths and immersion variables.

where b is the inner radius of the outer electrode, a is the outer radius of the inner electrode, z is the length of the *radial* part of the current path (see Figure 4), and G is the cell factor.

R_{liq}^{radial} is separated from R_{liq}^{fringe} by taking measurements at many immersions. Differentiation of equation (3) with respect to z yields

$$\frac{d\left(1/\left(Z_{liq}^{real}\right)^*\right)}{dz} = \frac{d\left(1/R_{liq}^{radial}\right)}{dz} \tag{5}$$

A $1/R_{liq}^{fringe}$ term does not appear because, as mentioned earlier, $1/R_{liq}^{fringe}$ is a constant and not a function of z /31/. Combination of equation (5) and the differential of equation (4) gives

$$\frac{d\left(1/\left(Z_{liq}^{real}\right)^*\right)}{dz} = \kappa\left(\frac{2\pi}{\ln(b/a)}\right) \tag{6}$$

Equation (6) predicts that the plot of $1/\left(Z_{lq}^{real}\right)^*$ *vs.* z must be strictly linear.

Depth of immersion,[5] ξ, and the length of the radial section, z, differ only by an additive constant (see Figure 4).[6] Therefore, their differentials are identical, $d\xi = dz$, and the value of the electrical conductivity of the liquid can be expressed as

$$\kappa = \frac{\ln(b/a)}{2\pi} \cdot \frac{d\left(1/\left(Z_{liq}^{real}\right)^*\right)}{d\xi} \tag{7}$$

It is evident from equation (7) that it is necessary to know only the *relative*, not the *absolute*, position of the

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[5] The measured immersion must be corrected to compensate for the effect of the liquid displaced by the electrodes. This displaced liquid increases the effective immersion, so that the actual immersion is equal to the sum of the vertical displacements of the electrodes and the displaced liquid.

[6] It is assumed that the shape of the meniscus is invariant with immersion.

electrodes. This is a most advantageous feature of the new technique; even when the liquid and electrodes are in clear view, wicking and other surface effects make it difficult, if not impossible, to determine absolute immersion. Furthermore, the constant $\frac{\ln(b/a)}{2\pi}$ is calculable from a knowledge of the electrode dimensions; there is, therefore, no need for calibration in a standard reference liquid. This is arguably the greatest advantage of the new technique.

III. CERTIFICATION

Using a specially constructed Pt electrode assembly,[7] the electrical conductivities of 1.0 D, 0.1 D, and 0.01 D KCl *(aq)* solutions[8] were measured at 20.5°C /39/, and the results matched the standard reference values within 0.5% /2, 40, 29/. Furthermore, values of the cell factor, $\frac{\ln\left(\frac{b}{a}\right)}{2\pi}$, calculated independently for all three KCl *(aq)* solutions using measured values of $\frac{d\left(1/\left(Z_{liq}^{real}\right)^*\right)}{d\xi}$ and the accepted standard values of κ, differed by less than 1.0% and were within 0.5% of the theoretical value, 3.515, calculated from the electrode dimensions.

The technique (comprising electrode design, experimental procedure, proposed equivalent circuit, and data analysis) was thus certified.

IV. APPLICATION TO RELATIVELY CONDUCTIVE, CORROSIVE LIQUIDS

IV.1. Molten Oxides

Using a specially constructed Mo electrode assembly and metal bellows device for high temperature measurements in inert atmospheres,[9] the electrical conductivities of two oxide melts in the CaO-MgO-SiO_2 system were measured as a function of temperature /31, 32/. As expected, both melts exhibited Arrhenius behavior – electrical conductivity increased with temperature, and $\ln(\kappa)$ varied linearly with $(1/T)$. This in conjunction with the derived values of the activation energy for electrical conduction, E_κ, indicated that the melts were ionic, as expected. These results serve to demonstrate the utility of the coaxial cylinders technique in molten oxides.

IV.2. Glass Melts

Using a specially constructed 80Pt-20Rh electrode assembly for high temperature measurements in air atmospheres,[10] the electrical conductivities of a liquid crystal display glass melt /41/ and two simulated nuclear waste glass melts /42/ were successfully measured as a function of temperature. As expected, these melts exhibited Arrhenius behavior – electrical conductivity increased with temperature, and $\ln(\kappa)$ varied linearly with $(1/T)$. These results serve to demonstrate the utility of the coaxial cylinders technique in glass melts.

V. LIMITATIONS AND SOURCES OF ERROR

V.1. Sources of Error

Sources of error fall into two categories: (1) those due to imperfections in the construction of the electrodes, and (2) those due to improper deployment of the electrodes. The first can lead to two problems: (i) if the central electrode is parallel to the outer electrode but off center, the technique will work, but the cell factor is no longer calculable from first principles, *i.e.*, the cell requires calibration; (ii) if the central electrode is not parallel to the outer electrode, the technique will not work, but fortunately, the plot of $1/\left(Z_{liq}^{real}\right)^*$ *vs.* ξ will fail to be linear, and the problem is easily recognized.

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[7] Complete details of the apparatus and experimental procedure are presented elsewhere /39/.

[8] Solutions were prepared according to the specifications of Janz and Tompkins /1/.

[9] Complete details of the apparatus and experimental procedure are presented elsewhere /32/.

[10] Complete details of the apparatus and experimental procedure are presented elsewhere /41, 42/.

The second source of error can lead to the following problem: if the electrodes too closely approach the floor of the container (within $2(b-a)$ /31/), the lower fringe is distorted and its conductance changes. Interaction between the lower fringe field and the container floor will result in a deviation from linearity in the plot of $1/\left(Z_{liq}^{real}\right)^{*}$ *vs.* ξ, and the problem is easily recognized.

V.2. Limitations

Like any technique, the coaxial cylinders technique has limitations, and successful use requires a thorough understanding of these limitations. The technique as presented above cannot be used to measure accurately liquids of extremely high or extremely low electrical conductivity (*e.g.* molten KCl and NaCl are examples of liquids that are too conductive) due to electrode non-idealities and the limitations of impedance measuring instruments. However, by taking a different approach to data analysis and improving the signal processing of the impedance measuring instrument (*e.g.* by way of a voltage amplifier), it may be possible to extend the useful range of the technique /31/.

V.2.1. Electrode Non-Idealities

When immersed in a highly conductive liquid like molten KCl, the electrodes are non-ideal, *i.e.*, they are not equipotential. The technique as presented above assumes that the electrode is either ideal or nearly ideal. For the purpose of this discussion, an ideal electrode has a negligible resistance which does not vary with immersion; a nearly ideal electrode has a very small resistance which does not vary with immersion; a non-ideal electrode has a small resistance which does vary with immersion. Figure 5 illustrates these three electrode types. The ratio of electrode resistance to solution resistance determines whether an electrode is ideal, nearly ideal, or non-ideal. Immersed in different solutions, the same electrode may be considered ideal in one case and non-ideal in another, *e.g.*, a Pt electrode immersed in motor oil is ideal; the same Pt electrode immersed in mercury is non-ideal. In brief, the problem is that when the measured resistance of the liquid is very small, the resistance of the electrode, although small, becomes a significant fraction of the total resistance, and the electrode cannot be modeled as ideal (resistanceless) or nearly ideal (lumped element). In this case the electrode must be modeled as non-ideal (distributed element, or transmissionline). Since the technique as described above treats the electrode as a lumped element, it fails when the electrodes are actually distributed elements, as in the case of molybdenum electrodes in molten NaCl.

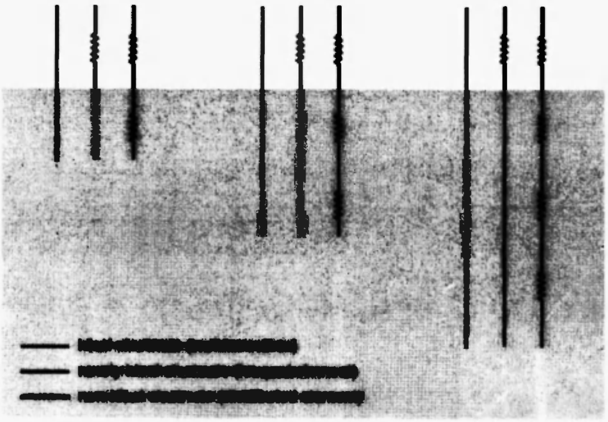

Fig. 5: Equivalent circuits of ideal, nearly ideal, and non-ideal electrodes at 3 immersions.

V.2.2. Limitations of the Impedance Measuring Instrument

The measured impedances in highly conductive liquids are too small for the impedance measuring instrument to accurately measure. There is a finite range of impedance and frequency over which the impedance measuring instrument can accurately measure absolute impedance. The accuracy is a function of both impedance and frequency, as shown in Figure 6 for a Solartron 1260 frequency response analyzer (1260 FRA). Typical impedances and frequency ranges of molten chloride measurements made with the Mo electrode assembly mentioned previously are also shown in this figure. As shown, the instrumentation errors associated with relatively small impedances at relatively high frequencies are quite large.

VI. SUMMARY

The coaxial cylinders technique was developed in response to the need for high-accuracy electrical

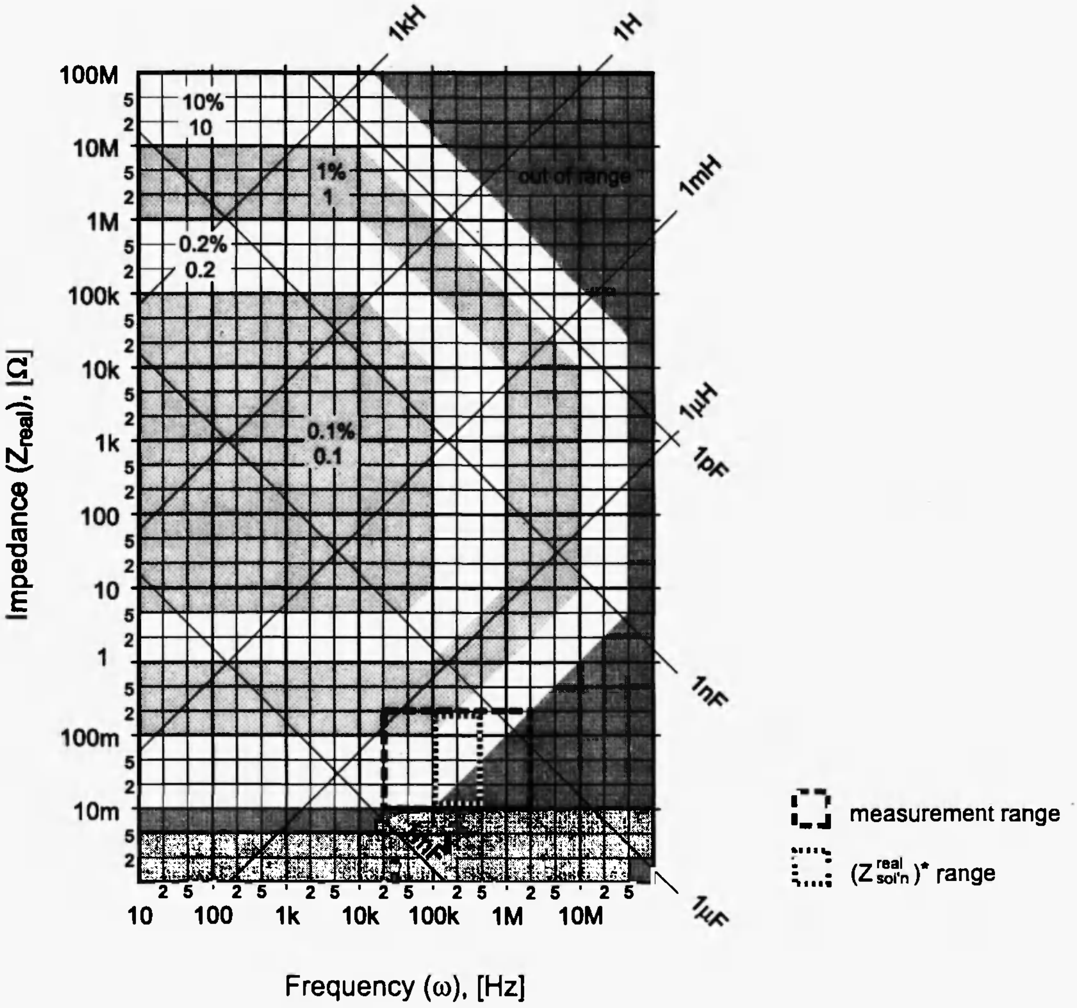

Fig. 6: Solartron 1260 FRA error chart showing typical ranges of impedance and frequency for molten chloride measurements.

conductivity measurements of relatively conductive, corrosive liquids. In addition to enabling measurement of previously inaccessible liquids, the coaxial cylinders technique has the unique advantage of being calibration free. The technique has been certified in standard aqueous solutions, and has been applied successfully to molten oxides and glass melts. Finally, electrode non-idealities and limitations of the impedance measuring instrument prohibit use of the technique (as presented in this paper) in highly conductive melts like molten chlorides.

VII. ACKNOWLEDGMENTS

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