The Distribution of Current in the Cu Electrolyte

Shiro SAKAI*, Shinobu SETOGUCHI**
Yoshio SHIMAGAYA***, Kunihiko HARADA***

Abstract

Nowadays electrolysis is widely utilized for industrial metal refining, electroplating, and so on.

The shape of the electrolytical bath and the intensity of electric current density determine the distribution of electric current in the solution.

But the distribution of electric current is not yet explained in detail.

If we can understand the distribution of electric current, we think it possible to improve the efficiencies of both the experiments and the work of electrolysis. Therefore, as the first attempt, we measured the cell voltage, overvoltage of anode and cathode, and the conductance of the copper solution in order to understand the flow of electric current.

We used an electronic computer in order to analyze the results speedily.

1. Apparatus

The circuit of electrolysis is shown in Fig. 1.

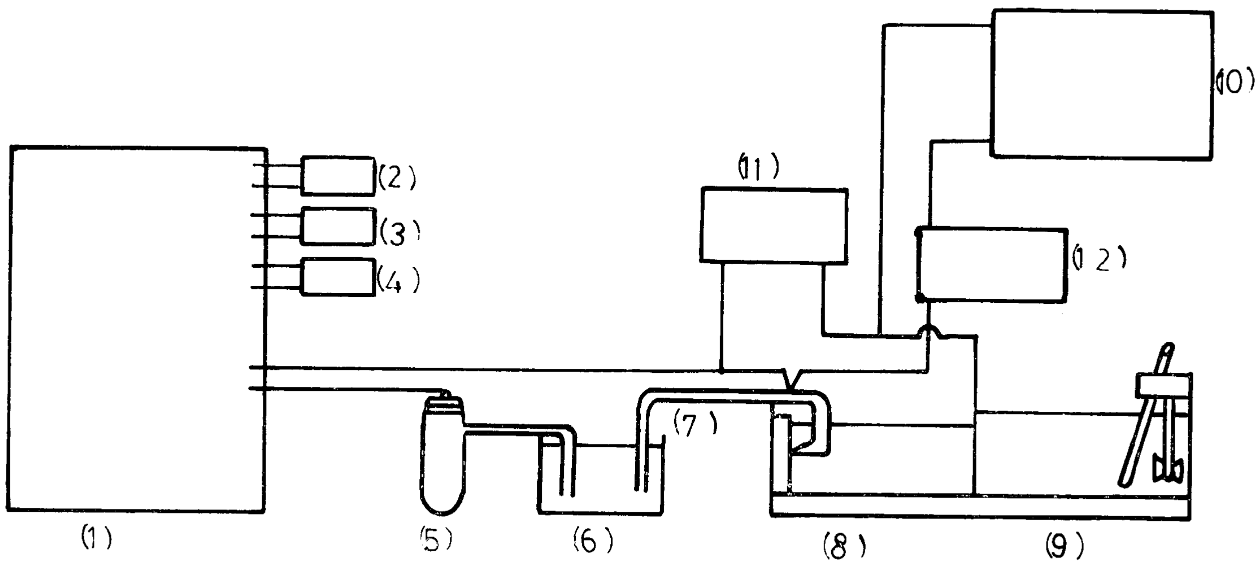

Fig. 1 Circuit of electrolysis

(1) Potentiometer (TYPE PO-30 DC-POTENTIOMETER SHIMAZU DENKI KEISOKUKI K.K. No. 574037—7)

(2) Galvanometer (TYPE 2707 YOKOGAWA)

(3) Cadmium standard cell (TYPE2742 SHIMAZU DENKI KEISOKUKI K.K. No.11602)

(4) Battery (2 v)

(5) Saturated calomel electrode

* The Kyushu Institute of Technology ** The Ube City Fire Station *** The Ube Technical College

(6) Saturated KCl solution

(7) Salt bridge

(8) Electrolytical bath

(9) Thermostat (TYPE MINEDR JUNIOR TOYO CHEMICAL INDUSTRY K.K.)

(10) Rectifier (TAKASAGO MODEL C-2 35V 2A)

(11) Voltmeter (TYPE 2051 YOKOGAWA)

(12) Amperemeter (TYPE 2051 YOKOGAWA)

The dimensions of electrodes are shown in Fig. 3, and the dimensions of electrolytic baths are shown in Fig. 2. (Dimension in mm)

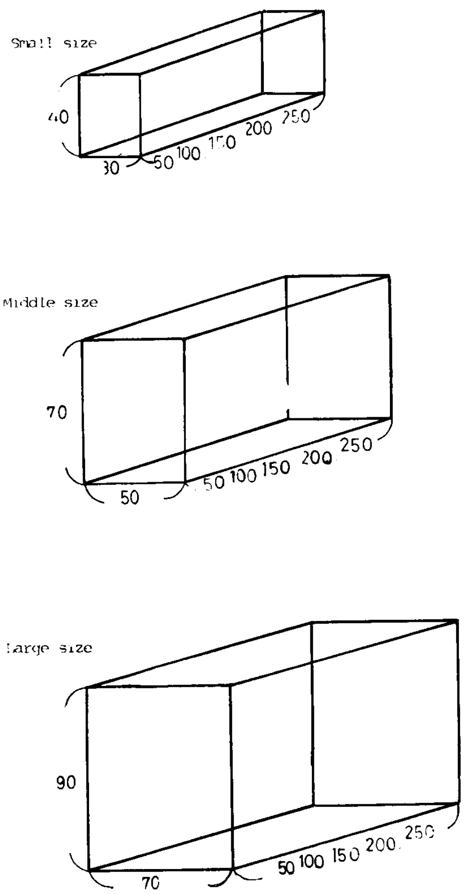

Fig. 2 Electrolytic bath

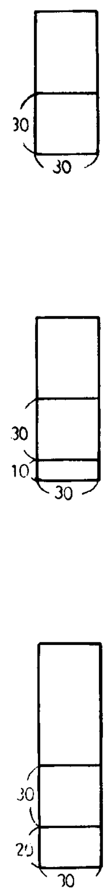

Fig. 3 Electrodes

We used Kohlrausch bridge (MY-8 SERIAL NO. 82601 YOKOGAWA) in order to measure conductance.

2. Symbols

a	surface-area of electrodes
ℓ	distance between electrodes
I	current
R	resistance
r	specific resistance

EOHM ohmic drop by resistance
EA electrodes potential of anode
EC electrodes poteotial of cathods
E cell voltage
EEOHM theoretical ohmic drop given by measured conductence

3. Experiment

(1) Method of measurement of conductance

First of all, we maintained the temperature at 55°C.

And we measured the cell constant by the conductance filled with 0.1 N Kcl solution.

Then we measured the conductance by the one filled with copper solution in order to calculate specific resistance.

(2) Method of electrolysis of copper solution

We measured single electrode potentials of both anode and cathode, and cell voltage when current density became 0.5, 1.0, and 2.0 A/dm^2.

Mathematically, EOHM may be defined by the equation.

$$EOHM = E - (EA - EC)$$

Now, according to Ohm's law, mathematically EEOHM may be evaluated as

$$EEOHM = R \cdot I = I \cdot r \cdot \ell / a = I \cdot r \cdot \ell / 9.0$$

where "a" is $9.0cm^2$, and "r" is obtained by measurement of conductance.

In the final discussion, we determined the relation between current density and electrode distance.

◦ SOLUTION Copper sulfate solution (approximately concentration of ;Cu^{2+} 40g/ℓ)
◦ TEMPERATURE 55°C
◦ CURRENT DENSITY 0.5, 1.0, 2.0A/dm^2

4. Result

(1) Result of measurement of the specific conductance.

$$k \cdot w = c$$

$$K = 0.02120 \ / \ ohm \cdot cm$$

Where w is the resistance of 0.1 N-KCl solution, c is the cell constant, and k is the specific conductance at 55°C.

$$w = 20.0330 \ ohm$$

Therefore,

$$c = 0.02120 \times 20.0330 = 0.424678 \ / \ cm$$

Then,

$$r = 1/k = w/c$$

In case of copper solution, w is 7.5757.

$$r = 7.5757 \ / \ 0.424678 = 17.6604 \ (ohm \cdot cm)$$

For example, when the distance between electrodes is 15 cm, and current density is 0.5 A/dm^2

$$EEOHM = I \cdot r \cdot \ell / a = 0.045 \times 17.6604 \times 15/9 = 1.3245 \ V.$$

(2) Result of measurement of E, EA, EC

The results of measurement are shown in Table. 1, 2, and 3.

We have had the experiences three times.

Table. 1

CURRENT DENSITY= 0.5 SMALL SIZE

DISTANCE	E	EA	EC
5	0.45	0.0987	0.0679
5	0.45	0.0977	0.0678
5	0.40	0.1000	0.0680
10	0.69	0.1024	0.0490
10	0.68	0.1013	0.0491
10	0.68	0.1017	0.0460
15	1.30	0.1094	0.0410
15	1.15	0.1061	0.0384
15	1.15	0.1041	0.0440
20	1.45	0.1234	0.0650
20	1.45	0.1239	0.0670
20	1.50	0.1289	0.0690
25	1.90	0.0948	0.0659
25	1.90	0.1025	0.0667
25	1.90	0.1029	0.0662

CURRENT DENSITY= 1.0 SMALL SIZE

DISTANCE	E	EA	EC
5	0.74	0.1083	0.0662
5	0.74	0.1096	0.0635
5	0.74	0.1096	0.0674
10	1.36	0.1016	0.0655
10	1.36	0.1010	0.0655
10	1.36	0.1030	0.0670
15	2.30	0.1030	0.0193
15	2.17	0.0893	0.0203
15	2.22	0.1190	0.0214
20	2.68	0.1438	0.0680
20	2.75	0.1389	0.0660
20	2.70	0.1469	0.0648
25	3.70	0.1049	0.0656
25	3.70	0.1037	0.0698
25	3.70	0.1053	0.0633

CURRENT DENSITY= 2.0 SMALL SIZE

DISTANCE	E	EA	EC
5	1.33	0.1112	0.0721
5	1.34	0.1130	0.0671
5	1.34	0.1114	0.0718
10	2.75	0.1061	0.0609
10	2.78	0.1051	0.0619
10	2.83	0.1055	0.0586
15	4.20	0.1300	0.0300
15	4.20	0.1120	0.0410
15	4.20	0.1280	0.0382
20	5.42	0.1354	0.0648
20	5.20	0.1586	0.0660
20	5.30	0.1328	0.0671
25	7.60	0.1069	0.0612
25	8.00	0.1033	0.0613
25	7.80	0.1029	0.0618

Table. 2

CURRENT DENSITY= 0.5 MIDDLE SIZE

DISTANCE	E	EA	EC
5	0.23	0.0929	0.0576
5	0.23	0.0972	0.0520
5	0.22	0.0970	0.0537
10	0.44	0.1167	0.0450
10	0.44	0.1160	0.0455
10	0.40	0.1138	0.0458
15	0.54	0.0996	0.0715
15	0.54	0.1001	0.0749

15	0.54	0.0983	0.0746
20	0.65	0.0944	0.0666
20	0.65	0.0940	0.0647
20	0.65	0.0943	0.0621
25	0.78	0.1084	0.0713
25	0.78	0.1096	0.0700
25	0.78	0.1124	0.0684

CURRENT DENSITY= 1.0 MIDDLE SIZE

DISTANCE	E	EA	EC
5	0.40	0.0930	0.0568
5	0.40	0.0980	0.0531
5	0.40	0.0930	0.0531
10	0.72	0.1123	0.0479
10	0.72	0.1101	0.0504
10	0.72	0.1116	0.0549
15	0.94	0.1039	0.0689
15	0.93	0.1015	0.0735
15	0.92	0.1022	0.0728
20	1.14	0.0961	0.0675
20	1.14	0.0990	0.0650
20	1.14	0.1001	0.0660
25	1.36	0.1035	0.0590
25	1.35	0.1277	0.0600
25	1.35	0.1322	0.0564

CURRENT DENSITY= 2.0 MIDDLE SIZE

DISTANCE	E	EA	EC
5	0.73	0.0934	0.0648
5	0.73	0.0959	0.0649
5	0.73	0.0973	0.0627
10	1.34	0.1085	0.0515
10	1.34	0.1110	0.0507
10	1.34	0.1066	0.0483
15	1.83	0.1090	0.0689
15	1.82	0.1133	0.0656
15	1.81	0.1076	0.0659
20	2.35	0.1057	0.0677
20	2.35	0.1019	0.0615
20	2.35	0,1000	0.0647
25	2.78	0.1043	0.0593
25	2.78	0.1028	0.0647
25	2.78	0.1004	0.0567

Table. 3

CURRENT DENSITY= 0.5 LARGE SIZE

DISTANCE	E	EA	EC
5	0.18	0.0954	0.0785
5	0.18	0.0941	0.0772
5	0.18	0.0936	0.0797
10	0.30	0.1012	0.0614
10	0.30	0.1032	0.0612
10	0.28	0.1014	0.0616
15	0.34	0.1006	0.0673
15	0.35	0.0985	0.0655
15	0.38	0.0985	0.0645
20	0.45	0.0857	0.0623
20	0.45	0.0888	0.0646
20	0.45	0.0890	0.0629
25	0.54	0.0974	0.0704
25	0.54	0,0942	0.0682
25	0.54	0.0929	0.0685

CURRENT DENSITY= 1.0 LARGE SIZE

DISTANCE	E	EA	EC
5	0.34	0.0942	0.0774
5	0.34	0.0959	0.0790
5	0.34	0.0957	0.0755
10	0.60	0.1162	0.0634
10	0.60	0.1133	0.0637
10	0.60	0.1100	0.0637
15	0.75	0.0983	0.0693
15	0.75	0.0989	0.0689
15	0.75	0.0988	0.0677
20	0.97	0.0867	0.0593
20	0.97	0.0884	0.0590
20	0.97	0.0876	0.0605
25	1.16	0.0946	0.0766
25	1.16	0.0946	0.0743
25	1.16	0.0984	0.0748

CURRENT DENSITY= 2.0 LARGE SIZE

DISTANCE	E	EA	EC
5	0.65	0.0958	0.0740
5	0.64	0.0957	0.0748
5	0.64	0.0949	0.0741
10	1.10	0.1269	0.0664
10	1.06	0.1249	0.0676
10	0.05	0.1261	0.0689
15	1.40	0.0994	0.0700
15	1.39	0.1014	0.0760
15	1.36	0 0985	0.0693
20	1·80	0.0877	0.0699
20	1.80	0.0875	0.0695
20	1.80	0.0889	0.0728
25	2.22	0.0978	0.0778
25	2.20	0.0990	0.0720
25	2.20	0.1000	0.0706

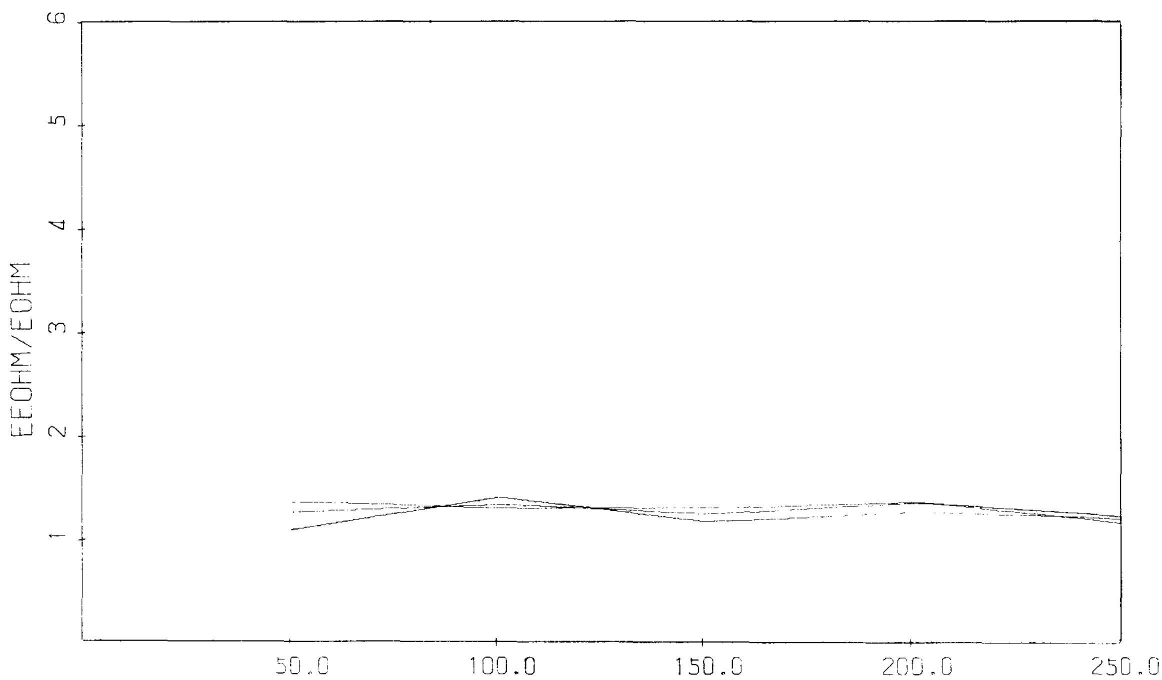

Fig. 4 EEOHM／FOHM against distance between electrodes

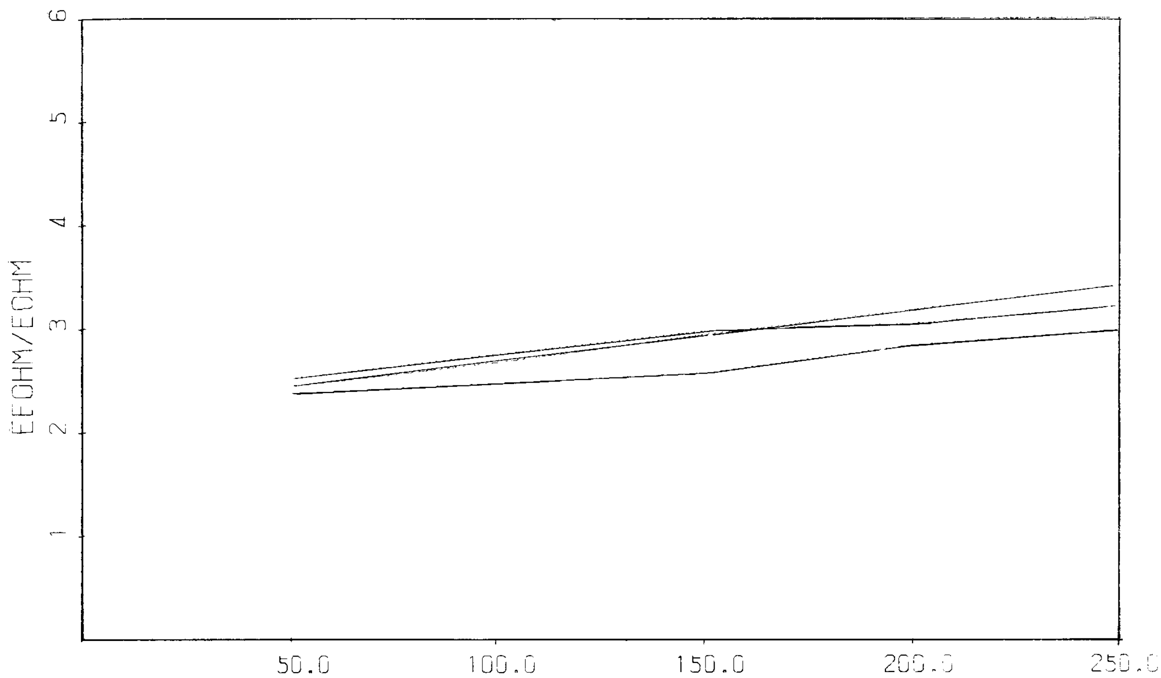

Fig. 5 EEOHM／EOHM against distance between electrodes

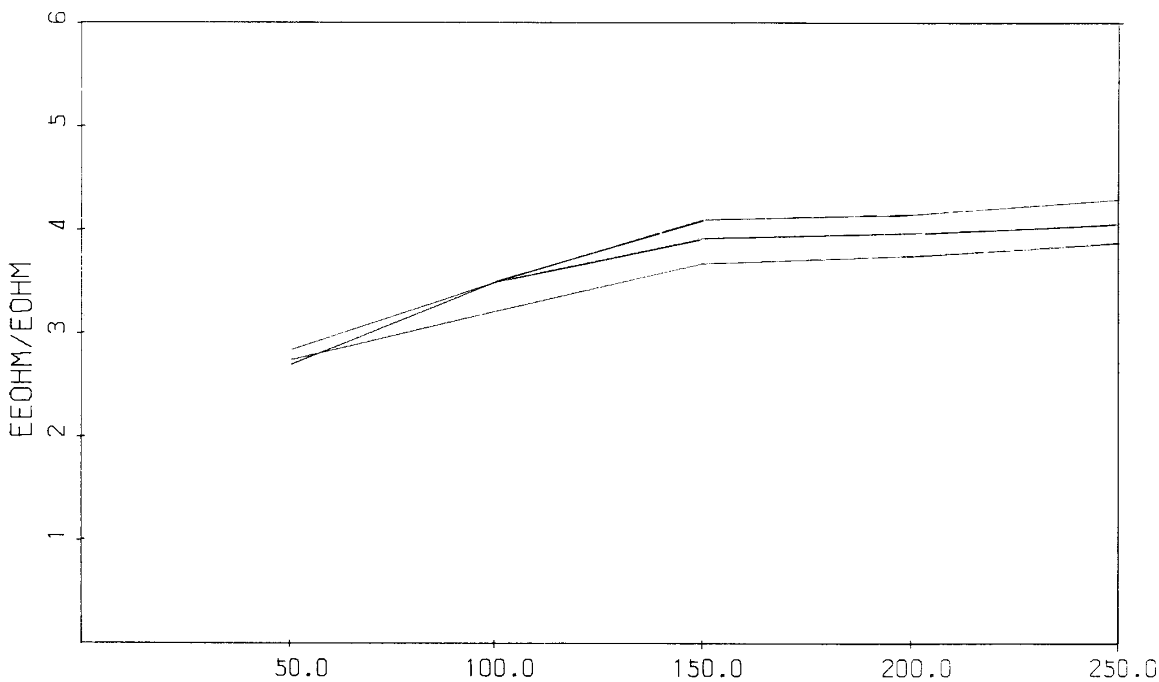

Fig. 6 EEOHM／EOHM against distance between electrodes

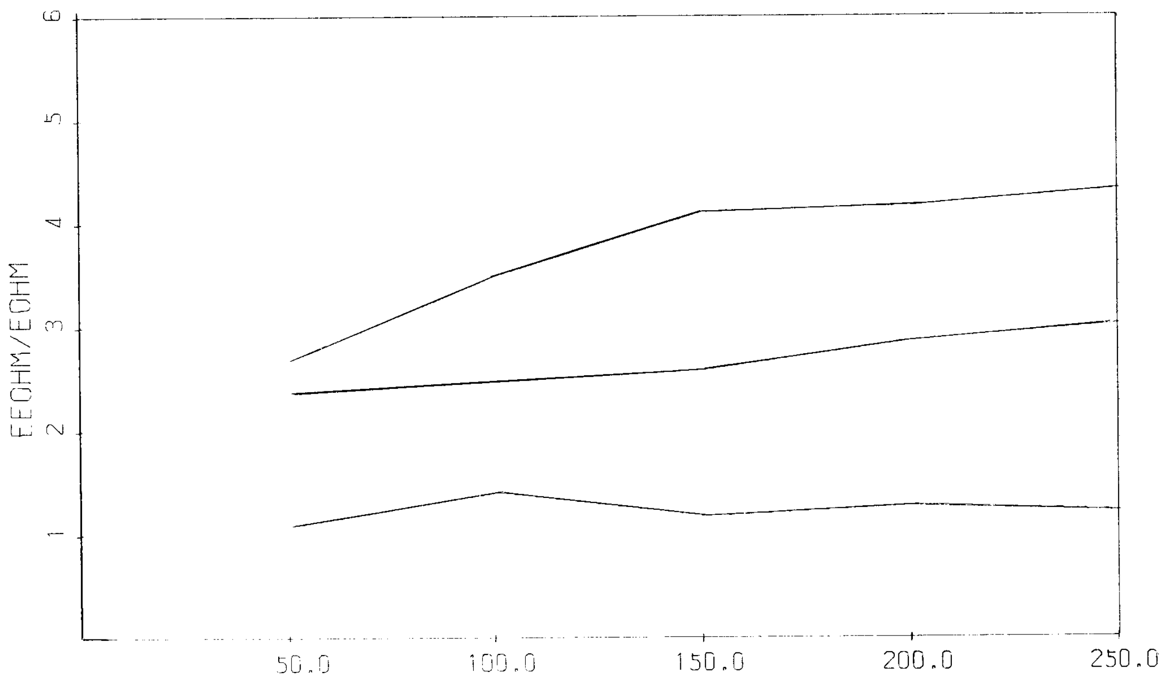

Fig. 7 EEOHM／EOHM against distance between electrodes

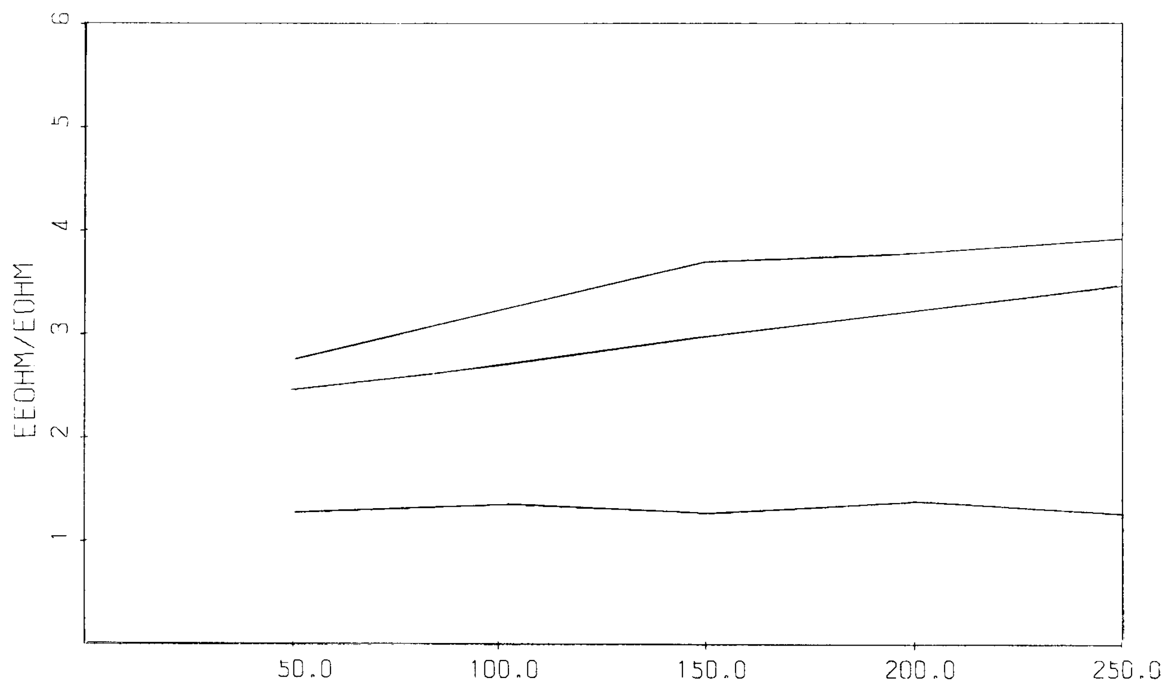

Fig. 8 EEOHM／EOHM against distance between electrodes

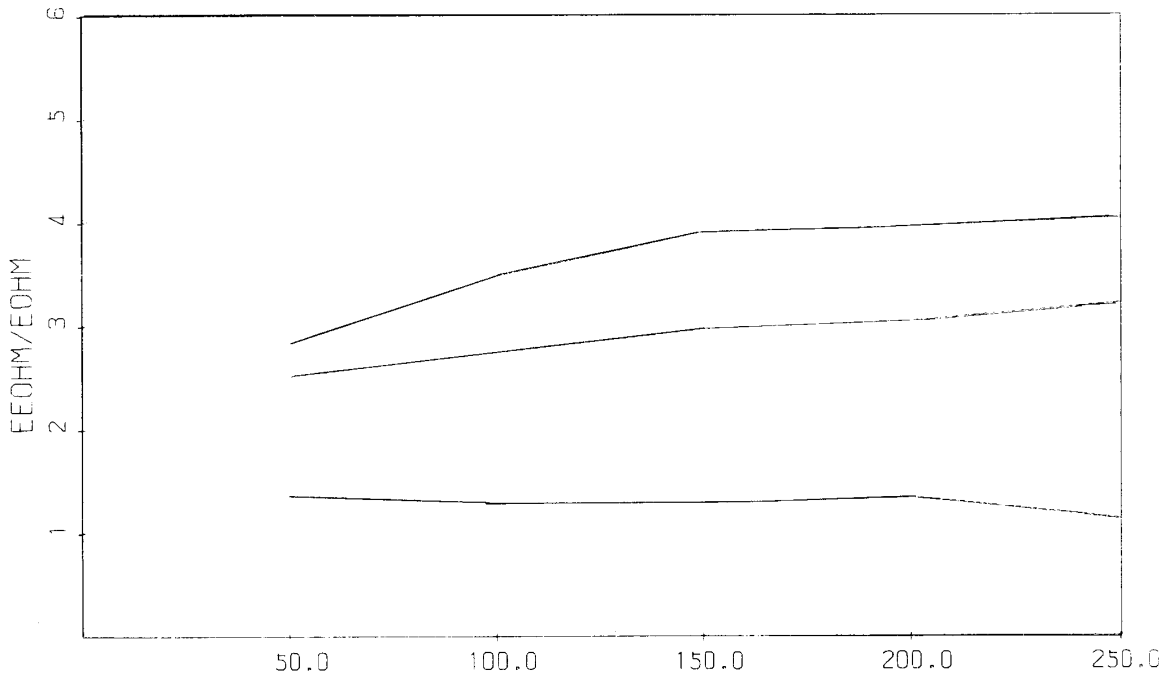

Fig. 9 EEOHM／EOHM against distance between electrodes

Then, we used the mean of the three results of measurements of E, EA, and EC in order to draw a true conclusion.

(3) Caluculation of EEOHM / EOHM

We calculated EEOHM / EOHM from the data by the computer (TOSBAC-3400).

Then, the relation between EEOHM / EOHM and electrode distance is shown in Fig. 4, 5, 6, 7, 8, and 9.

Table. 4

Fig. No.	Kind of eleetrolytic cell	size	Kind of current density	magnitude of current density
4	1	small size	3	0.5 1.0 2.0
5	1	middle size	3	0.5 1.0 2.0
6	1	large size	3	0.5 1.0 2.0
7	3	small size middle size large size	1	0.5
8	3	small size middle size large size	1	1.0
9	3	small size middle size large size	1	2.0

5. Discussion

The purpose of this reseach is to investigate the courses in which ion moves in solution.
We made several graphs in order to analyze the datas.
The results of measurement are shown in Fig. 4, 5, 6, 7, 8, and 9 respectively.
Table. 4 shows the experimental conditions in the 6 figures (No. 4, 5, 6, 7, 8, 9).
We think three hypotheses exist about the flow of current in solution.
The three hypotheses are as follows:
Hypothesis (1)
Copper ion runs straight from anode to cathode.
Hypothesie (2)
Copper ion runs all over the electrolytical bath.
Hypothesis (3)
Copper ion runs in a curve from anode to cathode.
Therefore, the trace is like a magnetic line.
One of these three hypotheses is the conclusion.
Hypothesis (1)
If copper ion runs straight, it flows only in the shaded portion in Fig. 10.

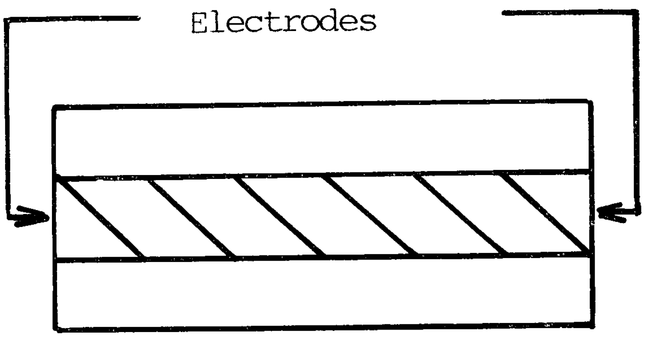

Fig. 10 (We look down the electrolytic bath.)

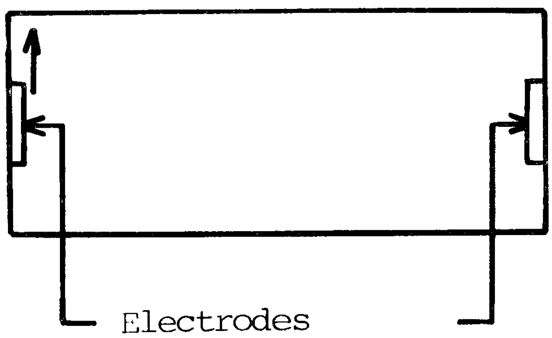

Fig. 11 (We look down the electrclytic bath.)

Therefore, EEOHM / EOHM should be approximately 1.000.
EEOHM / EOHM in Fig. 4 is approximately 1.000. So, Fig. 4 proves Hypothesis (1).
But, Fig. 5, 6, 7, 8, and 9 do not prove Hypothesis (1), because FEOHM / EOHM is over 2.000 in these figures.
Then, Hypothesis (1) is contradictory doubtlessly.
Hypothesis (2)
If copper ion runs all over the electrolytical bath, EEOHM / EOHM should be 5.444 (in a large-size one), 2.777 (in a middle-sized), and 1.000 (in a small-sized) regardess of current density.

Table. 5

size	surface -area	ratio
small	9 cm^2	1.000
middle	25cm^2	2.777
large	49cm^2	5.444

But in a large-sized one EEOHM is less than 5.444, and in a middle-sized less than 2.777.
Or, copper ion never runs in the direction shown in Fig. 11, as far as the force of cathode attracting cation remains.

Then Hypothesis (2) is contradictory donbtlessly.

Hypothesis (3)

We can explain in a large-sized one EEOHM / EOHM does not become 5.444, and in a middle-sized not 2.777 if copper ion runs in a curve.

In a small-sized one, the width and height of an electrode are the same as those of surface area of electrolytical bath.

As copper ion can not run in a curve, it runs straight.

For that reason, we think EEOHM / EOHM became approximately 1.000.

This hypothesis is in accord with the results.

(昭和54年 4 月13日受理)