

1. Study on Surface Electricity. (XIII)¹⁾

On Multi-electrode Phenomena in Solution

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When the potential differences at metal-electrolyte solution interfaces are altered slightly from their equilibrium states, several cases can be seen according to the amount of continuous current in the outer circuit. They are classified in three: (1) no continuous current is detected, (2) a stationary current flows which is determined by the ohmic resistance of the system and (3) (when the polarization back electromotive force is neglected) a smaller continuous current flows than is determined by Ohm's law. The former two are called (1) ideal polarized electrode -- which behaves like an electrical condenser without leakage -- and (2) ideal non-polarizable electrode -- its potential is independent on the amount of electricity which passes through it²⁾. The last one situates between these two. Though we have studied so far on those which belonged to the first category,³⁾ it is also a matter of importance to clarify the phenomena at the second kind of electrodes.

Here we used three electrodes each having different electrical potentials. This system corresponds to a triode valve, but, the resistance of solution being very small compared with the inner resistance of the valve, it is controlled by current rather than by voltage and resembles to the semiconductor triode. (e. g. Ge-transistor.)

This system differs from the one in which two of the three electrodes are in the same potential,⁴⁾ which is essentially the ordinary two electrode system and either of the two electrodes is divided in two parts. Of course our system obeys Kirchhoff's law and is no more than a combination of two electrode systems, but our interest lies in the variable polarization phenomena of such a network of circuits.

1. Circuit

Three electrodes 1, 2 and 3 are dipped in an electrolytic cell at the position of each apex of a regular triangle, and electromotive forces ${}_1E_2$ and ${}_2E_3$ and load resistances ${}_1R$ and ${}_2R$ are connected in series between 1 and 2 and also 2 and 3 as are shown in Fig. 1. This network has two independent closed

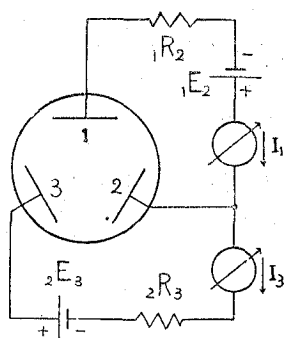


Fig. 1.

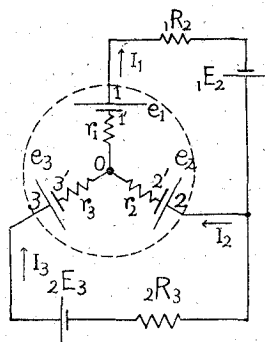


Fig. 2.

circuits, and so we need only to measure two current strengths, e. g. I_1 and I_3 .

Now we denote the single electrode potential differences¹⁾ of the electrodes at equilibrium (viz. the potential at the bulk of the solution) by e_1 , e_2 and e_3 . When currents flow through them, several polarization phenomena arise at each interfaces, which are included in e_i 's here. The solution resistances r_1 , r_2 and r_3 are taken for simplicity to be in star connection.

With these symbols and assumptions the equivalent circuit of this system can be pictured as in Fig. 2*. We now change E 's and R 's and observe the change in I_1 and I_3 (and I_2), from which Δe , Δr etc. are calculated.

2. Experimental

(1) Control of anodic oxide film. In case of a transistor, it is the change of space charge layer at collector (anodic) point contact by emitter (grid) current which controls the collector current.⁴⁾ In our case too, we considered a device to control the anodic current (I_1), applying the fact that the oxide film of an electrolytic condenser shows characteristic features against the change in potential or current. That is, we altered grid (electrode 3) potential near that of anode (electrode 2), by which the thickness of the anodic oxide film was changed and hence the current I_1 between electrodes 1 and 2 was also changed. (Resistance polarization).

A beaker of 100 c. c. was filled with 5 % $(\text{NH}_4)_2\text{B}_4\text{O}_7$ aq., in which electrodes 1 and 2 of clean aluminum foils were immersed. The forming of electrode 2 was performed with ${}_1E_2 = 6 \text{ V.}$, ${}_1R_2 = 100 \text{ k}\Omega$ and ${}_2R_3 = 10 \text{ k}\Omega$. Electrode 3 was a platinum wire. After a short time I_1 became constant and the forming ended. Now we changed ${}_2E_3$ (grid bias) from 8 V. to -1.0 V. , and observed I_1 and I_3 . They are tabulated in Table 1 column 2 and 3 (static character). The values of I_2 were calculated from $I_2 = I_1 - I_3$ and also shown in the forth column. If e_i 's and r_i 's were constant, I_1 , I_2 and I_3 would become linear functions of ${}_2E_3$ as easily shown by Ohm's law. The curves in Fig. 3 are these functions, which do not show linearity. From this fact we can deduce that the thickness of the oxide film at electrode 2 changed with ${}_2E_3$.

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Table 1.

${}_1E_2 = 6V.$ 5% 1: Al
 ${}_1R_2 = 100K\Omega$ $(NH_4)_2B_4O_7$ 2: Al
 ${}_2R_3 = 10K\Omega$ aq. 3: Pt

${}_2E_3$ (Volts)	I_1 (μA)	I_3 (μA)	I_2 $=I_1 - I_3$ (μA)	$I_3 \cdot {}_2R_3$ (Volts)	${}_2E_3'$ $={}_2E_3 - I_3 \cdot {}_2R_3$ (Volts)	${}_2E_0$ $={}_2E_3' - 1.5$ (Volts)	r_2 $={}_2E_0/I_2$ ($K\Omega$)
8.0	59.4	570.0	-510.6	5.70	2.30	1.28	2.5
7.5	59.8	520.0	-460.7	5.20	2.30	1.28	2.7
7.0	59.1	475.0	-415.9	4.75	2.25	1.23	2.9
6.5	59.0	425.0	-366.0	4.25	2.25	1.23	3.4
6.0	58.8	380.0	-321.2	3.80	2.20	1.18	3.7
5.5	58.5	335.0	-276.5	3.35	2.15	1.13	4.1
5.0	58.1	295.0	-236.9	2.95	2.05	1.03	4.3
4.5	57.7	255.0	-197.3	2.55	1.95	0.93	4.7
4.0	57.0	219.0	-162.0	2.19	1.81	0.79	4.9
3.5	55.7	189.0	-133.3	1.89	1.61	0.59	4.1
3.0	54.5	126.0	-71.5	1.26	1.74	0.72	11.0
2.5	54.0	88.8	-34.8	0.89	1.61	0.59	17.0
2.0	52.9	68.5	-10.6	0.64	1.35	0.34	32.0
1.5	50.3	48.3	2.1	0.48	1.02	0	
1.0	46.9	41.3	5.7	0.41	0.59	-0.43	76.0
0.5	44.0	27.8	16.3	0.28	0.22	-0.80	49.0
0.0	42.4	3.0	39.4	0.03	0.97	-0.05	1.3 (?)
-0.5	42.2	0.0	42.2	0.00	-0.50	-1.52	36.0
-1.0	42.2	-0.4	42.6	-0.004	-1.00	-2.02	47.0

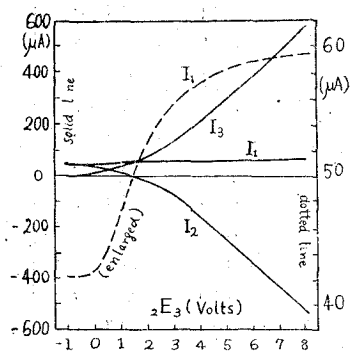


Fig. 3.

The voltage amplification coefficient $|\mu| = |{}_1R_2 \cdot \partial I_1 / \partial {}_2E_3|$ was always smaller than unity from the above figures. Between ${}_2E_3 = 0 - 3V$, the slope of I_1 was comparatively large.

To get the net potential differences between 2 and 3 we must subtract from ${}_2E_3$ the potential drop in ${}_2R_3$. The values of $I_3 \cdot {}_2R_3$ and ${}_2E_3' = {}_2E_3 - I_3 \cdot {}_2R_3$ are shown in column 5 and 6.

When $I_2 = 0$, the points 0 and 2' in Fig. 2 are in the same potential, i. e. ${}_2E_3 = 0$ (see later, chapter 3). From the above table, it was at ${}_2E_3 = 1.5V$ or ${}_2E_3' = 1.02V$, whence the potential differences between 0 and 2' were obtained from ${}_2E_0 = {}_2E_3' - 1.5$ (column 7).

Now, assuming boldly the constancy of e_2 , we can calculate r_2 by $r_2 = {}_2E_0 / I_2$ (anodic resistance polarization). Their values are tabulated in column 8, and $r_2 - {}_2E_0$ curve is shown in Fig. 4. A striking change from several $k\Omega$ to near $100k\Omega$ can be seen.

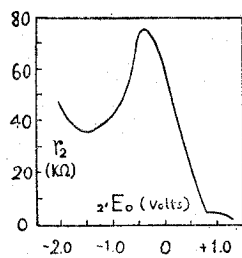


Fig. 4.

As is known commonly, oxide film of aluminum presents rectifying action⁸⁾ and it is hard for current to pass from aluminum metal to solution. In our case, when $I_2 > 0$ (or ${}_2E_0 < 0$), r_2 is higher and when $I_2 < 0$ (or ${}_2E_0 > 0$), it is lower. That is, the latter case shows normal resistance ($\overrightarrow{r_2}$) and the former inverse resistance ($\overleftarrow{r_2}$), and $\overrightarrow{r_2} < \overleftarrow{r_2}$.

The behaviors near ${}_2E_0 = 0$ (i. e. $I_2 = 0$) are interesting and a detailed examination between ${}_2E_3 = 0.3$ and 2.5 V. showed the results shown in Table 2 and Fig. 5.

Table 2.

${}_1E_2 = 6V$ 5% 1: Al
 ${}_1R_2 = 100K\Omega$ (NH₄)₂B₄O₇ 2: Al
 ${}_2R_3 = 10K\Omega$ aq. 3: Pt

${}_2E_3$ (Volts)	I_1 (μA)	I_3 (μA)	I_2 = $I_1 - I_3$ (μA)	$I_3 \cdot {}_2R_3$ (Volts)	${}_2E_3'$ = ${}_2E_3 - I_3 \cdot {}_2R_3$ (Volts)	${}_2E_0$ = ${}_2E_3' - 1.3$ (Volts)	r_2 = ${}_2E_0/I_2$ (Ω)
2.5	52.5	75.8	-24.3	0.77	1.73	0.91	$3.8 \cdot 10^4$
2.4	52.3	74.0	-21.7	0.74	1.66	0.84	3.9 "
2.3	51.9	70.0	-18.1	0.70	1.60	0.78	4.3 "
2.2	51.4	66.5	-15.5	0.66	1.54	0.76	4.9 "
2.1	50.8	63.5	-12.7	0.64	1.46	0.64	5.0 "
2.0	50.3	60.0	-9.7	0.60	1.40	0.58	6.0 "
1.9	49.9	57.3	-7.4	0.57	1.33	0.51	6.9 "
1.8	49.4	54.5	-5.1	0.55	1.25	0.43	8.4 "
1.7	49.0	52.3	-3.3	0.52	1.18	0.35	10.9 "
1.6	48.5	50.5	-2.0	0.50	1.10	0.28	14.0 "
1.5	48.0	49.0	-1.0	0.49	1.01	0.19	19.0 "
1.4	48.0	48.6	-0.6	0.49	0.91	0.09	15.0 "
1.3	48.0	48.0	0.0	0.48	0.32	0	
1.2	47.8	47.5	0.3	0.48	0.72	-0.10	33.3 "
1.1	47.0	47.2	-0.2	0.47	0.63	-0.19	95.0 "
1.0	46.2	46.5	-0.3	0.47	0.53	-0.29	96.7 "
0.9	45.4	45.7	-0.3	0.46	0.44	-0.38	123.7 "
0.8	44.8	45.0	-0.2	0.45	0.35	-0.47	235.0 "
0.7	44.0	44.5	-0.5	0.45	0.25	-0.57	114.0 "
0.6	43.3	43.0	0.3	0.43	0.17	-0.65	216.7 "
0.5	42.5	41.0	1.5	0.41	0.09	-0.73	48.7 "
0.4	42.2	36.0	6.2	0.36	0.04	-0.78	12.6 "
0.3	42.0	29.0	13.0	0.29	0.01	-0.81	6.2 "

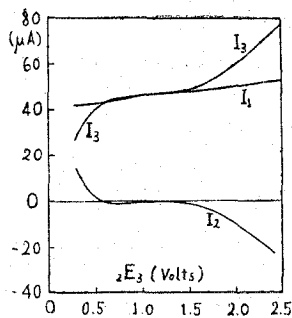


Fig. 5.

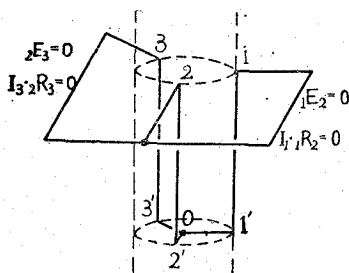


Fig. 6.

(2) Reversible electrode potential.⁷⁾

When the three electrodes 1, 2 and 3 are of the same material, their single electrode potentials are equal, i. e. $e_1 = e_2 = e_3 = e$. So, when ${}_1E_2 = {}_2E_3 = 0$, the potential distribution in the system can be represented as in Fig. 6. The usual electrochemical practice to avoid confusion resulting from the indefinity of single electrode potential⁸⁾ is to define the reversible hydrogen electrode potential e_H . This corresponds to cut the cylinder representing the solution at $e_H = 0$, by which the absolute distance from I to I' is determined.

Now it is when there is potential gradient on the solution plane ($1', 2', 3'$) that current flow occurs in the system.

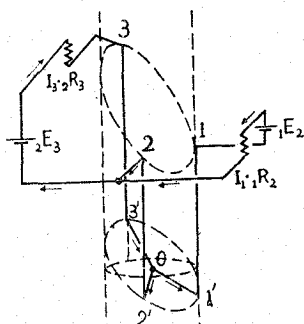


Fig. 7.

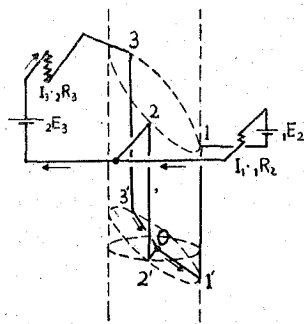


Fig. 8.

When ${}_1E_2, {}_2E_3 \neq 0$, the potential diagram is distorted as in Fig. 7, ${}_1E_2, {}_2E_3, I_1 \cdot {}_1R_2, I_2 \cdot {}_2R_3$, potential drop in solution and the polarization at electrodes being in equilibrium. Though, owing to the polarization at electrodes, the potential gradients at interfaces cause definite curvatures of solution plane at $1', 2'$ and $3'$, they are included for simplicity in $\triangle e_1, \triangle e_2$ and $\triangle e_3$. Here also star connection of current fluxes were assumed and its centre O was taken as the bulk of solution. When $I_2 = 0, 0$ and $2'$ are in equilibrium (Fig. 8), and there is no current flow through electrode 2, i. e. this is in reversible equilibrium potential. In other words, when $I_2 = 0$, the potentials of 1 and 3 are their overpotentials and $I_1 (= I_2)$ is the current flowing through them.

The experiment was performed with copper electrodes in 0.5 mol CuSO_4 aq., and ${}_1R_2$ and ${}_2R_3$ were each 10 $k\Omega$. Changing ${}_2E_3$ from 0.1 to 1.1 V., we measured the values of ${}_1E_2$ and I_1 so as to

make I_2 null. (I_2 was observed with a galvanometer). They are tabulated in Table 3, column 1, 2 and 3. From these values we can calculate the cathodic (1)

Table 3.

${}_1R_2=10K\Omega$ 0.5M. 1:Cu
 ${}_2R_3=10K\Omega$ CuSO₄aq. 2:Cu
 $I_2=0$ 3:Cu

${}_2E_3$ (Volts)	${}_1E_2$ (Volts)	I_1 $=I_3$ (μ A)	ΔE_C $={}_1E_2 - {}_1R_2 \cdot I_1$ (Volts)	ΔE_A $={}_2E_3 - {}_2R_3 \cdot I_1$ (μ A)	ΔE $=\Delta E_C + \Delta E_A$ (Volts)
1.1	1.0925	107.5	0.0175	0.025	0.0425
0.9	0.8945	87.9	0.0155	0.020	0.0355
0.7	0.6970	68.3	0.0144	0.016	0.0304
0.5	0.5011	49.3	0.0071	0.007	0.0141
0.3	0.3025	29.6	0.0035	0.004	0.0105
0.1	0.1020	10.0	0.0020	0.000	0.002

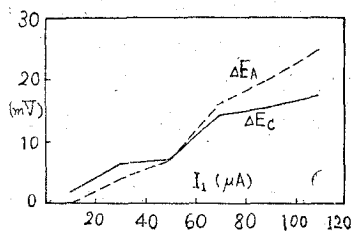


Fig. 9.

and anodic (2) overpotentials by

$$\Delta E_C = {}_1E_2 - I_1 \cdot {}_1R_2.$$

$$\Delta E_A = {}_2E_3 - I_3 \cdot {}_2R_3.$$

ΔE_C , $\Delta E_A - I_1$ curves are shown in Fig. 9, which indicate that the potential distribution in an electrolytic cell are in general not uniform.

Summary

We succeeded in controlling the resistance polarization at anodic surface film by a third electrode having slightly different potential from the anodic voltage. The circuit of this device resembled the Ge-transistor, but as the inner resistance in the solution was very low compared with that of the latter, it did not display the voltage amplification action.

When we controlled so as to putting the current passing through the central electrode to zero, this electrode was in the reversible equilibrium potential, which we could make the standard electrode against the other two electrodes. We tested the potential distribution between the anodic and cathodic portions when electrolysis was in operation between these two electrodes. We used copper as the three electrodes and 0.5 mol CuSO₄ as the solution. The overpotentials of the anodic portion was smaller than that of the cathodic portion at lower current densities and vice versa at higher current densities.

Acknowledgments

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References and Notes

- 1) This article was read before the semi-annual meeting of this Institute on Dec. 1, 1951.
- 2) Ueda and Watanabe, Chem. and chem. Ind., 4, 316 (1951); Grahame and Whitney, J. A. C. S., 64, 1548 (1942); Chem. rev., 41, 441 (1947); Craxford, Trans. Faraday Soc., 36, 85 (1940).
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- 4) Bardeen and Brattain, Phys. rev., 75 1238 (1949).
- 5) Hoar and Agar, Disc. of the Faraday Soc., No. 1, 162 (1947). etc.
- 6) It is impossible to measure this potential difference. We cannot avoid the absolute single electrode potential in picking up the potential of the bulk of solution. See for instance: Guggenheim, J. physic. chem., 33, 842 (1929); Lange und Misčenko, Z. physik. Chem. (A), 149, 1 (1930); Adam, "Physics and Chemistry of Surface", 3rd ed., p. 300, Oxford, London (1941).
- 7) Butler, "Electrocapillarity", Methuen & Co., London (1940).
- 8) Kameyama, "Theory and Application of Electrochemistry", p. 685.

* The signs of the emf's and currents are taken here as shown in this figure.