포텐티오메트릭 4-전극 용기에 의한 전도도 측정

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Electrolytic Conductance Measurement using Four-Electrode Cell and Potentiometric Circuit

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요 약. 4-전극 측정 용기와 정전위 전자회로를 써서 직독식 전기전도도 측정장치를 고안하여 KCl, HCl등 전해질 용액의 전기전도도를 측정하였다. 이 장치는 상용되고 있는 브럿지회로와 2-전극 용기를 쓰는 방법에서 당면하는 어려운 문제들, 특히 전극에서의 전기 이중층의 존재와 파라디임피던스 등으로 나타나는 전기화학적으로 복잡한 성질들로 인한 문제들을 피하여 정밀하고 간편한 측정에 쓰이도록 만들었다.

ABSTRACT. A direct-reading conductance measuring system using a potentiostatic circuit and a four-electrode conductance cell was devised. The difficulties with the traditional method of using the Wheatston bridge and a two-electrode cell due to the complicated nature of the electrochemical system, the double layer capacitance and the Faradaic impedance at the electrodes, etc., could be avoided in this method. The devised instrument proved to be convenient and suitable for precise measurements. The results of measured conductivities of KCl and HCl solutions are reported.

INTRODUCTION

The conventional method of measuring conductance of electrolyte solutions relies upon the use of ac current passing through the two-electrode conductance cell. Because of the low polarization and low impedance across the platinum-electrode/electrolyte interface the resistance measured by balancing the Wheatston bridge is taken to be solely that of the electolyte solution between the two electrodes. The low impedance at the electrode surface is due to the double layer capacitance and low degree of polarization. The existence of the double layer capacitance how-ever poses a problem in obtaining a precise measurement. The capacitance is in series with the electrolyte resistance and in parallel with the Faradaic impedance due to the electrode reactions. The complete cicuit across the two electrodes in a cell therefore constitutes an equivelent circuit of complex impedance that induces a phase shift in the imposed ac current.[1,2] Analysis of the electrode processes shows also that the Faradaic impedance is a complex quantity whose magnitude and phase angle depend on the ac frequency and voltage, thus complicating the situation further.[3~5] Even with the manually adjusted compensation circuit for

the phase shift in the bridge the detection of correct null point is not always easy and sensitive.

The platinized surface of the electrodes have large capacity for adsorption and makes itself difficult to clean, contaminating the eleclrolyte under study with whatever has been brought into conact with the surface previously. Braunstein and Robbins[6] discussed many of the difficult problems associated with the traditional method of conductance measurement due to the complex nature of the electrochemical system.

Another drawback of the method of two-electrode cell in an ac bridge is that it requires balancing of the bridge in order to obtain a reading. Many of the direct-reading or automatic controll instrumentations which have been used in less accurate measurements employ the off-null signals to indicate the changes in conductance. The off-null signals are not linear with the conductance or with the resistance changes over a wide range.

In order to avoid these difficulties, a different approach which does not employ the Wheatston bridge is attempted in devising the conductance measuring instrument reported in this paper. The (outer) potential difference between any two points in an electrolyte solution can be measured by placing at each point a small opening of a capillary whose other end is enlarged to contain a reference electrode. Such capillarries are often used in electrochemical experiments that require measurement or control of potential at the immediate neighborhood of an electrode and are usually called Luggin capillaries. [5]

In a previous work on conductance of a solid electrotyte in this laboratory[7], a pair of platinum pins was used as potential probes which were brought into pinpoint contact with the side of the cylindrical sample solid. Two metal discs were attached to both ends of the cylindrical

sample to make electrical contacts for the supplied current. The resistance of the middle portion of the sample between the two pins was measured by taking the ratio of the potential difference across the two pins to the current passing through the sample. The contact resistance or the magnitude of the capacitive impedance across the sample/metal disc interface is immaterial in this method unless they are prohibitevely large for passage of current of desired magnitude. Either ac or dc current can be used in principle. In an alternative method the two pin electrodes were connected to the inputs of a differential amplifier such that the current through the sample could be adjusted by means of a feedback to fix the potential difference across the pins at a desired precise value. The current is measured in this case since it is proportional to the conductance. The method is a modification of the four-point probe method used for semiconductor films. To apply this principle to liquid electrolytes, the Luggin capillaries have to be used in place of the pins.

INSTRUMENTION

Schematic drawings of the conductance cells are presented in *Fig.* 1. Cells of both type A and type B were used to obtain satisfactory results in the actual measurements. The outer two electrodes a and a' are made of circular platinum foil of radius 0.8 cm. These are the current supplying electrodes. The identical pair of reference electrodes, c and c', are placed inside the enlarged ends of the Luggin capillaries. While an electrode itself has in general a broad area of elecrical contact with the solution, the sharp capillary ending makes a pinpoint contact between the solution and the reference electrode. The voltage across the two identical reference electrodes is therefore the potential difference between the two points in the solution at the openings
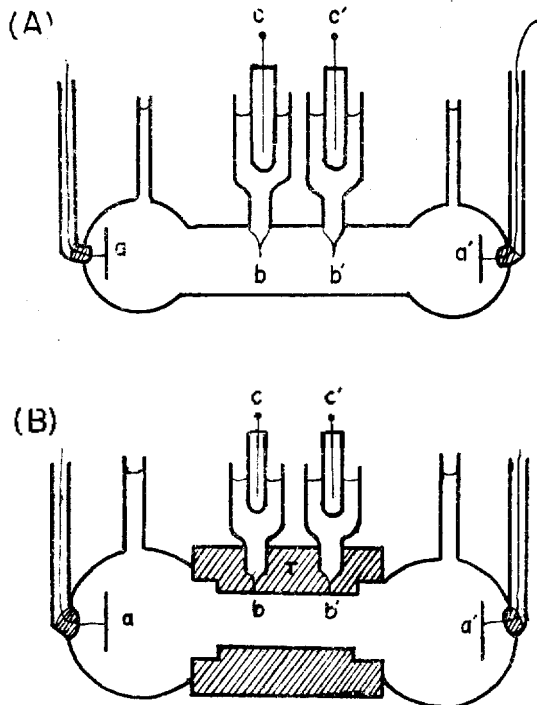
(A')

c c'

a a'

b b'

(B)

c c'

a a'

b b'

Fig. 1. Four-electrode conductance cells.

a, a' : current supplying electrodes, b, b' : Luggin capillaries, c, c' : reference electrodes, T : Teflon tube.

of the capillaries b and b. The capillaries are best filled with the same solution as the solution under study to avoid contamination of the solution being measured. The usual small sized electrodes such as silver-silver chloride or calomel electrodes are convenient to use as reference electrodes in the capillaries. The potassium chloride solutions in the electrode reservoirs in these chloride electrodes are separated from the solution in the capillaries by the asbestos wick junctions provided at the tip of the electrodes. The cell bodies and the capillaries are made of pyrex glass except the center part of the cell (B) which was made of Teflon.

Since the Teflon part of the cell(B) could be machined to a cylindrical symmetry of precise dimensions the cell constant can be known for an absolute measurement.

Fig. 2 illustrates the principles of the instru-

(A)

O

C

CONSTANT CURRENT
SUPPLY

(B)

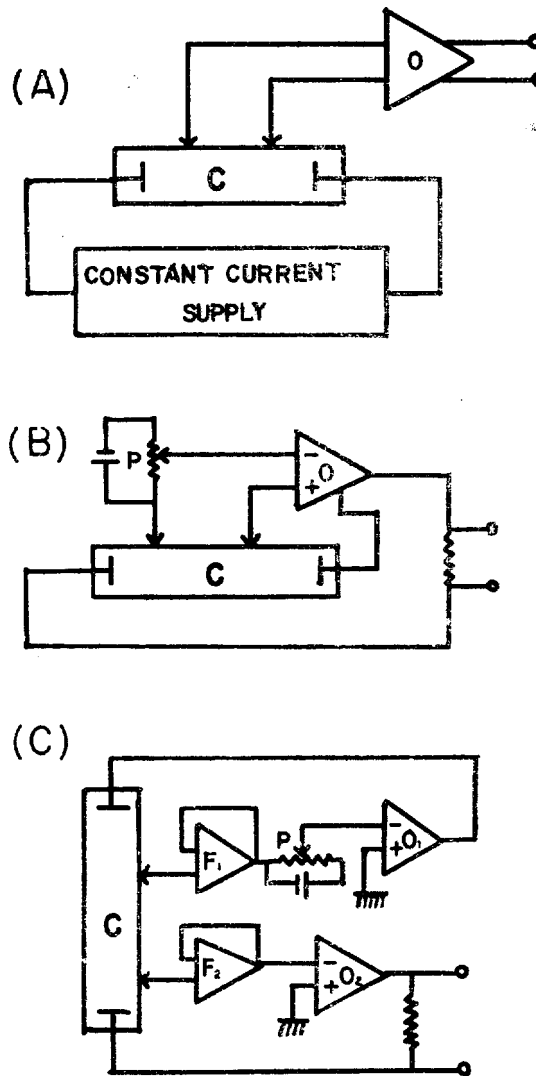P

+O

C

(C)

C

F₁ P +O₁

F₂ +O₂

Fig. 2. Block diagrams of instrumentation including four-electrode conductance cell.

F: Potential follower, O: operational amplifier, P: potentiometer, C: four-electrode cell.

mentation. In *Fig.* 2(A) the potential difference across the two probe electrodes due to the current is measured by means of a differential amplifier. Since amplifiers with extremely high imput impedance are available, the resistance of the solution in the fine capillaries does not constitute a problem. In the modification presented in *Fig.* 2(B) a desired fixed voltage is imposed

between the two points in the solution by means of a potentiometric circuit in the input stage of the differential amplifier and the feedback through the solution. This potentiotatic method proved more convenient because it does not need a precision constant current supply used in the first modification (A). A final refinement is made as in *Fig.* 2 (C) to avoid the common mode error of the differential amplifier. The system has double ended output for positive and negative currents with respect to the ground. In this circuit the common mode voltages of the input stages of all the amplifiers except the voltage follower F_1 are at the ground of the entire electrical system. The common mode input voltage of the follower F_1 is the same as the voltage fixed by the potentiometer P which does not exceed one volt in most cases, while in circuit (B) it can reach more than several volts off from ground. The voltage followers isolate the rather high resistance (up to $10 M\Omega$) of the
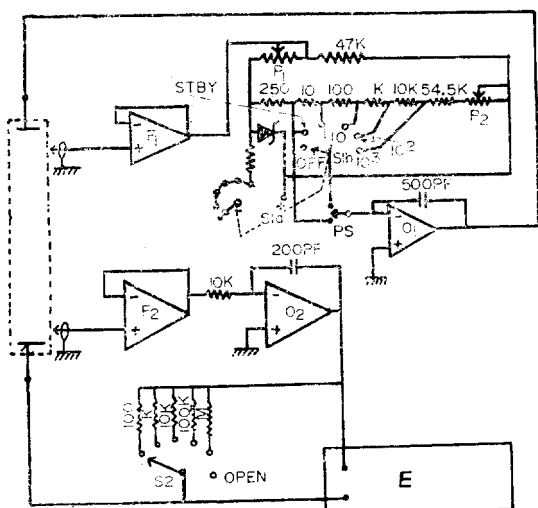

Fig. 3. Electronic circuit diagram of conductance meter.

E: electrometer or digital voltmeter, F_1, F_2: SU 536 operational amplifier with FET input stage, O_1, O_2: μA 741 operational amplifier, P_1, P_2: 1 k ohm helipot and trim potentiometer.

All resistors on S1 and S2 are selected to better than 0.1 % accuracy and are calibrated.

Luggin capillaries from the rest of the system. The system can be modified to use ac current instead of dc as presented here to prevent prolonged electrolysis. However, the alteration of the solution by the electrolysis with dc current can be held negligible by limitting the magnitude and duration of current necessary for each measurement(see DISCUSSIONS).

The actual circuit is presented in *Fig.* 3. The two voltage followers are high input-impedance operational amplifiers SU 536 and the two amplifiers used for the output stages are μA 741 stabilized by 200 pf feedback capacitors. The dc source of reference voltage in the potentiometer part between F_1 and O_1 is a regulated dc power supply and a precision zener diode. With the switch S1 at the stand-by position (0 volt) the trim potentiometer P_1 is adjusted so that there is no current through the cell and hence no voltage difference between the two Luggin capillaries. The other trim potentiometer P_2 is necessary for calibrating the input voltages at the positions of 1, 10, 100, and 1000 mV. The value of current flowing through the cell is obtained by measuring the voltage across the standard resistors. The push-botton switch PS was pressed at the time when reading is desired, this procedure being adopted to avoid unnecessarily prolonged electrolysis of the solution.

MEASUREMENTS

To test the performance of the instrument measurements were made for the conductance of 10^{-3}, 10^{-2}, 10^{-1}, and $10^0 N$ solutions of KCl and HCl. The solutions were made from the "analyzed reagents" of J. T. Baker Co. and conductance water whose conductivity was less than $10^{-7} ohm^{-1} cm^{-1}$. The cell is immersed in a thermostat water bath whose temperature is controlled to $25\pm0.01 °C$. While the solution inside the conductance cell reached the steady tem-

perature of the thermostat bath, the electronic system was readied by turning on the power and having the switch PS at the stand-by position and the switch S2 at proper voltage position. The magnitude of the input voltage is chosen for each sample solution such that it is not too small to cause a significant relative error in the operation of the system and not too large to cause a flow of large current through the cell to the extent of significant electrolysis of the electrolyte. Smaller input voltages were used for the more concentrated solutions and larger voltages were used for the more dilute solutions. The current-measuring standard resistors are selected accordingly with switch S2 to make the current measurement convenient. An electrometer or a digital voltmeter was used to measure the current. Several measurements were made for each solution by pushing the push-botton for about 5 seconds for each reading.

Since the accuracy of the measurement depends on the accuracy of the current and the applied voltage by the potentiometric circuit between the amplifiers F_1 and O_1, the standard resistors in the potentiometric circuit and the current measuring circuit were calibrated with a Leeds & Northrup universal potentiometer.

RESULTS and DISCUSSIONS

The cell constant of the type B cell used should be $3.504 \pm 0.046 \, cm^{-1}$, since its cross section is $0.4800 \pm 0.0061 \, cm^2$ and the distance between the two capillary tips is $1.682 \pm 0.001 cm$ as measured with a traveling microscope. With this value of the cell constant and the measured resistance values, the specific conductance values for KCl solutions are obtained as shown in *Table* 1. The agreement with the literature values is quite good.

The type A cell of *Fig.* 2 was tried later with equally successful results for KCl and HCl solutions, also shown in *Table* 1, when the cell constant is calibrated against a known solution. While the type B cell can be used for absolute measurement without calibration of the cell constant, type A cell can be more conveniently built.

The performance of the instrument with ac current was checked by replacing the dc power source with a sine wave generator and by viewing the current amplitude on an oscilloscope.

Table 1. Conductance, σ, and specific conductance, k, values

Electrolyte		$\sigma (ohm^{-1})$	$k_{obs.} (ohm^{-1} cm^{-1})$	$k_{lit.} (ohm^{-1} cm^{-1})$[8]	Type of cell used
$1 N$	KCl	$(3.179 \pm 0.037) \times 10^{-2}$	$(1.115 \pm 0.013) \times 10^{-1}$	1.1173×10^{-1}[**]	B
$1 N$	KCl	$(4.370 \pm 0.010) \times 10^{-2}$	$(1.118 \pm 0.004) \times 10^{-1}$	1.1173×10^{-1}	A
$10^{-1} N$	KCl	$(3.660 \pm 0.043) \times 10^{-3}$	$(1.284 \pm 0.015) \times 10^{-2}$	1.2896×10^{-2}	B
$10^{-1} N$	KCl	$(5.040 // 0.010) \times 10^{-3}$	$(1.289 \pm 0.005) \times 10^{-2}$	1.2896×10^{-2}	A
$10^{-2} N$	KCl	$(5.520 \pm 0.010) \times 10^{-4}$		1.4127×10^{-3}[*]	A
$10^{-3} N$	KCl	$(4.150 \pm 0.048) \times 10^{-5}$	$(1.470 \pm 0.017) \times 10^{-4}$	1.4695×10^{-4}	B
$10^{-3} N$	KCl	$(5.750 \pm 0.010) \times 10^{-5}$	$(1.471 \pm 0.005) \times 10^{-4}$	1.4695×10^{-4}	A
$1 N$	HCl	$(1.300 \pm 0.005) \times 10^{-1}$	$(3.326 \pm 0.013) \times 10^{-1}$	3.323×10^{-1}[***]	A
$10^{-1} N$	HCl	$(1.542 \pm 0.005) \times 10^{-2}$	$(3.945 \pm 0.015) \times 10^{-2}$	3.9132×10^{-2}	A
$10^{-2} N$	HCl	$(1.615 \pm 0.005) \times 10^{-3}$	$(4.133 \pm 0.016) \times 10^{-3}$	4.1200×10^{-3}	A
$10^{-3} N$	HCl	$(1.650 \pm 0.005) \times 10^{-4}$	$(4.222 \pm 0.016) \times 10^{-4}$	4.2136×10^{-4}	A

*This value used for calibration of the cell constant of the type A cell.
**from ref. 1
***from ref. 9

Up to frequency of 100 kHz measurement of the conductance gave same result as the dc measurement within the accuracy of the amplitude of the ac voltage. Since the accuracy of the dc voltage is better than that of ac voltage and with dc there is no spurious effects of stray reactances, the use of dc is preferred. The electrolysis of the solution with dc current does not cause a change in the composition of the solution to a significant extent. With the most dilute solution used, $10^{-3} N$ KCl, an input voltage of 10^3 mVolt causing current flow of about 6×10^{-2} mA was sufficient for good precision of measurement. The amount of charge passed during the 5 seconds of measurement is less than 10^{-8} Faraday. The maximum decrease of the electrolyte concentration or increase of hydronium or hydroxyl ion concentration in the 30 ml cell is less than $10^{-6} N$. For the concentrated solution, $1 N$ KCl, an input voltage of 10 mV causing current flow of 0.5 mA was a proper choice. The resulting concentration change during the 5 seconds measurement is less than $10^{-5} N$ at the maximum which is negligibly small compared to the concentration of the electrolyte itelf. The feasibility of dc measurement of conductance was also demonstrated earlier by Gunning and Gordon[10] at least for some solutions.

Since it is a direct reading instrument the measurement is faster compared to the time of manual adjustment of the Wheatston bridge in the traditional Kohlrausch method. The response of the circuit is fast enough to permit a recording of transient changes in conductance on a strip chart recorder or an oscilloscope. This is one of the particular feature of the system making it suitable for kinetics studies, conductometric titrations, or automatic control in the flow systems. A direct reading conductance apparatus recently designed by Cyr, Prudhomme, and

Zador[11] is an improvement over the previous direct reading instrumentations for better linearity. However, this device using still the two-electrode cell and ac current does not exclude the source of error due to the capacitive component of impedance through the electrochemical cell. Anderson, Brookes, Hotz and Spong[12] reported development of a four-electrode alternating current potentiometer device for conductance measurement. In their instrument a pair of platinum wire pieces were used as the potential probes and two bright platinum electrodes were used as the current suppliers. They reported that in this way the undesirable effects due to electrode polarization and to the use of platinized electrodes in the conventional method could be avoided. However, a bare platinum wire immersed in an electrolyte solution is poor reference electrode in the sense that it does not constitute a reversible electrode. A pair of such metal pieces can not only aquire a finite potential difference in the absence of current but also the voltage is quite unstable. An ac signal picked up by such a pair can be distorted therefore. The Luggin capillary reference electrode combination is therefore believed to be an ideal potential probe to be used in a four-electrode cell.

ACKNOWLEDGEMENTS

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