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Review

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The 66th special feature
"Novel Aspects and Approaches to Experimental Methods for Electrochemistry"

Electrical Conductivity Measurement of Electrolyte Solution[†,††]

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ABSTRACT

Methods for measuring and analyzing the electrical conductivity of electrolyte solutions are reviewed. The accuracy of conductivity measurements, which have been around for more than 100 years, depends on the physical properties related to ionic conductivity, especially the concentration of the reference material, the electrical signal at the time of measurement, and the temperature, each of which has been redefined each time according to changes in definitions and standards. This article summarizes elemental factors in electrical conductivity measurement, including the concentration and traceability of potassium chloride as a reference material, the history of the bridge method and types of measuring cells, and important notes and recent topics regarding the concept of temperature dependence.

Keywords : Principle of Electrical Conductivity Measurement, Concentration and Traceability of Potassium Chloride, Kohlrausch Bridge and Automatic Balancing Bridge, Temperature Dependence in Arrhenius and VTF Equations

1. Introduction

In the field of physical science, the electrical conductivity, σ, is defined as the coefficient of the electric field $\boldsymbol{E}$ on the current density $\boldsymbol{i}$ by Ohm's law as follows:

$$\boldsymbol{i} = \sigma \boldsymbol{E} \tag{1}$$

Based on this definition, measuring the electrical conductivity σ means placing a charged particle in an electric field and monitoring its movement. Most charged particles used in electrochemistry are electrons and ions, and in liquid electrolytes, the charged particles are exclusively dissolved ions (this paper does not deal with plasma in liquids). Therefore, the ionic conductivity is an important basic property of liquid electrolytes, and there are a wide range of considerations in its measurement, such as the theory of ionic conduction, measurement techniques (AC or DC measurement), and the type of conducting species (total or individual ionic conductivity) to be measured. For example, electrical conduction at the interface between the sample and the electrode (current collector) is caused by charge transfer reactions in which ions transfer electrons. In this case, not only the steady-state current caused by the transfer of charged particles, but also transient responses and polarization phenomena such as the reaction current in electrochemical reactions and the charging current in capacitors (charging of charged particles near the electrode) due to the electric field response and adsorption behavior of dipoles are involved. Therefore, it is necessary to select a measurement method that corresponds to phenomena with different time constants. Thus, it can be said that electrical conductivity measurement reflecting ionic conduction is a measurement and interpretation of the current response to changes in electric potential, and an appropriate measurement method should be selected in consideration of what kind of substance or charge transfer is occurring in the measurement system. Since ionic conduction is a mass transferring phenomenon, it is necessary to always consider the other conduction behaviors mentioned above, to distinguish between the factors that should be eliminated, which are often the cause of measurement errors, and to make accurate and precise measurements.

Methods and theoretical development of ionic conductivity measurement have long been conducted and established by Faraday, Hittorf, Kohlrausch, Debye, Hückel, Onseger, and others, and their genealogy can be traced in books and textbooks.[3] Most textbooks for beginners only describe the measurement of electrical conductivity according to early methods, using KCl as the reference material, using an AC Kohlrausch bridge at a given frequency, often 1 kHz, and measuring at a fixed temperature. However, this description of measurement conditions must be revised, as more meaningful measurement methods have been developed as concentration and temperature definitions and measurement techniques have evolved.

In the early days of electrochemistry, the concept of ionic conduction summarized by Kohlrausch, who systematically measured the electrical conductivity of electrolyte solutions, was the

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[†] This review is translated from an article in *Denki Kagaku*, **86**, 42 (2018)[1] with permission of the Electrochemical Society of Japan and is based on the original text lectured by the author at the 35th Electrochemistry Workshop organized by the Kansai Branch of the Electrochemical Society of Japan, published in November 2005, with substantial revisions and additions to the content to meet current IUPAC and Japanese Industrial Standards (JIS).

[††] This paper constitutes a collection of papers edited as the proceedings of the 51st Electrochemistry Workshop organized by the Kansai Branch of the Electrochemical Society of Japan. The author's profiles of this paper can be found on the preface.[2]

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M. Mizuhata orcid.org/0000-0002-4496-2215 basis for subsequent measurements of transport number and ionic conduction mechanisms, along with the establishment of the conductivity measurement method using the Kohlrausch bridge, which he modified from the Wheatstone bridge, and can be considered a sufficiently established method for measuring ordinary electrolyte solutions.[4] The conductivity of concentrated aqueous electrolyte solutions, which has been increasingly studied in recent years, has been considered as an extension of the theory of dilute solutions, such as the decrease in conductivity due to ion-pair formation. On the other hand, since the Walden rule was proposed for the correlation between viscosity[5] and conductivity[6–8] of viscous electrolyte solutions,[9–11] many researchers including Angell,[12,13] Watanabe,[14,15] and others have studied ionic conductivity not only in concentrated electrolyte solutions but also in molten salts, ionic liquids, and gel electrolytes from the viewpoint that ionic interactions affect physical properties.

Recently, due to restrictions on the amount of sample and atmosphere in which electrical conductivity must be measured, the conventional method of measuring aqueous solutions at room temperature and pressure (standard conditions) is becoming increasingly inapplicable. In addition, electrolytes, which are liquid materials, are not only used as they are in solution, but are also used in systems in which they coexist with porous solid materials (powders, fibers, fillers, etc.) to support their shape. Also, the conductive mechanisms of those ions have also been extensively studied.[16–29]

However, since explaining everything would be confusing and would not be appropriate for this paper, we will focus on how to accurately measure ionic conductivity, the reasons for doing so, and points to keep in mind. Reviews of ionic conductivity measurements have been published many times in predecessor and this journals, and the author and his coauthors have had the opportunity to write commentaries on electrical conductivity measurement methods[30] and their interpretations, focusing on impedance measurements in Japanese.[1,31,32] This manuscript is a translation of a Japanese version of a commentary previously written by the author,[1] in which the description includes international standards in addition to the content for Japan regarding industrial standards.

2. Specific Electrical Conductivity and Cell Constants

2.1 Resistance and electrical conductivity/specific electrical conductivity

The definition of electrical conductivity according to Ohm's law has already been described as Eq. 1, and additionally, the concept of concentration is introduced into the unit system convention and conductors in the field of electrochemistry. Some properties are defined as follows, together with the units used. When a current I (A) flows for an applied voltage E (V) in a measurement, its resistance R (ohm, Ω, or S^{-1}) is defined by Ohm's law as

$$R = E/I \tag{2}$$

where R is the reciprocal of the electrical conductivity, σ. The resistance R depends on the shape of the sample and is proportional to the reciprocal of the sample length l (m) and the cross-sectional area A (m^2). In order to calculate the intrinsic electrical conductivity of a material, the cell constant K_{cell} (m^{-1}) is given by

$$K_{\mathrm{cell}} = l/A \tag{3}$$

The specific electrical conductivity of each material is defined as κ (or σ) ($\mathrm{S\,m^{-1}}$) and is calculated by the following equation. The specific resistance, ρ, is the reciprocal of κ.

$$\kappa = \rho^{-1} = K_{\mathrm{cell}} R^{-1} \tag{4}$$

The above resistivity values can be measured directly for solid materials where the sample geometry can be fixed. However, it is difficult to directly measure the specific conductivity of liquids because the sample geometry is not fixed, and in the case of ionic conductors, there is the Parker effect[33,34] where the electric lines of force between the sample cross-sectional area and electrodes do not always coincide due to the state of the conductive path. Therefore, a measurement cell that is easy to reproduce is used, and the cell constant, K_{cell}, is determined for each cell by measuring the resistance R_{std} of a reference material with a known specific conductivity κ_{std}.

$$K_{\mathrm{cell}} = \kappa_{\mathrm{std}} R_{\mathrm{std}} \tag{5}$$

The standard material is an aqueous KCl solution as described in Section 2.2. The electrical conductivity of an ionic conductor is determined by the product of the number of ions as the conducting species and their mobility. The number of ions is expressed as the amount of substance of ions in a fixed volume of electrolyte. In usual electrochemical experiments, the concentration is often defined by the volume molar concentration C, and the electrical conductivity per volume molar concentration is called the equivalent conductivity Λ, as indicated as Eq. 6,

$$\Lambda = \kappa/C \tag{6}$$

Sometimes, the SI unit system is "strongly" recommended in textbooks, and in general rules for electrical conductivity measuring method in Japanese industrial standard: JIS K 0130–2008, which will be described later, it is defined using only basic units, so it is shown as in Eq. 6. However, in the past, "centimeter (cm)" was conventionally used as the unit of length in electrochemistry, and liter, L ($= \mathrm{dm}^{-3}$), was often used for volume. Therefore, $\mathrm{S\,cm^{-1}}$ and $\mathrm{mol\,L^{-1}}$ were so widely used as units of specific conductivity and concentration, respectively, that the following equation was used in the definition of equivalent conductivity,

$$\Lambda = 1000\kappa/C \tag{6$'$}$$

in the definition formula of equivalent conductivity. The coefficient "1000" will remain in the equation for the time being due to the customary notation of units.

2.2 Reconsideration of principals for electrical conductivity measurement

In the conductivity measurement by Kohlrausch et al. in 1898,[4] KCl was selected as the reference material because it is a strong electrical solution containing K^+ and Cl^- as dissolved species, it is easy to purify, weigh, and handle, and the mobility of the constituent ions, K^+ and Cl^-, is almost equal. The method for determining the absolute conductivity of aqueous KCl solution, which is used as a standard for calculating cell constants, requires an agreement on the substance and measurement environment that guarantees traceability and reproducibility.

As the electrical conductivity of aqueous solutions obtained from KCl is not calculated theoretically, it is determined by measuring the "absolute values" of electrical conductivity of aqueous KCl solutions at a given concentration. This concept remains unchanged to this day. Since the temperature standard of the SI unit system was redefined by ITS-90 in 1990,[35] the electrical conductivity of aqueous KCl solutions, whose measured values are greatly affected by temperature, had to be measured again. The current electrical conductivity measurements of aqueous KCl solutions based on the SI unit system standards are those reported based on the IUPAC verification in 2001.[36] The new values were established after a complete review of past measurements of the concentration of KCl as the reference material, the measurement cell, and the measurement method, and after identifying problems in the measurements. The Japanese Industrial Standards also revised the general rules for electrical conductivity measurement methods in accordance with these standards, which are now in operation as JIS K 0130–2008.[37]

Therefore, by verifying the past measurement methods for absolute values of electrical conductivity of aqueous KCl solutions, from which the IUPAC[36] and JIS[37] standards were derived, it is possible to determine how general electrical conductivity measurements can be made and how the measurement of electrical conductivity can be improved. The following is a description of the past methods for measuring the absolute value of electrical conductivity of aqueous KCl solutions, from which the IUPAC and JIS standards were derived. The purpose of electrical conductivity measurement of KCl aqueous solution is mentioned from the viewpoint of traceability by the Research Institute of Standards for Measurement, National Institute of Advanced Industrial Science and Technology (AIST).[38,39] There is no ISO standard equivalent to JIS K 0130-2008 mentioned above. ISO 7888:1985,[40] which is equivalent to JIS K 0102,[41] exists in Japan for electrical conductivity measurements for water quality control that contribute to environmental measurements. These differ in the concentration range of KCl applied, with JIS K 0130 covering aqueous solutions with values from 5 $\mathrm{S\,m^{-1}}$ to 200 $\mathrm{S\,m^{-1}}$, whereas ISO 7888 (JIS K 0102) refers to measurements from 1 $\mathrm{mS\,m^{-1}}$ to 500 $\mathrm{S\,m^{-1}}$. The reason why the lower limit of electrical conductivity for dilute solutions is set at 1 $\mathrm{mS\,m^{-1}}$ is that the contribution of $\mathrm{H^+}$ and $\mathrm{OH^-}$ to electrical conductivity due to water dissociation cannot be ignored.[41]

2.2.1 Aqueous potassium chloride (KCl) solution as standard solution for conductivity measurement

When measuring the electrical conductivity of liquids, aqueous potassium chloride (KCl) solutions prepared by the experimenters are usually used in many fields including electrochemical research.

KCl A reagent of KCl specified in JIS K 8121-2007[42] deviated from ISO 6353-3:1987[43] is used. Special grade reagents commercially available from reagent companies satisfy these regulations except for the water content, and may be used in ordinary experiments if stored under careful control. However, they must be dried in accordance with the regulations. The reagent should be powdered in an agate mortar, heated at 500 °C for 4 hours, and cooled in a desiccator.[42] By this process, the special grade reagent satisfies the specification for "KCl for electrical conductivity measurement." The original IUPAC standard for storage describes drying in a desiccator with $\mathrm{Mg(ClO_4)_2}$,[36] but $\mathrm{Mg(ClO_4)_2}$ is not suitable for drying solvents,[44] and in Japan it is a class 1 hazardous material, so in JIS, simply use airtight containers. Therefore, in JIS, an airtight container is simply used. Although not specified in JIS, drying in a vacuum desiccator using $\mathrm{P_2O_5}$ is a comparable drying method.

Water: Use pure water with an electrical conductivity of 0.2 $\mathrm{mS\,m^{-1}}$ (25 °C) or less.[36,45]

Weigh the amount of KCl: According to the molecular weight of KCl (74.552 $\mathrm{g\,mol^{-1}}$), weigh a predetermined amount of KCl pretreated as described above and dissolve it in 1 kg of water. In practice, it is difficult to precisely weigh the above amounts, so if the amount of KCl collected is within 1 % of the specified amount, the weight of water may be adjusted so that the KCl concentration is identical.[45]

It should be noted that the concentration of the solution specified here is defined as a mass molar concentration $\mathrm{mol\,kg^{-1}}$, i.e., a solution of a certain amount of KCl dissolved in 1 kg of solvent (water). JIS K 0130-2008, the general rule for electrical conductivity measurement methods specified in the Japanese Industrial Standards (JIS), also uses the electrical conductivity value based on this IUPAC measurement.[36] The three types of conductivity values, 1 $\mathrm{mol\,kg^{-1}}$, 0.1 $\mathrm{mol\,kg^{-1}}$, and 0.01 $\mathrm{mol\,kg^{-1}}$, are defined in the IUPAC standard above. 1 $\mathrm{mol\,kg^{-1}}$, 0.1 $\mathrm{mol\,kg^{-1}}$, and 0.01 $\mathrm{mol\,kg^{-1}}$, and for 0.001 $\mathrm{mol\,kg^{-1}}$, the literature value measured for aqueous KCl solutions specified in JIS K8121-2007 (potassium chloride (reagent)) is specified as the electrical conductivity of KCl.[46] The reason for using the molar concentration by weight is to ensure that changes in solution volume due to temperature change do not affect the concentration.[36] In a detailed experiment by Jones et al. in 1933, the unit of concentration for electrolyte solutions was the demal (the amount of solute dissolved in 1 kg of solution, sometimes referred to as "D").[47] This unit was used for many years until the determination of the electrical conductivity of KCl, which was defined by IUPAC, the SI system of units, according to the IPTS-68 temperature standard.[48] There was confusion due to the difference between the academic field using the SI unit system as the standard and the industrial field using the JIS standard as the standard. In JIS K0130-2008, for the first time in JIS standards, a measurement method based on IUPAC units was made as the general rule, thereby defining a reference material for electrical conductivity that is consistent both academically and industrially. Hence, the problem of determining the concentration of the reference solution has now been almost eliminated. It should be noted that recent revisions can be found in currently published textbooks, handbooks, and procedures, some of which are based on the previous plan such as JIS K0130-1995.

Standard solutions of KCl prepared under the guarantee of traceability based on such concentration specifications are supplied in many countries. In addition, disposable standard samples for which the value of electrical conductivity is specified without specifying the type of electrolyte are sold as ISO 17025 Conductivity Calibration Standards,[49,50] and reagent manufacturers in various countries are selling reagents complying with these standards.

In Japan, electrical conductivity standard solutions (aqueous KCl solutions) based on certification issued by the National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (AIST) began to be distributed in 2015.[51] As of 2017, three types of KCl solutions (1 $\mathrm{mol\,kg^{-1}}$, 0.1 $\mathrm{mol\,kg^{-1}}$, and 0.01 $\mathrm{mol\,kg^{-1}}$) were delivered. Currently, electrical conductivity reference materials are sold by companies that comply with ISO 17034:2016 "General requirements for the competence of reference material producers."[52] KCl is generally used and is a disposable product whose packaging is defined by its electrical conductivity value, not by the concentration of the electrolyte solution. However, these solutions are extremely expensive and are rarely used in practice, except when it is necessary to prove that the measurement equipment and data handling based on the measurement results conform JIS. For ordinary measurements, standard solutions that conform to JIS standards with sufficient accuracy are available from reagent manufacturers at low prices, and these can be used.

2.2.2 Measuring cells

Jones et al. precisely measured the electrical conductivity of KCl in the 1920s and 1930s firstly. They made a major contribution to the establishment of the electrical conductivity measurement method by improving the accuracy of measurements with the Kohlrausch bridge. They made a number of improvements in elemental techniques related to the verification of actual measurements of electrical conductivity by AC bridge,[53] improvement of the power supply (AC oscillator) and detector,[54] cell shape,[55] validity of Ohm's law in electrolyte solutions,[56] effect of polarization on the application of AC,[57] fabrication of platinum black electrodes,[58] and use of oscilloscopes,[59] and in 1937, he proposed a standard value for the electrical conductivity of aqueous KCl solutions finally.[47,60] In the IUPAC measurements reported in 2001, the Jones' cell was used as one of the measuring cells, and its accuracy was verified.[36] Two measurement methods were used: 0.01 $\mathrm{mol\,kg^{-1}}$ and 0.1 $\mathrm{mol\,kg^{-1}}$ KCl solutions, the Jones' cell shown in Fig. 1a was used to measure AC impedance values at frequencies $f = 1$, 2, and 5 kHz, respectively using Jones' bridges.[47,53] The impedances at each frequency were extrapolated to $f \to \infty$ and the resulting values were used as resistance ones.

However, this method is difficult to use for a 1 $\mathrm{mol\,kg^{-1}}$ KCl solution with high electrical conductivity because of its electrode polarization. Therefore, the cell shown in Fig. 1b was used and the

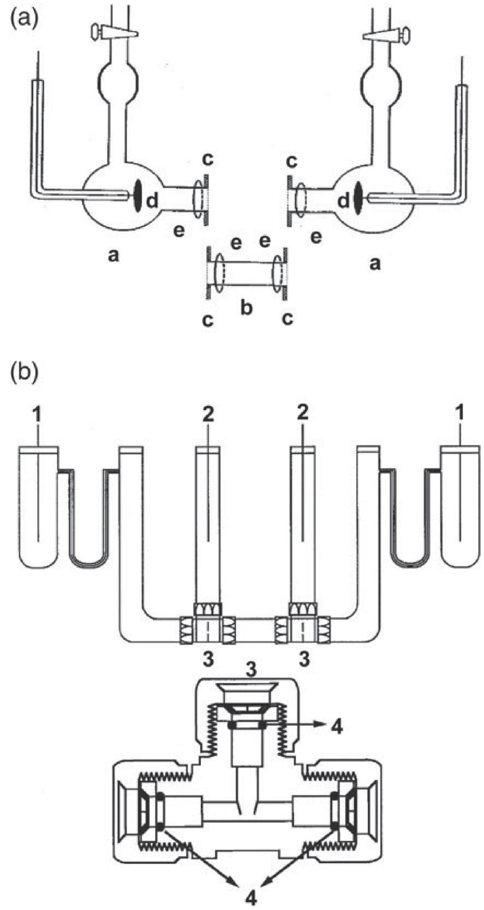


Figure 1. Jones' cell for electrical conductivity measurement. (a) Diagram of the AC conductivity cell used for the absolute measurements: a; end sections (half cells), b; center extension tube, c; flanges, d; Pt electrodes, e; O-rings. A plastic band (not shown) surrounds the outer circumference of the mating flanges to hold them coaxially and a compression clamp (also not shown) presses on the O-rings to hold the mating flanges together, and (b) Diagram of the DC conductivity cell used for the absolute measurements: 1; current electrodes, 2; potential difference sensing electrodes, 3; Nylon tee joints, 4; O-rings. Reprinted from Ref. 36, Copyright 2001 IUPAC.

DC 4-terminal method was used. Here, nylon Swagelok joints are used to connect the vessels. Resistance was determined by applying a given current between the outer electrode 1 and measuring the potential difference between the two electrodes. Since polarization occurs only at the current probe, the conductivity of KCl can be determined directly from the cell shape since there is almost no change in concentration between the potential probes. After confirming the reproducibility of the conductivity obtained, the values shown in Table 1 were recorded and used as the IUPAC standard values. However, there are some important points to be recognized when considering the method of conductivity measurement of electrolyte solutions.

1. The appropriate measurement method must be used depending on the magnitude of the electrical conductivity. That is, the best possible measurement method depends on the conductivity of the material.
2. AC measurements are made at 1, 2, and 5 kHz and extrapolated to $f \to \infty$.
3. The position of the potential probe in a 4-terminal DC measurement is not defined by the electrode insertion position, but by the liquid entanglement.

Table 1. The value of specific electrical conductivity κ of KCl standard solution newly established by IUPAC based on the temperature indication of ITS-90.[36]

t/°C	0.01 mol/kg KCl	0.1 mol/kg KCl	1 mol/kg KCl (10^4 κ/S m^{-1})
0	772.92 ± 0.23	7116.85 ± 2.85	63488 ± 25
18	1219.93 ± 0.37	11140.6 ± 4.5	—
20	1273.03 ± 0.38	11615.9 ± 4.6	99170 ± 40
25	1408.23 ± 0.42	12824.6 ± 5.1	108620 ± 43
30	1546.63 ± 0.46	14059.2 ± 5.6	118240 ± 47

These conditions suggest that the best method should be considered on a case-by-case basis, depending on the nature of the liquid sample we are measuring, especially its electrical conductivity. When measuring ionic conductivity in solids, the sample geometry directly defines the cell constants, meaning that we are measuring absolute values of conductivity. In contrast, for liquid samples, electrodes are placed at arbitrary positions in the measurement cell, so one should always be aware that there are many things to be verified in terms of electrode size, contact conditions, and distance between electrodes. General information on the measurement cell is described in section 4.

3. Circuit for Electrical Conductivity Measurement

3.1 Kohlrausch bridge

A well-known circuit for electrical conductivity measurement is the Kohlrausch bridge which is a derivative of the Wheatstone bridge equipped with an AC power supply. This circuit combines an RC circuit with a known resistor element in parallel with a variable capacitor, a variable resistor, and a current meter as shown in Fig. 2, and uses the AC method for measurement. Here, the resistance value of the sample, R_s, is given by

$$R_s = R_1 R_2 / R_3 \tag{7}$$

Whereas this equation is valid for a circuit consisting of only a resistance component without a capacity one, in the case of ionic conductors, there is a capacitance component due to the time delay required for ion transfer and polarization phenomena at the electrodes. Jones proposed the use of a variable capacitor to compensate for the phase difference in the AC current caused by the capacitance of the sample in the conductivity measurement cell and made significant improvements to subsequent measurements using bridges in which the description is written in the section of "*Conditions of Balance of the Bridge Analyzed*" in Ref. 53. As described above, the bridge method has been widely used in

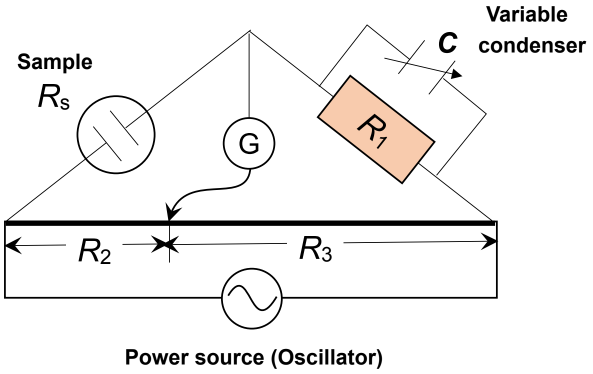


Figure 2. Circuit diagram of a Kohlrausch bridge, R_1: fixed resistor, R_2, R_3: variable resistors, G: galvanometer.

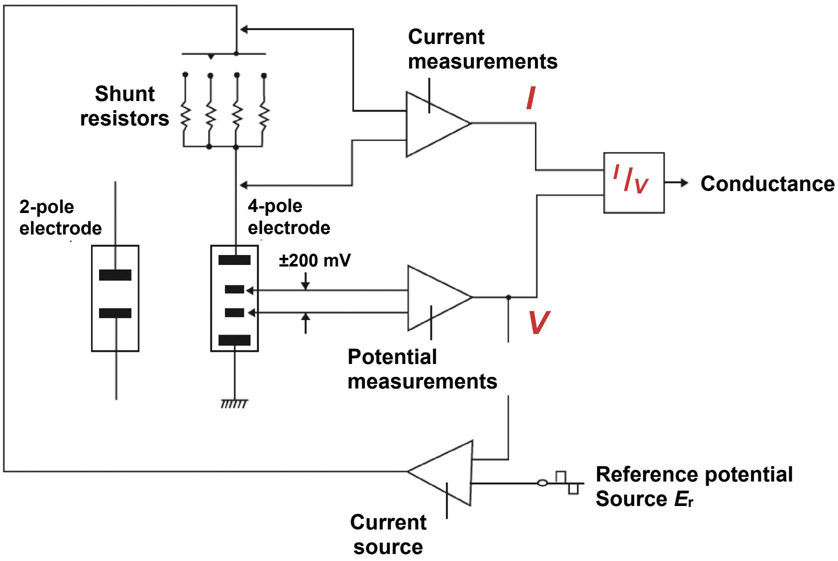


Figure 3. Automatic balancing of linear AC bridge circuits.

conductivity measurements because it can provide very accurate values with a simple oscillation circuit. However, as shown in the next section, automatic balanced bridge circuits are now widely used, and commercially available bridges for measuring the electrical conductivity of electrolyte solutions are rarely available.

3.2 Automated balanced bridge

The auto-balancing bridge circuit is currently the most typical circuit used to measure electrical conductivity by the AC method and is a typical circuit system for impedance meters and LCR meters. The potential is generated by a power supply (AC oscillator) as shown in Fig. 3, and the potential difference generated in the connected sample is measured. In this case, either the 4-terminal method or the 2-terminal method is used, depending on the electrode configuration. The current value is converted to a current value by measuring the potential difference generated in a fixed resistance (shunt resistance) connected in series with the sample. Since a fixed resistor with a value similar to that of the sample is suitable for measuring the potential, an appropriate resistance value is automatically selected for the current measurement. The sample resistance is measured from the potential difference between the samples and the current value through an A/D converter and a division operation circuit. Since an alternating current is applied, the resistance value obtained is treated as an impedance as for the Kohlrausch bridge, and the phase of the current and potential is also measured. The applied AC frequency varies according to the manufacturer, but values in the range of 1–100 kHz are used, and the higher the frequency, the smaller the resistance value (the greater the electrical conductivity).

3.3 DC four-terminal method

When measuring the resistance of a sample showing a low resistance value, such as a highly concentrated electrolyte solution, AC resistance measurement is often difficult in terms of frequency selection because of excessive current flow. Therefore, the DC four-terminal method (sometimes called Kelvin method) is used. The cell configuration is shown in Fig. 1b. Since electrode reaction and polarization are inevitable when using direct current, this method requires that the electrode section and the voltage measurement section be separated in the cell to prevent the effect of electrode polarization on the section measuring the potential difference. A DC power supply is connected to the electrodes at both ends of the cell, and an electrometer with a high internal impedance of at least $10^{13}\,\Omega$ is used to measure the potential difference and calculate the resistance value. In this case, since the amount of current can be varied over a wide range, the resistance should be calculated from the slope of the I-V response after confirming linearity. A volt meter or tester with low internal impedance is not suitable for the measurement because it itself becomes a power source. The method of measuring conductivity with KCl standard solution, calculating the cell constant, measuring the sample resistance, and calculating the electrical conductivity using Eq. 5 is the same as the AC method. Although this method was partially applied in IUPAC measurement,[32] the direct current method is not recommended in JIS K 0130-2008.

4. Sample Cells

4.1 Shape of measuring cell

There are many designs of electrical conductivity cells as shown in Fig. 4, including cells of various shapes invented by Kohlrausch and currently available on the market, and the most suitable shape depends on the amount of sample, resistance, and stability of the sample. In particular, electrical conductivity is highly dependent on temperature and must be measured while maintaining the electrolyte at a constant temperature. For this reason, there are cells in which the sample is injected into a solution bath for measurement for Figs. 4a–4e, and cells in which the sample is flown through the cell for measurement as shown in Fig. 4f.

Recently, commercially available cells for electrical conductometers are increasingly being used. Generally, as shown in Fig. 5, a platinum resistance thermometer, thermistor, or thermocouple, and a glass tube containing conductors connected to the electrodes, with platinum electrodes installed above and below on a ring, are widely used as an integrated type. In the case of using an integrated cell, a protection cell is used. Regarding the thermometers provided here, the temperature standard ITS-90, which was the reason for the revision of JIS K0130-2008, defines a platinum resistance thermometer as a supplementary instrument at 13.8033 K–961.78 °C. When an integrated cell is used, it is often equipped with a protective tube. The following precautions should be taken as follows.

- The protective tube shall not be taken for the above purpose as shown in Fig. 5a. The protective tube is used to avoid the influence of external diffusion currents and to keep the lines of electric force only within the protective tube to avoid large changes in the cell constants due to large or small conductivity of the electrolyte. When the protective tube is removed, the value of the electrical conductivity may increase. This value is due to the spread of the lines of electric force inside the vessel and is not a correct value.

- For the measurement under the condition for Fig. 5b, no air bubbles shall be allowed to enter or adhere to the protective tube around the electrode in order to avoid the internal volume of the electrolyte solution changing and continuity being lost.

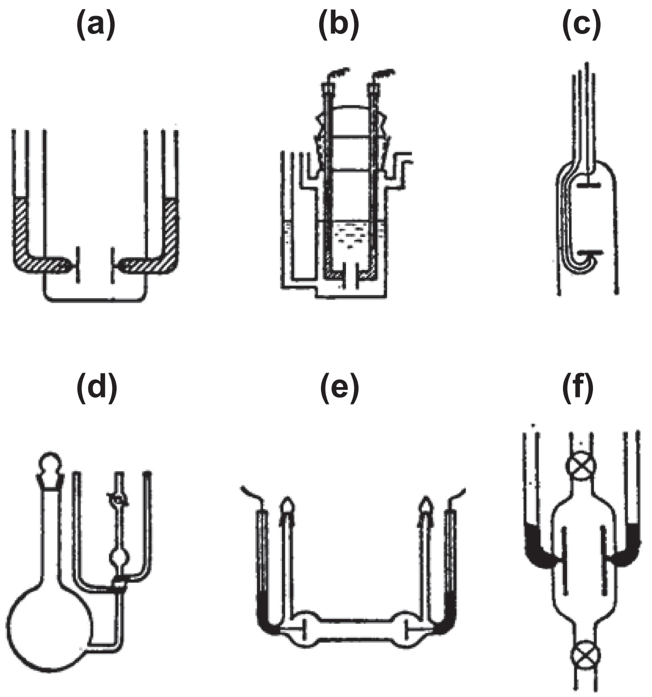


Figure 4. Typical structures of electrodes for an electrical conductivity measurement. (a) Simplified type, (b) and (c) Insertion type, (d) For dilute solution, (e) For precise measurement, and (f) Flow cells.

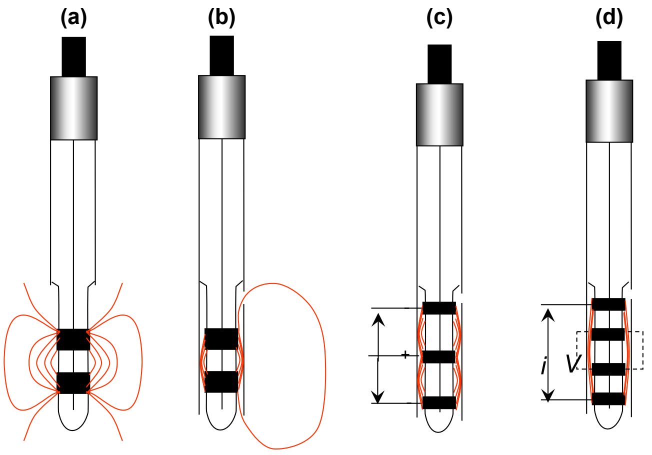


Figure 5. Schematics of commercially available insertion-type conductivity cell with electric lines of force generated during measurement. (a) Shield removed two-pole cell. An unshielded electrode causes the lines of electric force to spread so much that they depend on the shape of the measurement bath. (b) The two-pole cell with the shield. Since lines of electric force leak through the air holes in the upper part of the cell a little, they are considered to have little effect. (c) A two-pole cell with identical poles on the top and bottom to prevent leakage of lines of electric force to the outside. (d) A four-pole cell. The current and voltage probes are independent.

- Although the cell shown in Fig. 5c appears to have "three poles," the upper and lower poles have the same polarity. Therefore, the leakage of lines of electric force does not occur as in Fig. 5b, and the cell constants are extremely accurate.
- The quadrupole cell shown in Fig. 5d has current and voltage probes arranged independently.

For conductivity measurements of highly resistive solutions, the distance between electrodes should be narrower and the electrode area should be larger. A conductivity cell with extreme geometries, such as Keysight 16452A liquid test fixture is commercially available for measuring the capacitance component of electrolyte solutions and solvents with very high resistance values. It has a diameter of 38 mm and a very small cell constant with spacers that allow the distance between electrodes to be adjusted from 1.3 mm to 3.0 mm for capacitive measurements. The cross-sectional area and distance between the electrodes are defined, so the cell is capable of measuring absolute resistance.

4.2 Platinum-black electrode

Electrodes are often made of platinum or platinum-black because they must be resistant to corrosion by the electrolyte, but since JIS K 0130 specifies that electrodes must be "impervious to specimens," titanium and stainless steel (SUS316 etc.) are sometimes permitted in commercial products. When using a platinum electrode, it is recommended to use a platinum-black electrode in which a platinum electrode is inserted into a platinum chloride acid solution to secure a sufficient effective area at the electrode, and a black velvety platinum dendrite is formed by electrolysis as shown in Fig. 6. The method of producing platinum black is as follows. (See Ref. 34, p. 5)

(a) Removal of platinum black

Platinum black can be easily removed by electrolyzing a

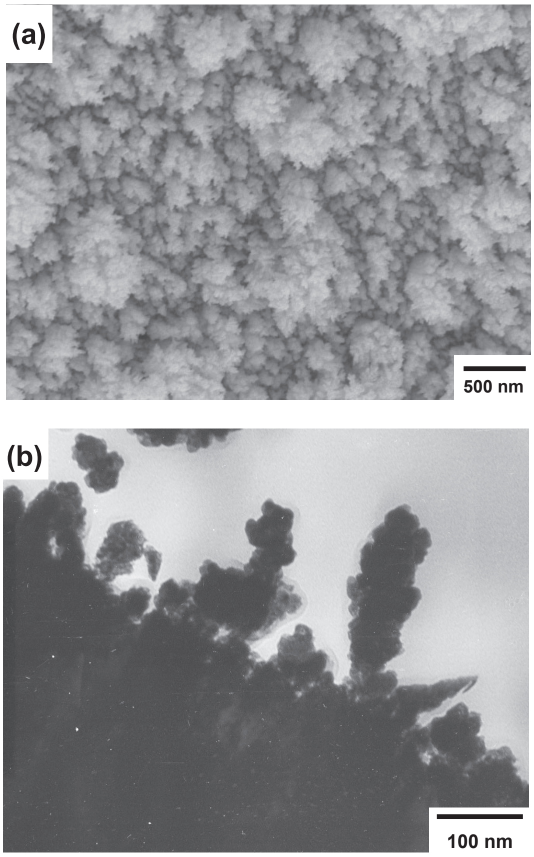
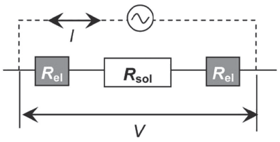
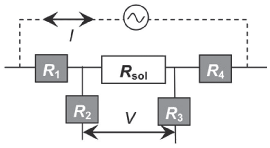


Figure 6. (a) Surface SEM image and (b) cross-sectional TEM image of a platinum electrode with platinum black deposited by Pt plating from H_2PtCl_6 solution as described in Section 4.2.

Table 2. Comparison of 2-pole and 4-pole methods.

	2-pole method	4-pole method
Schematic of equivalent circuits		
Features and advantages	- Easy maintenance - Inexpensive because of their simple structure. - Suitable for use with highly viscous samples and colloidal solutions.	- The current-potential response is linear in any conductivity region. - The conductivity regions in the calibration and conductivity measurements can be different. - Ideal for samples with high conductivity. - Applicable for samples with low conductivity if the effect of stray capacitance is compensated.
Disadvantage	- The electrodes must be placed in the center of the container to avoid electric field effects. - The effect of polarization cannot be ignored in the case of samples with high conductivity. - It is desirable to use two types of samples with conductivities that differ by about two orders of magnitude when calibrating conductivity.	- Not suitable for small samples because all four electrodes must be in contact (immersed) with the sample. (3–4 cm distance between electrodes is required.) - Not suitable for flow method.
Measurement range	With Pt black: $>3\,\mathrm{mS\,cm^{-1}}$ Without Pt black: $>1\,\mathrm{mS\,cm^{-1}}$	With Pt black: applicable in wide range of conductivity Without Pt black: $>100\,\mathrm{mS\,cm^{-1}}$

platinum (black) electrode as an anode in about $1\,\mathrm{mol\,L^{-1}}$ hydrochloric acid.

(b) Plating method

Weighed 30 g of $H_2PtCl_6\cdot 6H_2O$ and 0.25 g of $(CH_3COO)_2Pb\cdot 3H_2O$ are dissolved in water, and 1 L of electrolyte is prepared. A platinum electrode is placed in the electrolyte, and the electrolyte is energized (35–$140\,\mathrm{kC\,m^{-2}}$) for approximately 10 min, switching polarity several times at a constant current density (100–$400\,\mathrm{A\,m^{-2}}$) while stirring the electrolyte using a power supply of approximately 6 V DC.

Next, the platinum black is energized in $0.033\,\mathrm{mol\,L^{-1}}$ sulfuric acid for about 30 min, changing the current direction occasionally, to remove adhered or absorbed hexachloroplatin(IV) acid and chlorine gas. Since polarization is inhibited once Pt black is applied, care should be taken with the applied voltage to prevent dissolution of the Pt black on the anode side.

Once a Pt/black electrode is dried, surface wetting is impaired and diffusion of the electrolyte into the Pt/black is inhibited. Therefore, it is necessary to take care of the maintenance of both commercial and home-built cells. This indicates that the cell is not suitable for non-aqueous electrolytes, electrolyte solutions in which dissolved species are adsorbed or react with the Pt black, or colloidal solutions. In the case of the measurement of the electrical conductivity of non-aqueous electrolytes, a Pt plate can be used. However, since polarization tends to occur, it is desirable to measure at a frequency at which polarization hardly occurs, based on an understanding of the frequency dispersion state by AC impedance. Recent electrical conductivity measurement equipment often measure conductivity in a relatively high-frequency range and have a circuit system that minimizes the polarization effect at the electrode, so it may be better to use a platinum plate electrode when the electrical conductivity is somewhat small. In any case, even when platinum plate electrodes are used, care should be taken to ensure that the shape and arrangement of the electrodes, the orientation of the electrodes, and the parallelism between the electrodes in the case of opposing plate electrodes do not change.

4.3 Two-pole and four-pole cells

JIS K 0130-2008 recommends the AC 2-electrode method, the AC 4-electrode method, and the electromagnetic induction method as electrical conductivity meters as mentioned in 4.2. The former two methods are usually applied in electrochemical measurements, and often comprise a 2-pole cell and a 4-pole cell, respectively. The characteristics of these methods are shown in Table 2. The two-pole method serves as both a current collector and a voltage measuring device, and is affected by the polarization of the electrodes. The quadrupole method, on the other hand, separates the current-carrying electrode from the voltage-measuring electrode, and since the voltage-measuring electrode is connected to a high-impedance voltage measuring device, only a very small amount of current flows through it and is not affected by electrode polarization. Therefore, the polarization resistance indicated by R_2 and R_3 is almost negligible. The quadrupole method minimizes the electric field effect of the sample container in the sample cell because the area where the electric field is applied is limited to the vicinity of the electrodes. Therefore, the sample volume and container volume have little influence on the measured values.

4.4 Connection between cell and device

The connection between the cell and the device is made with a conductor of good electrical conductivity. Normally, commercially available conductors are used as they are, and little attention is paid to the following points, including the AC method.

- Avoid using unnecessarily long connectors to avoid errors due to low terminal voltage. When connecting electrodes with clips, etc., avoid increasing contact resistance due to corrosion by cleaning, polishing, etc.
- In the case of the AC method, long conductors cause a decrease in terminal voltage and a decrease in line-to-line capacitance. In particular, when using an impedance meter to measure conductivity, it is necessary to use a coaxial cable and ground the conductor itself as an inductance component in the high-frequency range and to ground the conductor in parallel between the cell and the device because of the contribution of

the stray component of superimposed interline capacitance. It should be noted that coaxial cables must be used and grounded to equipment.

5. Electrical Conductivity Measurement by AC Method and Frequency Dependence

However, the appropriate measurement frequency range differs depending on the sample resistance. Since the frequency at which polarization occurs is often different for each sample, the value measured with the KCl standard solution is not necessarily applicable at all frequencies. When measuring liquid electrolyte solutions by frequency dispersion, it is necessary to apply an AC voltage within the potential window where no electrode reaction occurs, and the semicircle corresponding to the charge transfer resistance component in the electrochemical impedance is not seen, and only the polarization impedance on the electrode at the low frequency side is obtained. Only the polarization impedance can be obtained, so only a straight line is often seen in the complex impedance plot, as shown in Fig. 7. If conductivity is calculated by impedance measurement, conductivity can be easily calculated by taking the solution resistance as the point where the straight line and the real axis intersect. Here, we would like to make a note on the frequency dependence of the AC measurement at an arbitrary AC frequency without impedance measurement.

Figure 8 shows the frequency dependence of various electrolytes as a Bode diagram. Due to the effect of electrode polarization, the absolute value of impedance $|Z|$ increases at low frequencies. However, the frequency at which the increase is observed depends on the characteristics of each sample and shows different values, indicating that it is not desirable to calculate all conductivity values using only the value measured at 1 kHz, for example. The resistance of each electrolyte should be measured at the higher frequencies where the polarization resistance is no longer observed, thus indicating that impedance measurement is suitable for liquid samples as well, since the frequency dispersion can be easily determined. In practice, it is known that commercially available cells select an appropriate AC frequency according to the resistance of the sample to be measured. For example, Radiometer Analytical uses 94 Hz for the 4–40 µS range and 46.9 kHz for the higher range. The relaxation times corresponding to these phenomena correspond to the reciprocal of the frequency, and thus capture phenomena on the order of millisecond to microsecond. The adsorption and desorption of ions near the electrode and the orientation of the solvent occur on this timescale and are responsible for the polarization phenomena. However, the Debye-Falkenhagen effect,[61–64] a phenomenon in which the ionic atmosphere follows the electric field based on the electric field gradient around the ion in the bulk, is a relaxation phenomenon in the picosecond to nanosecond range, and thus the resistance value varies in the GHz range. If the conductivity of an aqueous electrolyte solution measured in the kHz range shows no frequency dependence, it is reasonable to assume that the conductivity is the reciprocal of the resistance at that time.

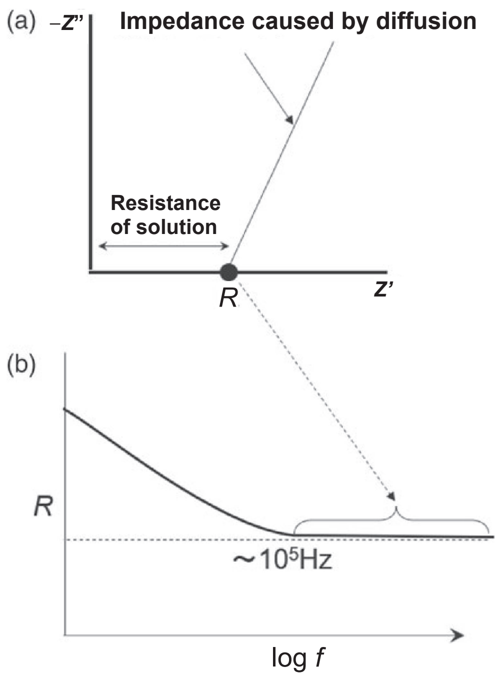


Figure 7. (a) Complex impedance plot and (b) corresponding Bode plot of a typical solution resistance measurement. When polarization at the electrode interface does not occur at high frequencies, the phase difference between the applied voltage and current disappears and the plot is on the real axis. On the Bode diagram, the resistance is independent of frequency and shows a constant value as shown in (b).

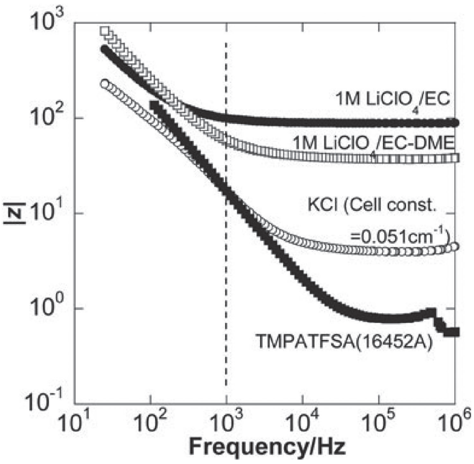


Figure 8. Frequency dependence of absolute AC impedance $|Z|$ for various electrolytes (Bode's plots). 16452A in TMPATFSA (Tetramethylpropylammonium tetrafluoro-bisulfonamide) indicates a Keysight (formerly Agilent Technology) cell.

6. Temperature Dependence of Electrical Conductivity

6.1 Accuracy of measurement temperature

It is widely known that electrical conductivity is a transport property of ions and that it depends sensitively on temperature. In other words, the temperature control of the measurement system must be precise. In general, a 1 : 1 electrolyte such as KCl at a concentration of about $1\,\mathrm{mol\,kg^{-1}}$ shows a conductivity change of about 2 % per degree. Therefore, if we require three significant digits of conductivity (expanded uncertainty 0.1 %), stability at temperatures below 0.01 °C must be ensured.

To guarantee this accuracy, in Japan, the temperature measurement is equivalent to using a calibrated platinum resistor guaranteed by a calibration laboratory registered under the Japan Calibration Service System (JCSS),[38] so it is necessary to fully consider how much accuracy can be achieved in the interpretation of the measured value of electrical conductivity. In general, thermocouples and thermistors are often used because relative comparisons of electrical conductivity are often acceptable from an academic standpoint, rather than absolute measurements. On the other hand, when summarizing results for which a description of accuracy is required, specifically the temperature measurement method and its instruments should also be described in the paper.

When measuring temperature, it is desirable to insert the sensor part of the thermometer into the cell and measure the temperature of the electrolyte directly. If this is not possible due to the shape of the cell or the nature of the electrolyte, the temperature stability of the thermostatic bath should be maintained to the same degree, and the stability of the temperature in the cell should be confirmed by a constant value of electrical conductivity to be used as the measurement value.

6.2 Differences between industrial standards and scientific analysis

Interpretations of the temperature dependence of electrical conductivity vary widely depending on the purpose of the measurement. Commercially available electrical conductivity meters must conform to some industrial standard, and the same applies to the handling of temperature. In conclusion, the temperature compensation function of electrical conductivity meters should not be used when measuring the variation of electrical conductivity with temperature (temperature dependence) from an academic standpoint or when measuring an unknown sample at an arbitrary temperature. The reason for this is explained in a note using JIS K0130-2008 or ISO 7888:1985, which is used in domestic commercial products as an example. (See Appendix A) The temperature dependence of the electrical conductivity of KCl is expressed by a polynomial approximation in Jones's study,[47] IUPAC,[36] and JIS,[37] and has no physicochemical meaning. In the case of temperature compensation by nonlinear approximation, the function used is also a polynomial function centered on the electrical conductivity of an aqueous solution of KCl at 25 °C, and it is clear that it cannot be applied to other samples. In other words, if the temperature compensation function of the conductometer is turned on when measuring the electrical conductivity of a sample, the electrical conductivity will only be corrected with respect to the 25 °C KCl solution according to the temperature compensation coefficient of KCl.

6.3 Temperature dependence and activation energy of conductivity

The temperature dependence of the electrical conductivity of electrolytes in which ions move as charged particles is generally explained by Eyring's Transition State Theory. In other words, charged particles (ions) respond to an electric field, and position exchange (rearrangement of materials) occurs through the transition state, which is considered as an electrical conductivity phenomenon. Based on the transition state theory, it is assumed that the energy required to reach the transition state in the movement of ions (meaning the rearrangement of matter) is the activation energy ΔE_a, and that even if charged particles exist in the system, only charged particles that have obtained this energy can move. As a result, using the same approach as for general chemical reactions, the electrical conductivity σ is

$$\sigma = \sigma_0 \exp(-\Delta E_a/RT) \tag{8}$$

or

$$\log\sigma = -\Delta E_a/2.303RT + \log\sigma_0 \tag{9}$$

where σ_0 and R are a constant and a gas constant ($8.314\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$). Therefore, if a linear correlation is obtained on a $\log\sigma$ vs. $1/T$ plot, commonly called Arrhenius plots. Here, the slope $\mathrm{d}\log\sigma/\mathrm{d}(1/T)$ is

$$\mathrm{d}\log\sigma/\mathrm{d}(1/T) = -\Delta E_a/2.303R \tag{10}$$

and the activation energy ΔE_a is calculated as follows:

$$\Delta E_a = -2.303R[\mathrm{d}\log\sigma/\mathrm{d}(1/T)] \tag{11}$$

The activation energy is often used as a measure of the ease of ionic migration, and is applicable to any shape of ionic conductors such as liquids, solids, and gels.

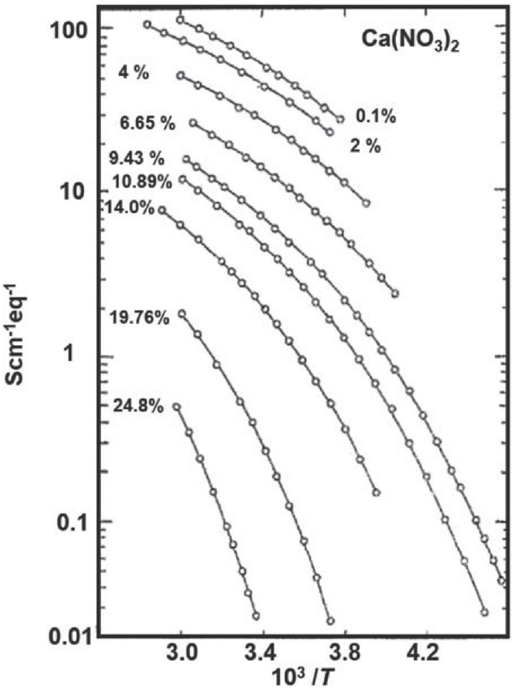


Figure 9. Temperature dependence of electrical conductivity of aqueous $Ca(NO_3)_2$ solutions. Concentration unit is % by weight. Reprinted from Ref. 65, Copyright 1972 American Chemical Society.

6.4 Nonlinear Arrhenius plots and VTF equation

When the temperature dependence of electrical conductivity is measured, a convex upper temperature dependence is often observed. As a typical example, Fig. 9 shows the electrical conductivity of an aqueous solution of $Ca(NO_3)_2$ measured by Angell et al. over a wide concentration range.[65] When the temperature dependence has a nonlinear response in a $\log\sigma$ vs. $1/T$ plot as in this example, an empirical formula called the VTF formula

$$W = A\exp[-B/(T - T_0)] \tag{12}$$

is often applied, where W is a number indicating the possibility of rearrangement of the material (e.g., electrical conductivity, fluidity, diffusivity, etc., indicating flow), A is the pre-exponential term constant, and B is a constant. This equation was derived by Vogel[66] and Fulcher[67] from measurements of the temperature dependence of the viscosity constant of glass, and was applied to a wide range of glassy materials by Tammann[68] and thus became known as the VTF equation. Since then, Angell has systematized not only viscous flow but also various transport properties of electrolyte, such as ionic conduction in electric field and ionic diffusion in concentration gradient.

For the VTF equation for electrical conductivity proposed by Adam and Gibbs, Angell derived from free volume theory.[69] The VTF equation is indicated that

$$W = AT^{-1/2}\exp[-B/(T - T_0)] \tag{13}$$

of which pre-exponential term is proportional to $T^{-1/2}$.[70–74]

The derivation of the pre-exponential term $AT^{-1/2}$ by free volume theory was performed in a system with molten salts by Angell et al.[74,75] After the derivation of this equation, the comparison with the experimental data was done using the equation derived by Adams et al. as described in Appendix B. The term "1/2" attached to the pre-exponential term has a less significant effect on the equivalent conductivity.

The application of transition state theory to the interpretation of ionic conduction assumes that given the energy required to activate a charged particle in an electric field, there is always an exchange of ionic positions that contributes to ionic conduction. Thus, in the situation described by the Arrhenius equation, is the following conditions must be satisfied.

- Ion migration is not disturbed by other dissolved species.
- The law of independent ion transfer at infinite dilution (Kohlrausch) holds.
- Debye-Hückel theory (point charge transfer in a continuous medium) is assumed.

These conditions are unlikely to be satisfied because charged particles in reality have finite sizes and the interactions exist between charged particles in ion transfer. Therefore, it is more common for the VTF equation to hold in electrolyte solute.

When the VTF equation is applied, the apparent activation energy can have a variety of meanings. If one were to adapt transition state theory and take only the transition energies, it would be strictly arithmetic to go back and find the value of $z^*\Delta\mu$ in Eq. B1 in Appendix B.[69] However, if the phenomenon of ionic conduction is not only caused by the movement of individual ions, but also by the coordination of other dissolved species (ions, solvents, molecular chains in case of polymers, etc.), the calculation of transition energy based on the VTF equation, of which gradient varies with temperature, should take into account the molecular motion and entropy effect of the system. From this point of view, assuming that the linearity is maintained in the microscopic temperature range, it is not meaningless to treat the differential coefficient of the VTF equation at each temperature (the slope in the VTF plot) as the apparent activation energy. Calculating the differential coefficients of Eqs. 12 and 13, they are expressed as follows:

from Eq. 12,

$$\frac{\mathrm{d}\ln W(T)}{\mathrm{d}(1/T)} = \frac{\Delta E_w(T)}{R} = -B\frac{T}{T-T_0} \tag{14}$$

and from Eq. 13,

$$\frac{\mathrm{d}\ln W(T)}{\mathrm{d}(1/T)} = \frac{\Delta E_w(T)}{R} = -\frac{1}{2}T - B\frac{T}{T-T_0} \tag{15}$$

On the other hand, the discussion of various parameters in the VTF equation is tied to the correlation with the structure of the electrolyte. In particular, the discussion of T_0 has been applied to various ionic conductors with random structures, such as concentrated solutions,[75] ionic liquids,[76,77] molten salts[78] and polymer gels,[79] in addition to the application to glass materials, which were the origin of the introduction of VTF, and the correlation with structural properties is often made based on this interpretation. The interpretation of the results is often correlated with the structural properties.

In addition to cases where the temperature dependence follows either the Arrhenius or VTF equation, which is a continuous function within the measurement temperature range, there are also cases where the temperature change is abrupt and discontinuous based on phase change (melting point, transition point) or structural change (change in coordination number to ions, etc.) in the electrolyte solution. If the activation energy is calculated based on the gradient of the plot across these abrupt changes, an extremely large activation energy value is obtained. Since these abrupt changes are due to factors other than migration phenomena in the solution, the gradient should not be considered as the activation energy. At the very least, it is necessary to confirm the cause of the abrupt change in electrical conductivity, and to calculate the activation energy only in the temperature region where the stability of the system with temperature is maintained.[19,25,26]

6.5 Choice between log(σT) and log σ on the vertical axis of an "Arrhenius plot" of ionic conductivity

The temperature dependence of electrical conductivity is often plotted over a wide temperature range, and as noted in 6.3 and 6.4, the temperature dependence is shown in semi-logarithmic plots. The vertical axis is denoted here as $\log\sigma$, and on the basis of the Arrhenius equation derived from the transition state theory in ionic conduction, the plots show that a linear correlation can be obtained between $\log\sigma$ and the reciprocal of temperature, $1/T$.

On the other hand, based on the Nernst-Einstein equation, the relationship between the electrophoretic force (ionic mobility, u) acting on ions in an electric field and the driving force (diffusion coefficient, D) due to the concentration gradient in ion migration in an ion-conducting medium is expressed by the following formula,[80]

$$D = \frac{uRT}{|z|F}\left(= \frac{ukT}{|z|e}\right) \tag{16}$$

where $k = R/N_A$, $e = F/N_A$, and substituting $\lambda \equiv |z|Fu$ into this equation yields the following relationship,

$$D = \frac{uRT}{|z|F} = \frac{\lambda RT}{z^2F^2} \tag{17}$$

By the way, based on the transition state theory and free volume theory described in 6.3, as shown in Appendix B, all of the physical properties related to mass transfer, such as electrical conductivity, fluidity, and diffusion constant, show a temperature dependence based on the Arrhenius equation. However, if it is assumed that the electrical conductivity is based on diffusion phenomena in a material placed in an electric field based on the Nernst-Einstein equation, the temperature dependence of electrical conductivity is to be derived based on Eq. 16 as follows,

$$D = D_0 \exp\left(\frac{-\Delta E_a}{RT}\right) \tag{18}$$

Then,

$$\log D = \log D_0 - \left(\frac{\Delta E_a}{2.303RT}\right) \tag{19}$$

substituting Eq. 17 into Eq. 19,

$$\log D = \log(R\lambda T/z^2F^2) = \log D_0 - \left(\frac{\Delta E_a}{2.303RT}\right) \tag{20}$$

$$\log \lambda T = \log(D_0 z^2F^2/R) - \left(\frac{\Delta E_a}{2.303RT}\right) \tag{21}$$

If it is assumed that only specific (single) ion contributes to conductivity at certain concentration, i.e., $\lambda = \sigma/C$, the Arrhenius-type temperature dependence is shown to be satisfied by setting $\log\sigma T$ on the vertical axis. This difference is reflected as a slight difference when the same data is illustrated. Temperature dependence of the calculated electrical conductivities of a material following the equation (a) $\log\sigma = \log A - \Delta E_a/2.303RT$ and (b) $\log(\sigma T) = \log A - \Delta E_a/2.303RT$ for Arrhenius plots in Fig. 10. In the case of the electrical conductivity $\sigma = 1\,\mathrm{S\,m^{-1}}$ at the measured temperature $T = 500\,\mathrm{K}$ and the activation energy is $\Delta E_a = 38.29\,\mathrm{kJ\,mol^{-1}}$, adjusted electrical conductivity is $10^{-6}\,\mathrm{S\,m^{-1}}$ at 200 K for equation (a). Using equation (b), the value of σ should be compensated by the temperature change and a little more than the value for equation (a).

In considering the temperature dependence, the plots based on the transition state theory or the free volume theory, or based on the diffusion behavior are chosen. This is not a question of which to choose, but rather a necessary choice in the interpretation of the data obtained. For this reason, "$\log\sigma T$" is used when specific ions are moving or in solids such as crystals and semiconductors where the path of movement is fixed, and "$\log\sigma$" is used when multiple ions are moving along random paths.

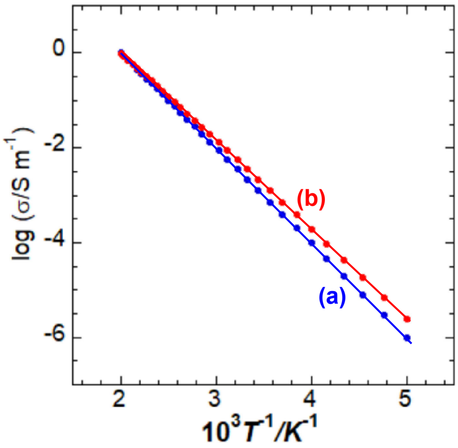


Figure 10. Temperature dependence of the calculated electrical conductivities of a material following the equation (a) $\log\sigma = \log A - \Delta E_a/2.303RT$ and (b) $\log(\sigma T) = \log A - \Delta E_a/2.303RT$ for Arrhenius plots, where the electrical conductivity $\sigma = 1\,\mathrm{S\,m^{-1}}$ at the measured temperature $T = 500\,\mathrm{K}$ and the activation energy is $\Delta E_a = 38.29\,\mathrm{kJ\,mol^{-1}}$ for which value, the electrical conductivity is adjusted $\sigma = 10^{-6}$ at 200 K for equation (a).

7. Summary

In a scientific purpose, the study of electrical conductivity and temperature dependence is very useful in discussing the physical properties of other dissolved species in solution, such as viscosity and diffusion coefficient, and since these physical properties are very sensitive to changes in these properties and vary greatly, more accurate and precise measurements are necessary.

The contents described in this paper can be understood by constructing a measurement system using a self-made cell, impedance meter, LCR meter, etc., and understanding the characteristics of each device and verifying its operation. On the other hand, commercially available electrical conductivity meters, whose primary purpose is to be used for environmental analysis, often have an interface system that prioritizes convenience, such as a temperature compensation function and other measurement modes compliant with industrial standards. Therefore, it is necessary to carefully check the operational status of the device to ensure that there is no discrepancy between theory and practice, as described in this paper.

No matter how much the accuracy and simplicity of the measurement device improves, the last remaining issue is to understand the liquid entanglement and contact around the cell, especially at the interface between the electrode and the sample, and the polarization phenomena that occur there. Even though the AC method is now commonly used, care must be taken in handling the sample. Conductivity measurement should be performed in a condition that does not affect the composition as much as possible, contrary to CV measurement that traces electrochemical reactions, and it is necessary to consider how to remove the influence of polarization while obtaining accurate measurement values.

Appendix A. Temperature Compensation of Electrical Conductivity

In ISO7888:1985 and JIS K 0130-2008, the temperature correction of the electrical conductivity of an electrolyte solution is treated as follows, assuming that the value of the electrical conductivity depends linearly on temperature.

The reference temperature for the temperature correction is 25 °C. If the electrical conductivity at that temperature is κ_{25} and the electrical conductivity at the measurement temperature at T is κ_T, the temperature compensation coefficients $\alpha_{\theta,25}$ are calculated by the following equation.

$$\alpha_{\theta,25} = \frac{\kappa_\theta - \kappa_{25}}{\kappa_{25}(\theta - 25)} \tag{A1}$$

Using the coefficients obtained here, the electrical conductivity κ of the sample is calculated from the electrical conductivity κ_θ at any temperature θ using the following equation.

$$\kappa = \kappa_\theta/\alpha_{\theta,25} \tag{A2}$$

As can be seen from this relationship, the temperature dependence of the electrical conductivity varies linearly and is based on the relationship calculated from the temperature coefficient. Since the temperature coefficient of a sample is not linear from a point of view in physicochemical properties, and the differences are very large depending on the substance and its concentration, if the electrical conductivity needs to be measured in scientific purpose, the temperature compensation function of the electrical conductivity meter or all the input temperature coefficient values must be made ineffective.

The need to introduce a temperature coefficient is due to the high need for temperature compensation when developing conductivity meters with excellent outdoor portability, such as for environmental measurements. In other words, in conductivity measurements of electrolytes containing trace amounts of ions, such as the measurement of ionic quantities in both seawater and freshwater, it is not necessary to discuss the temperature coefficient so strictly, and in many cases, emphasis is placed on concentration detection. Therefore, the priority is to calculate the temperature coefficient of typical electrolytes in advance, and to use a conductivity cell with a temperature compensation function to easily measure and compare electrical conductivity outdoors.

Appendix B. Derivation Process of the Equation Proposed by Adam and Gibbs in Ref. 69

Adam and Gibbs[69] assumed that in highly concentrated electrolyte solutions with low fluidity, ion transfer is due to the cooperative movement of all particles in a locally independent microscopic space in the liquid from a statistical point of view. The Arrhenius-type temperature dependence of the transition state theory induced by the statistical interpretation is expressed by the following Eq. B1 in terms of the probability function W for the rearrangement to occur.

$$W = A\exp(-z^*\Delta\mu/kT) \tag{B1}$$

where

z^*: Size of the smallest region where cooperative migration occurs (number of particles in the region)

$z^*\Delta\mu$: Potential energy required for rearrangement of particles in the region

k: Boltzmann constant

By the way, the rearrangement entropy per mole S_c in the macroscopic range is the sum of the product of the entropy $s_c{}^*$ in the smallest region where cooperative rearrangement occurs and the number of smallest regions in the system from a statistical mechanics viewpoint. Therefore, since all phenomena in the minimum region can be assumed to be identical, the following equation is obtained using the Avogadro constant, N_A,

$$s_c{}^*/z^* = S_c/N_A \tag{B2}$$

Substituting Eq. B2 into Eq. B1, respectively, we obtain

$$W = A\exp(-s_c{}^* N_A \Delta\mu/kT\,S_c) \tag{B3}$$

$$= A\exp(-C/T\,S_c) \tag{B4}$$

where $C = s_c{}^* N_A \Delta\mu/k$ (constant), where $s_c{}^*$ and $\Delta\mu$ are statistical constants independent of temperature.

On the other hand, using the entropy of the macroscopic system, the heat required for rearrangement in the system is expressed as the integral of the constant pressure molar specific heat, ΔC_p, integrated over a given temperature range, and thus,

$$S_\mathrm{c} = \int_{T_0}^{T} (\Delta C_\mathrm{p}/T)\mathrm{d}T \tag{B5}$$

where T_0 is the theoretical glass transition temperature at which the entropy with respect to the particle array of the entire system is zero. According to the experimental results by Angell et al., the value of ΔC_p inversely proportional to temperature in such systems.[65] Therefore, substituting the integral from Eq. B5 into equation Eq. B4, we obtain,

$$W = A\exp[-C'T/(T - T_0)] \tag{B6}$$

$$= A\exp[-B/(T - T_0)] \tag{B7}$$

Where, C' and B are constants. The assumption used to derive this equation is that ion transfer occurs cooperatively in a medium in a locally independent microscopic space. The temperature dependence of the electrical conductivity of a material with this assumption does not show a linear Arrhenius plot. A derivation of the equation for the same reason has been calculated by Angell et al. from Bond-Lattice theory.[81] The temperature dependence of the various physical properties obtained from the derivation of this probability function are expressed as follows.

Ionic conductivity $\lambda = \lambda_0 \exp[-B/(T - T_0)]$ (B8)

Fluidity $\varphi = \varphi_0 \exp[-B/(T - T_0)]$ (B9)

Ionic diffusivity $D_\mathrm{i} = D_\mathrm{i0} \exp[-B/(T - T_0)]$ (B10)

CRediT Authorship Contribution Statement

Minoru Mizuhata: Conceptualization (Lead), Data curation (Lead), Formal analysis (Lead), Investigation (Lead), Methodology (Lead), Validation (Lead), Writing – original draft (Lead)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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