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A high-accuracy, calibration-free technique for measuring the electrical conductivity of liquids

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A high-accuracy, calibration-free technique to measure the electrical conductivity of liquids has been developed — the coaxial cylinders technique. Because the liquid under investigation comes in contact only with metal and not with anything dielectric, this technique enables the measurement of the electrical properties of liquids inaccessible by classical high-accuracy techniques. Two coaxial cylindrical electrodes are immersed in the liquid to an arbitrary initial depth, and ac impedance is measured over a wide range of frequency. This process is repeated at many immersions. The electrical conductivity is calculated from the change in measured conductance with immersion. This technique was validated in 1.0, 0.1, and 0.01 D KCl(*aq*) solutions at room temperature. Measured electrical conductivities were within ±0.5% of the standard reference values. © *1998 American Institute of Physics.* [S0034-6748(98)04909-0]

I. INTRODUCTION

In applications ranging from batteries to electrolysis cells, design and optimization can be greatly enhanced with accurate knowledge of the electrical conductivity of the electrolyte, as this property figures prominently in establishing the thermal balance of the system. Molten oxides have been identified as candidate electrolytes for prospective high-temperature electrochemical processes,[1,2] and since all applicable classical high-accuracy techniques for measuring electrical conductivity rely on the use of dielectric materials, it was necessary to invent a technique that prevents contact between these highly reactive melts and dielectric materials. The result is the coaxial cylinders technique, which uses a cell in which only metal contacts the liquid.[3] This article describes the technique and offers proof of concept.

II. REVIEW OF AVAILABLE TECHNIQUES

Although the electrical conductivities of various molten oxides have been measured in the past, it is the opinion of the authors that these data are, by and large, inaccurate. In this section we review available techniques and explain why, as currently practiced, they are incapable of supplying high-accuracy data, i.e., absolute error $<\pm 1.0\%$, under the extreme conditions encountered in such melts. Table I lists 11 techniques and classifies them according to accuracy.

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

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

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. In *all* of the techniques reviewed, determination of electrical conductivity is a comparative procedure dependent on calibration in a standard liquid.[25] Calibration is accomplished by measuring the resistance of the standard, R_{std}, and calculating the cell factor G, by the relationship $G=\kappa_{\mathrm{std}}R_{\mathrm{std}}$.[26] The conductivity of the liquid of interest, κ_{liq}, is then determined by measuring its resistance and using the measured cell factor, $\kappa_{\mathrm{liq}}=G/R_{\mathrm{liq}}$. The procedure is valid only when the cell factor is constant, i.e., when the current path is invariant with the electrical properties of *all* of the following: (i) the liquid under investigation, (ii) the electrodes, and (iii) the container. High-accuracy techniques satisfy these conditions; low-accuracy techniques do not.

A. Low-accuracy techniques

Seven low-accuracy techniques based on five electrode designs were identified. These are depicted schematically in Fig. 1.

In the two-wire technique, the current path is not confined. Current spreads out in all directions to an extent dictated by the electrical properties of the liquid (conductivity κ and dielectric constant ϵ) and the proximity of the electrodes to the container walls and floor. For this reason, calibration of this type of cell is problematic — the cell factor so determined is in fact not constant, but an unknown function of κ and ϵ of the liquid.

The four-wire technique suffers from the same current-path problem as the two-wire technique. While some of the effects of electrode–electrolyte interfacial impedance, contact resistance, and spreading resistance are avoided, there is no improvement in accuracy.

The four-wire with double immersion technique is an

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TABLE I. Available techniques for measuring the electrical conductivity of a liquid.

Technique	Types of liquids investigated
Low accuracy	
(1) Two wire	Aqueous solutions (Ref. 4); molten oxides (Refs. 5–11)
(2) Four wire	Molten fluorides (Ref. 12)
(3) Four wire/double immersion	Molten oxides (Refs. 13 and 14)
(4) Crucible	Molten oxides (Refs. 15 and 16); molten fluorides (Refs. 17 and 18)
(5) Differential crucible	Molten fluorides (Refs. 19 and 20)
(6) Ring	Aqueous solutions (Ref. 21); molten oxides (Ref. 22); molten fluorides (Ref. 23)
(7) Two toroid	Aqueous solutions (Ref. 24)
High accuracy	
(1) Interdigitated	Cryogenic liquids (Ref. 31)
(2) Capillary	Aqueous solutions (Ref. 28); molten chlorides (Ref. 32); molten oxides (Refs. 33–36) molten fluorides (Ref. 37); molten chloride–sulfide solutions (Ref. 38)
(3) Differential capillary	Aqueous solutions (Refs. 39 and 40); molten fluorides (Refs. 29 and 41)
(4) Meandering winding	Aqueous solutions (Ref. 42)

improvement over both the two- and four-wire techniques. The procedure used by Ohta *et al.*[13] accounts for the current that spreads out below, but fails to account for the current that spreads out radially beyond, the four electrodes. Not surprisingly, measurements were extremely sensitive to the radial position of the electrodes with respect to the crucible wall. As a result, Ohta *et al.*[13] were unable to measure the conductivities of KCl(*aq*) solutions with great accuracy.

The crucible technique is a low-accuracy technique because the current distribution is a function of κ and ϵ of both the liquid and the electrodes. Hence, for the same reasons as those discussed above, calibration of this type of cell is problematic. By way of example, there are two studies in which the electrical conductivity of molten CaF_2 was measured in cells of identical geometry but constructed of different materials. Ogino *et al.*[18] used crucible cells, one of molybdenum and another of graphite. At 1500 °C, the measured values of κ differed by nearly 30%. In contrast, Kim and Sadoway[29] used differential capillary cells, one fitted with tungsten electrodes and another with graphite electrodes. The values of κ measured in the two cells differed by less than 1%. Clearly, the wide variation in the data taken in the crucible cells by Ogino *et al.*[18] derives from the fact that the current path, and thus the cell factor, is a function of the electrical properties of the electrodes.

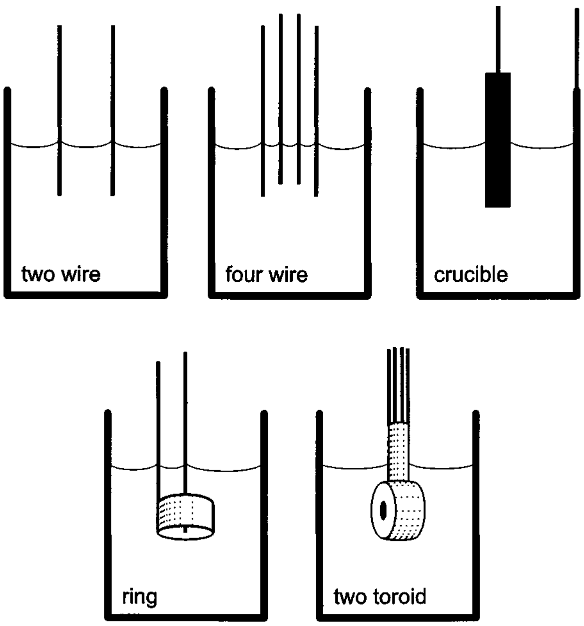

FIG. 1. Low-accuracy techniques for measuring electrical conductivity.

In the differential crucible technique, measurements are taken with the central electrode positioned at several depths of immersion. The measured resistance R_{meas} is related to the conductivity by[19]

$$R_{\text{meas}}=\frac{G}{\kappa}+R_{\text{leads}}, \tag{2}$$

where G is the cell factor. However, since the cell factors are determined in a single calibration at each depth of immersion, this technique suffers from the same current distribution problem as the crucible technique.

In the ring technique, the current path is well defined (i.e., strictly radial and invariant with κ and ϵ of the liquid under investigation) between the cylindrical electrodes. However, the current is not confined to the space between the electrodes; so-called fringe currents stray above and below the interelectrode gap and are dependent on κ and ϵ of the liquid under investigation. This is a low-accuracy technique because the simple expression used to calculate the electrical conductivity from the measured resistance does not account for these fringe currents.

So-called electrodeless conductance measurements have been made via the two toroid technique. In this technique, one toroid radiates an ac electric field and the other acts as a receiver to pick up the small current induced by the moving ions in a conducting loop of liquid. As applied to date, this is

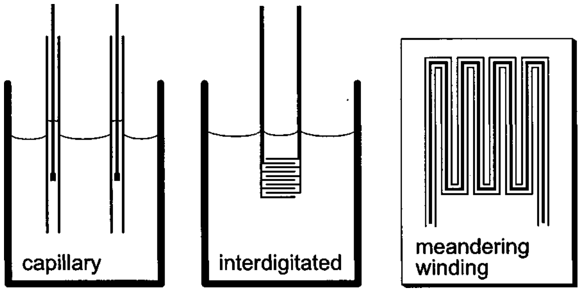

FIG. 2. High-accuracy techniques for measuring electrical conductivity.

a low-accuracy technique because the current distribution is a function of κ and ϵ of the liquid under investigation.

In closing, it is important to point out that if appropriate measures are taken, e.g., modifying the experimental procedure along with the data reduction method, it may be possible to make high-accuracy measurements using cell designs cited in this section. For example, recent work in this laboratory has demonstrated how to get high-accuracy data with a two-wire cell.[30]

B. High-accuracy techniques

Four high-accuracy techniques based on three electrode designs were identified. These are depicted schematically in Fig. 2. Factors to consider in choosing one of these techniques for a specific application include (i) the range limits of the available impedance measuring instrument, (ii) the conductance of the liquid under investigation (i.e., the conductivity as seen through the cell factor of the particular electrode configuration), and (iii) chemical compatibility between the liquid under investigation and cell materials. The interdigitated electrode design, featuring relatively short and wide current paths, is best suited for use in highly resistive liquids (e.g., transformer oil), while the capillary design, featuring relatively long and narrow current paths, is best suited for use in highly conductive liquids (e.g., molten NaCl). The meandering winding method, which has been used for measuring the electrical conductivity of solid metals, is, in principle, suitable for use with highly conductive liquids. As for the molten oxides of interest, their high conductivity excludes the interdigitated design while their incompatibility with dielectric materials excludes both the capillary techniques and the meandering winding method.

III. THE COAXIAL CYLINDERS TECHNIQUE

The coaxial cylinders technique employs cylindrical electrodes: the inner electrode is a rod situated coaxially inside the outer tube electrode (see Fig. 3). The two electrodes are positioned by dielectric separators that never contact the liquid under investigation. The electrodes are immersed in the liquid to an arbitrary initial depth, and ac impedance is measured over a wide frequency range. This process is repeated at many immersions, and the electrical conductivity is calculated from the change in measured conductance with depth of immersion.

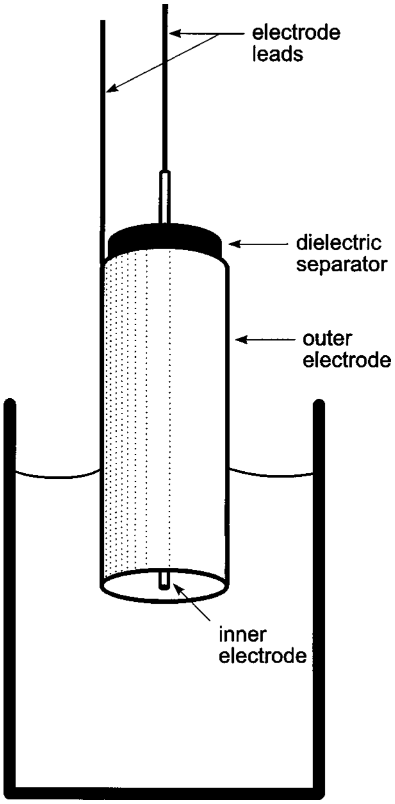

FIG. 3. Schematic illustration of coaxial cylinder electrodes as deployed in measuring the electrical conductivity of a liquid.

A. Theory

The electrical conductivity of the liquid is derived from its impedance, $\tilde{Z}_{\text{liq}}$, (the tilde denotes a complex number). In the present investigation, impedance was measured by electrochemical impedance spectroscopy.[43–45] An impedance measurement $\tilde{Z}_{\text{meas}}$ necessarily contains contributions from other sources, i.e., electrodes, leadwires, etc., so that $\tilde{Z}_{\text{meas}} \neq \tilde{Z}_{\text{liq}}$. The primary goal of the technique is extraction of κ from $\tilde{Z}_{\text{meas}}$.

The equivalent circuit for the measurement is shown in Fig. 4.[46] Summing series impedances give: $\tilde{Z}_{\text{meas}} = \tilde{Z}_{\text{leads}} + \tilde{Z}_{\text{electrode}} + \tilde{Z}_{\text{liq}}$, where $\tilde{Z}_{\text{leads}}$ is the impedance of the leadwires from the impedance measuring instrument, $\tilde{Z}_{\text{electrode}}$ is the impedance of the electrodes, and $\tilde{Z}_{\text{liq}}$ is the impedance of the liquid under investigation.

Since κ derives solely from $\tilde{Z}_{\text{liq}}$, $\tilde{Z}_{\text{leads}}$ and $\tilde{Z}_{\text{electrode}}$ must be eliminated from $\tilde{Z}_{\text{meas}}$. This is done by measuring the impedance of the system with the electrodes shorted, then subtracting this from $\tilde{Z}_{\text{meas}}$.[48]

As κ influences only resistance (not capacitance or inductance), it is necessary to isolate the *purely resistive* part of $\tilde{Z}_{\text{liq}}$, denoted here as $(Z_{\text{liq}}^{\text{real}})^*$. $(Z_{\text{liq}}^{\text{real}})^*$ contains radial and fringe resistances related as follows:

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

where $1/R_{\text{liq}}^{\text{radial}}$ is the radial contribution to the liquid conduc-

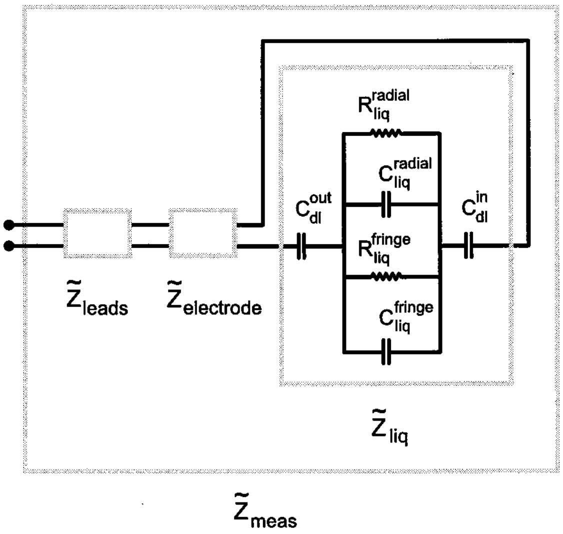

FIG. 4. Equivalent circuit of coaxial cylinders cell.

tance, and $1/R_{\mathrm{liq}}^{\mathrm{fringe}}$ is the fringe contribution to the liquid conductance. Figure 5 schematically illustrates the fringe and radial current paths. Because it is *purely* radial, 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, are influenced by the electrical properties of the liquid. Fortunately, over a wide range of electrode immersion, as evidenced by measurements made in this laboratory, the extent of the fringe section is constant.

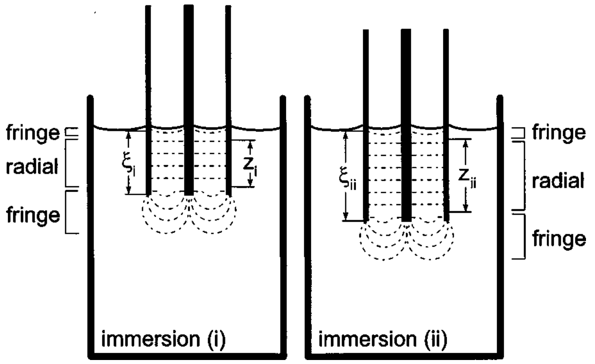

FIG. 5. Definition of radial and fringe current paths and immersion variables.

$(Z_{\mathrm{liq}}^{\mathrm{real}})^*$ was isolated from $\tilde{Z}_{\mathrm{liq}}$ by electrochemical impedance spectroscopy. The value of $Z_{\mathrm{liq}}^{\mathrm{real}}$ corresponding to the minimum in $(-Z_{\mathrm{liq}}^{\mathrm{im}})$ is taken as the purely resistive part of $\tilde{Z}_{\mathrm{liq}}$ and denoted $(Z_{\mathrm{liq}}^{\mathrm{real}})^*$ (mathematical justification of this assignment can be found in Ref. 47).

For the coaxial electrode geometry, κ is related to $R_{\mathrm{liq}}^{\mathrm{radial}}$ as follows:[49,50]

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

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 Fig. 5), and G is the cell factor.

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

$$\frac{d[1/(Z_{\mathrm{liq}}^{\mathrm{real}})^*]}{dz}=\frac{d[1/R_{\mathrm{liq}}^{\mathrm{radial}}]}{dz}. \tag{5}$$

A $1/R_{\mathrm{liq}}^{\mathrm{fringe}}$ term does not appear because, as mentioned earlier, $1/R_{\mathrm{liq}}^{\mathrm{fringe}}$ is a constant and not a function of z.[47] Combination of Eq. (5) and the differential of Eq. (4) gives

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

Equation (6) predicts that the plot of $1/(Z_{\mathrm{liq}}^{\mathrm{real}})^*$ versus z must be strictly linear.

Depth of immersion[51] ξ and the length of the radial section z differ only by an additive constant[52] (see Fig. 5). Therefore, their differentials are identical, $d\xi=dz$, and the value of the electrical conductivity of the liquid can be expressed as

$$\kappa=\frac{\ln(b/a)}{2\pi}\,\frac{d[1/(Z_{\mathrm{liq}}^{\mathrm{real}})^*]}{d\xi}. \tag{7}$$

It is evident from Eq. (7) that it is necessary to know only the *relative*, not the *absolute*, position of the electrodes. This is a most advantageous feature of the coaxial cylinders 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. The constant $\ln(b/a)/2\pi$ is calculable from a knowledge of the electrode dimensions. This means that there is no need for calibration in a standard reference liquid. This is arguably the greatest advantage of this technique.

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 by the formula presented herein, 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 $1/(Z_{\mathrm{liq}}^{\mathrm{real}})^*$ versus ξ will fail to be linear, and the problem is easy to recognize. The second source of error can lead to the

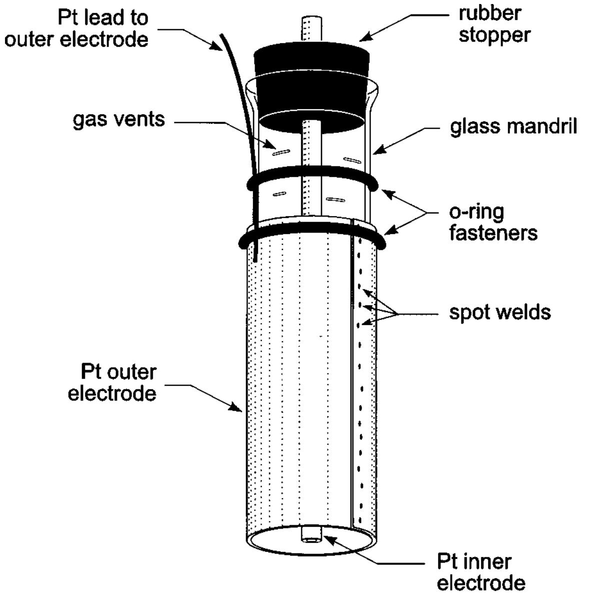

FIG. 6. Platinum electrodes for measurements in aqueous solutions.

following problem: if the electrodes too closely approach the floor of the container, i.e., come within $2(b-a)$ of the container floor,[47] the lower fringe is distorted and its conductance changes. Interaction between the lower fringe field and the container floor will manifest itself as a deviation from linearity in the plot of $1/(Z_{\mathrm{liq}}^{\mathrm{real}})^*$ versus ξ, making the problem easy to recognize.

IV. VALIDATION IN AQUEOUS SOLUTIONS

Electrical conductivity measurements of KCl(*aq*) solutions spanning three decades of concentration yielded results with errors less than ±0.5%. This validated the electrode design, experimental procedure, attendant data analysis, and the proposed equivalent circuit.

The electrode assembly is shown in Fig. 6. Made of platinum, the outer electrode measured 1.8 cm i.d. ×5 cm long and was formed by spot welding platinum foil, 0.0381 cm thick, around a tubular glass mandrel, which became its permanent support. Rubber o rings secured the outer electrode to the glass tube and formed a pressure contact between a platinum leadwire and the outer electrode. The inner electrode was a platinum tube, 0.3 cm o.d. and 10.4 cm long, coaxially positioned by way of a rubber plug in the top of the glass mandrel. Slits in the glass mandrel allowed gas to escape when the electrodes were lowered into the solution. The entire assembly was held by a clamp attached to a freestanding height gauge, which accurately measured the vertical displacement of the electrodes.

Standard 1.0, 0.1, and 0.01 D KCl(*aq*) solutions were prepared according to the specifications of Janz and Tomkins.[53] The proper amount of KCl (99.999%, water content <0.1%, Cerac) was weighed out in a glove box and later dissolved in high-purity water in a glove bag. Appropriate corrections were made for buoyancy, temperature, pressure, and humidity.[28]

Conductivity experiments were conducted in a glove bag filled with ultra-high-purity argon (99.999%), which had bubbled through a KCl(*aq*) solution identical to that under investigation. Following a purge of the bag with ultra-high-purity argon for at least 2 h, the solution was transferred to a 100 ml tall-form beaker and deaerated by bubbling argon gas for 10 min. After deaeration the solution was left for 2 h in order to reach thermal equilibrium. The temperature of the solution was measured with a thermometer and recorded.

TABLE II. Frequency ranges for impedance measurements of KCl(*aq*) solutions.

Concentration	Frequency range
0.01 D	2 MHz–1 kHz
0.1 D	3 MHz–50 kHz
1.0 D	3 MHz–10 kHz

The electrodes were immersed in the solution at least 2.0 cm below the surface — this was done to ensure that the top and bottom fringe fields were not contiguous; i.e., $z>0$ in Fig. 5. Next, impedance measurements were taken at regular frequency intervals over a wide range. The measuring instrument was an impedance/gain-phase analyzer (Solartron 1260, Solartron Instruments, Allentown, PA). The frequency range spanned for each solution (see Table II) was wide enough to reveal the ''notch'' (critical point) in the impedance plane plot. The ac excitation voltage was set at a value between 30 and 50 mV. Results were independent of the magnitude of the excitation voltage. The electrodes were then immersed farther, and the measurement procedure was repeated. Measurements were made at a minimum of five immersions. Data acquisition, storage, and analysis were controlled by a personal computer using the Z60 impedance program (Scribner Associates, Inc., Southern Pines, NC). In a separate experiment, the electrodes were shorted at the bottom via copper foil, and impedance measurements were made over exactly the same frequency range and at the same intervals as for the corresponding solution. The data were then analyzed in accordance with the theory described previously to yield the electrical conductivity κ of the solution.

The electrical conductivities of KCl(*aq*) solutions spanning three decades of concentration were measured at 20.5 °C. The results for the 1.0, 0.1, and 0.01 D KCl(*aq*) solutions differ from standard reference values by less than 0.5%.[28,54,55] Furthermore, values of the effective cell factor, $\ln(b/a)/2\pi$, calculated independently for all three KCl(*aq*) solutions using measured values of $d[1/(Z_{\mathrm{liq}}^{\mathrm{real}})^*]/d\xi$ and the accepted values of κ, differed by less than 1.0% and were within 0.5% of the theoretical value, 3.515, calculated solely from the electrode dimensions. The technique was thus validated.

V. DISCUSSION

These results are unambiguous in their validation of the coaxial cylinders technique. Three attributes make the coaxial cylinders technique especially well suited for studies of molten salts and other highly aggressive liquids. The first is that no dielectric material contacts the liquid under investigation. Indeed, high-accuracy measurements have now been made in molten oxides.[56] The second is that it is necessary to know only the *relative* electrode immersion. Uncertainties in absolute immersion due to wicking and surface effects are, therefore, avoided. The third is that the effective cell factor is calculable from first principles, which obviates the need for calibration in a standard solution.

ACKNOWLEDGMENTS

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[51] 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, ξ_{actual}, is equal to the sum of the vertical displacements of the electrodes, ξ_{imm}, and the displaced liquid, ξ_{liq}.

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

[53] The demal (D) is a concentration unit used in connection with the electrical conductivity of aqueous solutions and is defined as follows: a 1 D solution consists of 71.1352 g KCl per kg solution, a 0.1 D solution consists of 7.419 13 g KCl per kg solution, and a 0.01 D solution consists of 0.745 263 g KCl per kg solution (Ref. 27).

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