*The Alternating Current Polarisation with Respect to Hetero-Pair Electrodes**

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Introduction

It was long ago when the galvanic polarisation such as the polarisation capacitance and the polarisation resistance, caused by alternating current, came into our knowledge.

As was shown in some reviews made recently by one of the present authors[1] and also by Shaw and Remick[2], many investigators have been concerned with the problem either theoretically or experimentally for the past 70 years or more.

In spite of the fact that the theoretical treatments were carried out in detail from the various standpoints, the experimental investigations did not give us any satisfactory explanation for the nature of the polarisation effect. One of the causes of the present meagre experimental knowledge is the difficulty of the measurement of this sort. Above all it is serious that exact reproducibility can never be attained. In fact, all the investigators have stated that the observed values change, not only from one sample of the liquid to another, or from one set of the electrodes to another, but also change with time for the same set of electrodes and the same sample of liquid.

Here we want to verify a fundamental character of polarisation effect, caused by the application of alternating current, which has been assumed tacitly by prior investigators. In other words, our main subject is to know whether the polarisation characters, measured as to a whole cell, can be attributed to each single electrode or not.

No such attempt has been made so far as we aware.

Robertson[3] attempted to determine the polarisation capacitance for a single platinum electrode immersed in hydrochloric acid solution, along the line indicated by Grahame[4] for dropping mercury electrode.

Though his experiments were carried out also for the polarisation capacitance of the single electrode of solid metal, the effect observed was essentially the direct current polarisation, in which the steady state may be reached, We are going to study the problem in a different way.

Experimental

The measuring devices consist of an ordinary impedance bridge and an audio frequency generator. The latter was made in our laboratory. The frequency was kept at 1440 cycles per second, which was corrected with a standard oscillator. A variable air condenser attached to the balancing arm of the bridge changes in its capacity from 1.11μF. to 0.0001μF.

Since the principal purpose of this experiment was the attribution of the polarisation characters to each component electrode (electrode/soln. interface), several kinds of metals were prepared for electrode materials, each having the same dimension, that is, the disk plate having 2 cm. in its diameter. Metals prepared were Pt, Ni, Cu and Ag. Copper electrode was electropolished before each measurement. Nickel and silver electrodes were prepared by means of electroplating on the copper surface. The solutions investigated were N/100, N/10 and 1N KCl aqueous solution. Alcoholic solutions of KCl in two different concentrations were also investigated. One of these alcoholic solutions was made in the following way: 2 cc. of 1N KCl aqueous solution was dropped into 1 litre of 96% ethyl alcohol and after vigorous shaking the bottle was kept still at 0°C for a day, then the excess precipitation of potassium chloride was separated by careful decantation. A portion of the saturated solution, thus obtained, was diluted by ninefold amount of ethyl alcohol.

Measurements were carried out at 28°C and at 0°C, the former temperature was obtained by means of well regulated thermostat and the latter was kept by means of ice-water mixture.

Figure 1a shows the conductivity cell which is made of Telex glass and has been used for all of the experiments. As is clearly seen, from the figure, both of the two electrodes are allowed to move so as to be able to determine the polarisation resistance in such a way as will be explained in the following article.*

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* The terms homo-pair electrodes and hetero-pair electrodes are defined as a set of electrodes consisting of the same or different metals, respectively.

[1] S. Nagaura, *J. Electrochem. Soc. Japan*, **19**, 249 (1951).

[2] M. Shaw and A. Remick, *J. Electrochem. Soc.*, **97**, 324 (1950).

[3] W. Robertson, *J. Electrochem. Soc.*, **100**, 195 (1953).

[4] D. C. Grahame, *J. Am. Chem. Soc.*, **68**, 301 (1946); *Chem. Revs.*, **41** 441 (1947).

A Short Explanation of the Equivalent Series Circuit

Though most investigators have treated their measured quantities of the polarisation phenomena using the equivalent series circuit, no serious discrepancy has appeared in such treatment.

Warburg first suggested and developed the idea that the diffusion is responsible for the incomplete reversibility of the electrode reactions. By the integration of Fick's law of diffusion with suitable boundary conditions he reached the conclusion that polarisation causes a capacitance in series with the resistance of the electrolyte. His theory has been extended by many authors thereafter, but owing to their different viewpoints, there exist several kinds of equivalent circuits for an electrolytic cell (See Ref. 1). Some of them, however, can not be adopted practically because of the complexity of their circuit elements.

Kohlrausch first found that the inverse electromotive force, Ep, caused by polarisation, is proportional to the amount of electricity passed through the cell, i.e.,

$$Ep=1/C\int Idt. \tag{1}$$

If the current, I,is alternative and expressed as $I=Io$ sinωt, Eq. 1 then becomes

$$Ep=Io/\omega C\ \sin(\omega t-\pi/2). \tag{2}$$

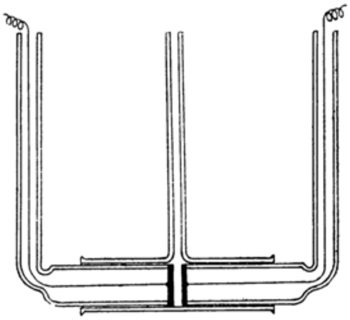

Fig. 1 a. Conductivity cell

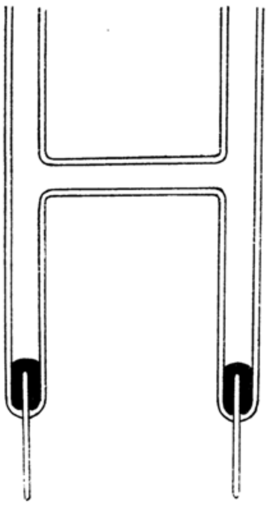

Fig. 1 b. H-Form electrode

This means that Ep is equal to the voltage drop which occurs when a.c., $I=Io$ sinωt, passes through a condenser of capacity C.

Wien suggested that the formula on Ep must have a term with regard to the phase difference, φ, i.e.,

$$Ep=Io/\omega C\ \sin\left\{\omega t-(\pi/2-\varphi)\right\}. \tag{3}$$

This equation means that Ep is equal to the voltage drop which occurs when a.c. is applied to a series circuit consisting of a condenser of capacity $C/\cos\varphi$ and a resistor of resistance $\sin\varphi/\omega C$.

Figure 2a is a schematic expression of the equation 3.

In this work we assume the identical behavior of the two electrodes, thus the equivalent circuit can be expressed as in Fig. 2b.**

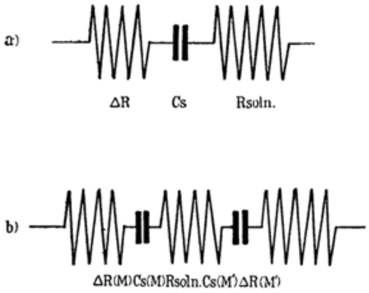

Fig. 2a. Equivalent circuit

Results and Discussion

Reproducibility of the Measurements.—At first, the effect of the immersion time and the reproducibility of the measurements were detected.

Shaw and Remick reported that when the platinum electrodes are combined together electrically and used as the anode for the electrolysis of alkaline cyanide solution before each conductivity measurement, reproducible results were obtained. As far as we repeated their experiment, however, the satisfactory agreement with them was not recognised. Moreover the systematic influence of the electrolysis was not observed. This is shown in Table 1. In Table 1, Rp and Cp are the values of bridge readings and Rs and Cs are of those converted into series circuit, respectively.

From the Table we can not see any regenerative effect of the electrolysis. (Some atten-

TABLE I.*

Immersion time (min.)	$Rp(\Omega)$	$Cp(\mu F.)$	$Rs(\Omega)$	$Cs(\mu F.)$
1) Anodic treatment; 15 min..				
0	711	0.1051	48.7	3.33
80	628	0.0914	49.4	4.27
220	619	0.0884	49.6	44.4
2) Anodic treatment; one hour.				
0	615	0.0899	49.1	4.45
3) Anodic treatment; 12 min..				
0	760	0.1063	49.3	3.03
10	752	0.1059	49.7	3.11
50	757	0.1068	49.1	3.04
105	762	0.1079	48.8	3.03
4) Anodic treatment; 20 min..				
0	789	0.1068	49.3	2.71
20	775	0.1059	49.5	2.71
50	776	0.1080	49.4	2.58

* The values are arranged in order of the measurements.

It is seen from the table that the values do not depend on the time of anodic treatment but on the immersion time.

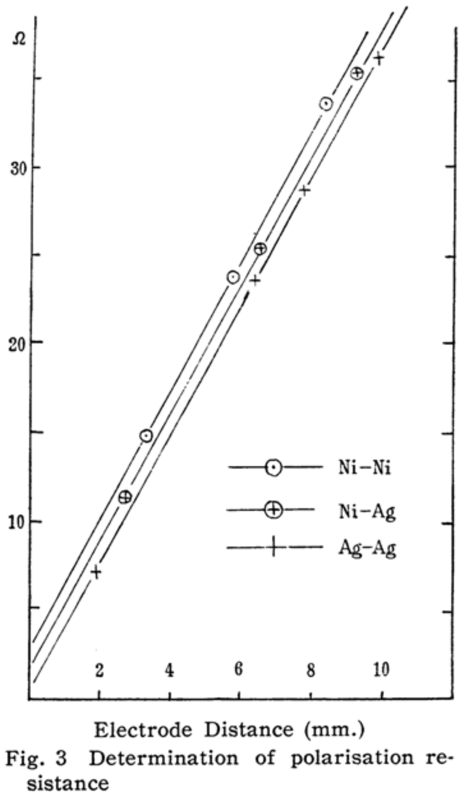

Fig. 3 Determination of polarisation resistance

tion must be given to zero minute values.)

These observations were made by H-form platinum electrodes, which are shown in Fig. 1b, in a wide porcelain bath at room temperature.

Shaw and Remick also stated the effects of immersion as follows:

1) The electrodes were immersed for one hour before taking a reading. Then they were removed from the measuring solution and washed with hot water just before boiling. Finally, the electrodes were returned to the cell and Cs was immediately determined. The result was the same to " one hour value ".

2) The changes of Cs with time, whatever their nature, were essentially independent of any application of the current.

These results were in agreement mostly with our trace experiment.

In consequence, we conclude that the " aging process " of the electrodes makes it impossible to determine the absolute values of the polarisation impedances for all the individual electrode, owing to the incomplete reversibility of the a.c. electrode reactions, and special precautions have to be taken even to obtain relative values which are comparable.

A similar opinion was reported by jaffé and Rider⁵⁾ recently. In this connection, Jones and Christian⁶⁾ reported that their Cs value with silver electrodes was greater than that for platinum, while Wien had obtained the contrary results. Thus it is also doubtful whether it is possible to determine the order of the Cs values of various metals. From the above arguements, it must be said that absolute order can not be obtained in practice, owing to instability of each metal surface against the action of alternating current and this inability is not because of the experimental mistake.

Thus in the following experiments we took

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5) G. Jaffé and A. Rider, *J. Chem. Phys.*, **20**, 1077 (1952).

6) G. Jones and S. Christian, *J. Am. Chem. Soc.*, **57**, 272 (1935).

great care to get reliable data; we need the data only for comparison. In other words, a series of experiments should be completed without delaying.

Additivity of the Polarisation Characters with Respect to a Single Electrode.—Since the arrangement of the balancing arm of the bridge is in parallel, impedances of each element of Fig. 2a is easily calculated by the following relations;

$$Rs = Rt + \Delta R = n(Rp/1+\omega^2 Cp^2 Rp^2) \qquad (4)$$

$$Cs = 1/n \cdot Cp(1+1/\omega^2 Cp^2 Rp^2) \qquad (5)$$

where n is the arm ratio of the bridge, and suffixes s and p are taken to mean the series and parallel values, respectively.

As far as we deal with the homo-pair measurements, these series values are easily divided into two parts corresponding to each metal/soln. interface. The values for hetero-pair electrodes may be calculated from the values of homo-pair measurements and also by direct measurements. The results thus obtained for aqueous KCl solutions are tabulated in Table II. Values in Table III are those for KCl saturated ethyl alcohol.

In general, the same kind of experiments were carried out two or three times and the tabulated values are the averages of them.

Although it seems that *Cs* values for N/100 KCl aq. soln. disprove the simple additivity of the polarisation characters, most of them for N/10 KCl aq. solns. and especially for alcoholic solutions confirm our assumption with relatively high concordance. The *Cs* values of Cu-Pt system in Table II is something erratic, perhaps due to chemical instability of copper in aqueous solution, while the same system in alcoholic solution gives a good agreement between the observed value and the calculated one. The discrepancies which appear in " N/100 measurements " were

TABLE II

ADDITIVITY OF POLARISATION IMPEDANCES FOR AQUEOUS SOLUTIONS

A) N/10 KCl aq. soln. at 28°C

System	$\Delta R(\Omega)$		$Cs(\mu F.)$	
	Obs.	Calc.	Obs.	Calc.
Pt-Pt	3.0	—	12.2	—
Ni-Ni	12.6	—	4.5	—
Cu-Cu	3.4	—	21.4	—
Ag-Ag	1.5	—	25.5	—
Ag-Pt	1.5	2.2	11.4	16
Cu-Pt	3.5	3.2	9.3	14
Ni-Pt	6.7	7.8	6.7	6.6
B) N/10 KCl aq. soln. at 0°C				
Ni-Ni	2.6	—	16.1	—
Ag-Ag	0.8	—	37.0	—
Ag-Ni	1.6	1.6	22.3	21.3
C) N/100 KCl aq. soln. at 0°C				
Ni-Ni	40	—	1.4	—
Ag-Ag	5	—	7.6	—
Pt-Pt	uncertain	—	1.6	—
Ag-Ni	10	20	6.8	2.4
Pt-Ni	uncertain	uncertain	4.7	1.5

TABLE III

ADDITIVITY OF POLARISATION IMPEDANCES FOR ALCOHOLIC SOLUTIONS

System	$\Delta R(\Omega)$		$Cs(\mu F.)$	
	Obs.	Calc.	Obs.	Calc.
Ni-Ni	70±30	—	4.8	—
Ag-Ag	130 „	—	12.5	—
Pt-Pt	uncertain	—	9.1	—
Cu-Cu	30±30	—	20.1	—
Ag-Ni	70±„	uncertain	6.5	6.9
Pt-Ni	140 „	„	6.1	6.0
Pt-Cu	50 „	„	12.6	12.5
Pt-Ag	140 „	„	11.1	10.4

not changed by the second runing reexamined one month after the first experiment.

It may be thought that in a dilute solution the solvent molecule as a role to make these discrepancies. In this connection, we made a series of experiments using a dilute alcoholic solution. The result confirmed the additive characters of the effect. This is seen in Table IV.

TABLE IV

ADDITIVITY FOR DILUTE ALCOHOLIC SOLUTIONS

System	Cs (μF.)	
	Obs.	Calc.
Ag-Ag	21.8	—
Ni-Ni	5.0	—
Ag-Ni	8.2	8.1

" N/100 values ", however, are only two sets of electrodes, therefore more detailed investigations with various sets of electrodes are necessary. At the same time the study must be carried out about more dilute solutions.

The polarisation resistance, ΔR,which is often called excess resistance, can be determined by changing the distance of electrodes; since the polarisation resistance is characteristic only of the electrode/solution interface and not affected by inter-electrode distance, if the frequency is kept constant.[1,6] Therefore we can obtain the ΔR value by plotting measured series resistance, Rs, against the electrode separation and read the extrapolated value of Rs at zero distance. Fig. 3a is one of the representative diagram for ΔR determinations. ΔR values for N/100 aqueous potassium chloride solutions and also for alcoholic solutions are very erratic, because our conductivity cell has no elaborate attachment to determine the interelectrode distance and therefore we can read only the order of the magnitude, when the solution is less conductive.

Summary

1) We attempted to prove that the polarisation characters, being measured as to a whole cell, can be attributed to each single electrode. This attempt was verified by most of the experiments.

2) The above success may be one of the experimental justifications to use a simple series circuit as the equivalent circuit of a conductivity cell.

3) Discordant results appearing in " N/100 measurements " are to be studied in more details.

The authors wish to express their great thanks to the effort made by Mr. Koichi Karaki, our former collaborator.

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