

ELECTRO-DEPOSITION AND ELECTRO-DISSOLUTION OF METALS IN FUSED SALTS

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Introduction

Production of metals by fused salt electrolysis is popular as well as that by electrolysis in aqueous solutions in extractive metallurgy. The fundamental research on this matter, however, developed in recent twenty years. Concerning to basic research on electrodeposition of metals in fused salts most works were carried out in the field of analytical chemistry¹⁾²⁾. In author's laboratory the electrodeposition of simple metals such as silver in chloride melts has been investigated in the course of the fundamental studies for the production of active metals and the reprocessing of nuclear fuels by fused salt electrolysis. From the practical and thermodynamical points of view this paper concerned with the electro-deposition and dissolution of a steady state.

In Chapter I the measurements of overpotentials with a back side reference electrode (Nanis' electrode) which was immersed in a working electrode and procedures to obtain a transfer coefficient were described.

In Chapter II theoretical considerations of deposition and dissolution of a simple metal in fused salt electrolysis in a steady state were described. In this process it was considered that mobile equilibrium between activated species on the electrode and reactant ions in solution was established with an overpotential. The concept of mobile equilibrium in a steady state yielded the physical meaning of transfer coefficient which was ambiguous. Furthermore the number of reactant ions was suggested from the transfer coefficient. In the electrodeposition of silver from chloride melts activated species were considered as Ag° ions and in dissolution as Cl_2^- ions on the electrode.

In Chapter III the absorption spectra of silver chloride of solid, melt and fused salt solutions are described as a supplementary note. The absorption spectra in visible and near infrared region support the existence of Ag° and Cl_2^- ions.

Chapter I. Measurement on Overpotentials of Electro-deposition and Dissolution of Silver in AgCl-KCl (70 : 30)³⁾⁴⁾

1. Introduction

Even in an aqueous solution reproducible results of over-potentials for the electrodeposition of metals in a steady state were rare⁵⁾ except flowing method⁶⁾⁷⁾. Apparently measurement in a steady state has almost ignored⁸⁾⁹⁾. In this chapter experimental details for measurement of overpotential of deposition and dissolution of silver in chloride melt with back side reference electrode will be described. In order to know the electrode processes in a steady state it was attempted to eliminate the diffusion current as possible by using the fused salt solution in rather high concentration of AgCl and a large working electrode which reduces current densities. As a result consistent values were obtained.

2. Experimental

2.1. Chemicals and apparatus

Silver chloride (99.6% up) and potassiumchloride (JIS Special quality) were melted respectively in a flowing atmosphere of dry purified chlorine.

Two types of silver working electrode illustrated in Fig. 1 were made, and those purity was 99.3% up. The electrode Type I shown in Fig. 1 was originally designed and constructed by L. Nanis. This type of electrode has a trouble of

the collapse of insulator made of pyrex glass or quartz tube. Mainly type II was used. Area of an electrode of type I and type II was 0.7 cm² and 1.8 cm² respectively. A reference electrode (ϕ 0.8 mm) and a counter electrode (ϕ 45 \times 5 mm) were made from silver of the same purity to a working one. A working electrode with a reference one was polished first by emery papers, electropolished with KCN solution and cleaned with absolute alcohol. All electrodes were situated in a pyrex vessel as illustrated in Fig. 1. An electrical resistance furnace was used to heat the vessel and its temperature was controlled within $\pm 1^\circ\text{C}$ in the range of 370–500°C.

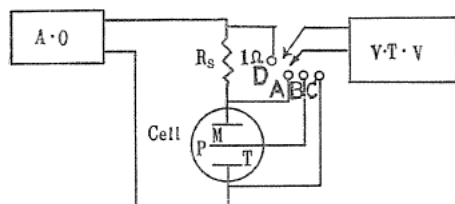


FIG. 2. Block diagram of measuring resistance between working electrode (M) and reference electrode (P)

A.O: Audio Oscillator Type OV-21 A (YEW)

Rs: 4-dial type resistoy Type REC-401 (YEW)

V.T.V: Vacuum valve volt meter Type MV-951 A (Matsushita)

2.2. Measurement of ohmic overpotentials

A precise value of ohmic resistance between a reference and a working electrode is required in order to get a ohmic over-potential. Two methods *i.e.* voltage measurement with alternating current and initial voltage jump in dc, were compared. In Fig. 2 the block diagram of measurements of resistance with alternating currents in the range 10–10⁴ cycle was introduced. A current passed through the cell was obtained by a voltage drop across a resistance of R_s shown in the figure. Experimental results obtained at 450°C are indicated in Table 1. Notation in this table imply as follows: V_s ; voltage drop across the resistance R_s , i ; a current, V_{TM} ; a voltage drop between a counter electrode (T) and a working electrode (M), R_{TM} ; a resistance between T and M electrode, V_{PM} ; a voltage drop between a reference electrode (P) and a working electrode (M), and R_{PM} ; a resistance between P and M electrode. It should be noticed here that the values of R_{PM} and R_{TM} increase with frequencies beyond 500 cycle. It was recognized that this tendency stronger in R_{PM} than in R_{TM} . Values of R_{PM} from 370°C to 550°C were shown against $1/\sqrt{f}$ in Fig. 3. The ohmic resistance of R_{PM} was obtained by interporation to 0 for $1/\sqrt{f}$ from low frequencies (high values of

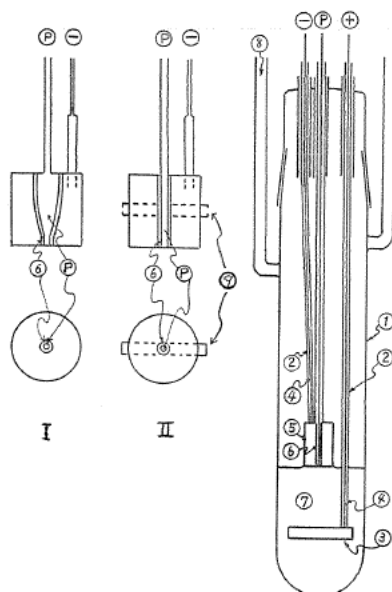


FIG. 1. Cell and electrode.

- 1: Reaction vessel (pyrex) (ϕ 50 mm)
- 2: Pyrex tube, 3: Auxiliary electrode
- 4: Lead wire (Ag) (0.8 mm)
- 5: Working electrode (Ag) (ϕ 12.5 mm)
- 6: Insulator (pyrex), 7: Fused salts
- 8: Argon gas inlet
- 9: P: electrode supporting screw
- P: Reference electrode

$1/\sqrt{f}$). These values were almost consistent with those obtained by dc potential jumps. Other simple useful method proposed by Bockris *et al.* was tested. In Fig. 3 the block diagram of this method which we call as dc potential jump. In Fig. 4 a display on oscilloscope is represented. Precision of this method was rather inferior to the ac method.

TABLE 1. Changes of resistance with frequencies of alternating currents (70 : 30 mol. ratio) melt at 450°C

f (cycle)	$1/\sqrt{f} \times 10^2$	V_s (V)	i (A)	$V_{TM} (\times 10^2)$ (V)	R_{TM} (Ω)	$V_{PM} (\times 10^3)$ (V)	$R_{PM} (\times 10^2)$ (Ω)
10	31.62	0.124	0.248	4.63	0.187	5.56	2.24
20	22.36	0.124	0.248	4.66	0.188	5.58	2.25
50	14.14	0.124	0.248	4.66	0.388	5.58	2.25
100	10	0.124	0.248	4.66	0.188	5.58	2.25
200	7.07	0.123	0.246	4.62	0.188	5.54	2.25
500	4.47	0.123	0.246	4.62	0.188	5.56	2.26
1,000	3.16	0.122	0.244	4.61	8.189	6.76	2.36
2,000	2.236	0.120	0.240	4.58	0.191	5.55	2.73
5,000	1.414	0.112	0.224	4.57	0.204	10.8	4.81
10,000	1.000	0.087	0.174	4.02	0.231	18.3	10.5

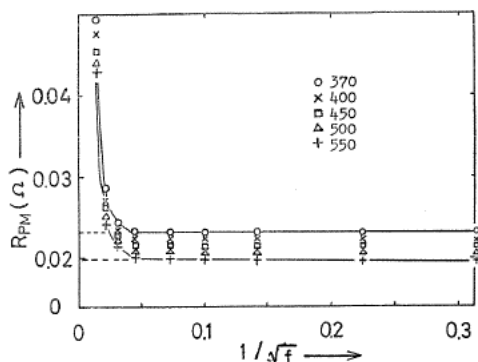


FIG. 3. Relationship between R_{PM} and $1/\sqrt{f}$ in aAgCl-KCl (70 : 30 mol. ratio) melt.

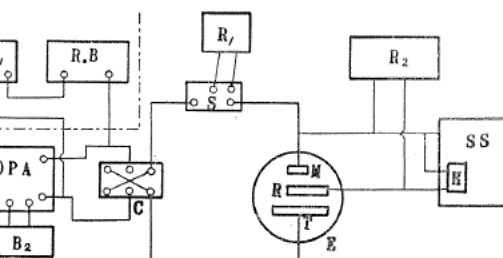
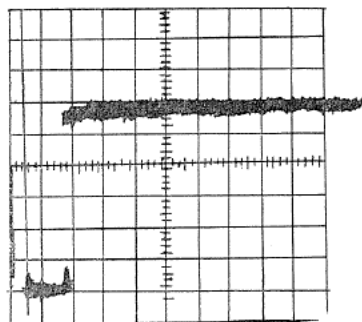


FIG. 4. Block diagram of measurement of resistance and overpotential by synchroscope. B_1 : Battery (p-6) E: Cell O.P.A.: Aparatus for measurement of overpotentials M: Working electrode (Ag) T: Counter electrode (Ag) B_2 : Battery (PYB-6) R: Reference electrode (Ag) C: Switch R_1, R_2 : Recorder S: Shunt S.S.: Synchroscope (Iwasaki DS-5015) R.B.: Resistance box for generating constant current

FIG. 5. Initial jump of potential caused by ohmic resistance between P and M electrode.

Sensitivity (vert.): 0.2 mV/div.

Sensitivity (hori.): 2 msec/div.

V_{PM} : 1.08 mV J : 47.5 mA R_{PM} : 0.0227 Ω

2.3. Measurements of overpotentials

A constant voltage method was applied to measure overpotentials. The apparatus used in this experiment are shown in Fig. 5. A constant voltage was applied to the cell through the low variable resistance (R) to which a variable transformer (Slidac) of 10 A, 100 V ac was applied. Resistances of R and r were about 2Ω . A current through the cell and a potential between P and M electrode was measured with recorders R_1 and R_2 respectively. Ranges of the recorder R_1 were 0-200 mA and 200 mA-400 mA, and a width of the chart was 250 mm. The recorder R_2 have the range of 2, 5, 10, 20, and 50 mV. A working electrode was used alternatively as a cathode or an anode. In order to minimize the change of the electrode a duration of anodic current was determined by the coulomb used in a previous cathod current. Both cathodic and anodic overpotentials were calculated in the way that the ohmic overpotential obtained by ac method described in foregoing section was subtracted from the measured one.

It should be noticed that the position of the end of a reference electrode would yield a great influence on the stability of a potential between a working electrode and a reference one. Potentials and currents with a reference electrode in a different position are illustrated from Fig. 7 to 8. Therefore the end of a reference electrode must be on the surface of a working electrode to determine a correct potential value.

The results shown in Fig. 7 under 350 mA/cm^2 are in the condition above mentioned. As shown in this figure at a current density over 350 mA/cm^2 at 450°C the potentials between P and M electrode were not kept constant. Accordingly such values were rejected. In that case small dendrites were observed with a microscope. Those current densities decreased with a decreasing temperature.

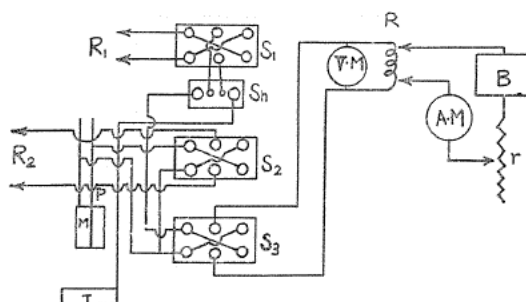


FIG. 6. Block diagram of measurement of overpotential.

B: Battery (6 V) A.M.: Ammeter
S: Shunt R₁, R₂: Recorder
r: Slide resistor (YWS) VM: Voltmeter
R: Slidac S₁, S₂, S₃: Switch

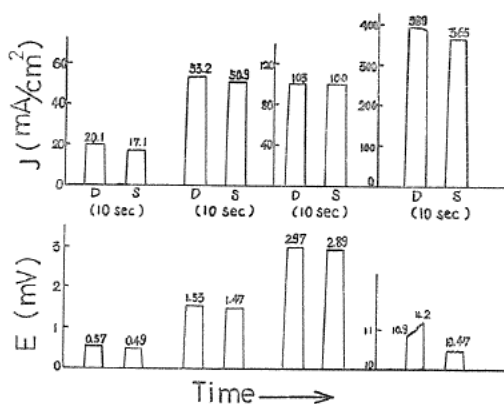


FIG. 7. Currents and potentials between a reference electrode and a working electrode during electrodeposition (D) and dissolution (S) of silver in AgCl-KCl (70 : 30) at 450°C in the case that the end surface of the reference electrode coincides with the plane of the end surface of the working electrode.

3. Results and consideration

3.1. Procedures to obtain overpotentials from measurements

In order to get a real overpotential from the measurements of overpotentials with a backside reference electrode which does not exist in equilibrium concentration of the solution, it is necessary to consider some theoretical approach for yielding a real overpotential with that electrode.

In the case the supply of oxidant to electrode is sufficient, and electrode reactions determine the rate of the reaction *i.e.* Oxidant \rightleftharpoons Reductant (1). Then the following relation is fulfilled:

$$J_c = \vec{i} - \tilde{i} = J_0 \{ e^{-nFA\eta_c/RT} - e^{nF(1-A)\eta_c/RT} \} \quad (2)$$

$$J_0 = nFa^\circ \mathcal{M}_o k_f \quad (3)$$

where J : current densities, \vec{i} : cathodic currents, \tilde{i} : anodic currents, J_0 : exchange currents, n : numbers of electrons transferred, F : faraday, η_c : cathodic overpotentials, and A : transfer coefficients for cathodic processes. Notations a° and \mathcal{M}_o are activities of an oxidant in an equilibrium state and numbers of mole of an oxidant per cm^2 in a reference state of an activity respectively. k_f is a reaction rate constant for forward direction. In this type of relation, overpotentials must be determined from equilibrium state of reaction (1). If a reference electrode is not in an equilibrium position but in any position where the following conditions:

$$\begin{aligned} nFA\eta_c &= nF\alpha_0\eta_{pc} \\ nF(1-A)\eta_c &= nF\beta_0\eta_{pc}, \end{aligned} \quad (4)$$

and

are satisfied, then the equation (2) becomes

$$J_c = J_0 \{ e^{-nF\alpha_0\eta_{pc}} - e^{nF\beta_0\eta_{pc}} \} \quad (5)$$

The conditions of equation (4) are equivalent to

$$\eta_c = (\alpha_0 + \beta_0)\eta_{pc} \quad (6)$$

since the sum of the two relation of (4) is unity. From (4) and (6)

$$A = \frac{\alpha_0}{\alpha_0 + \beta_0} \quad (7)$$

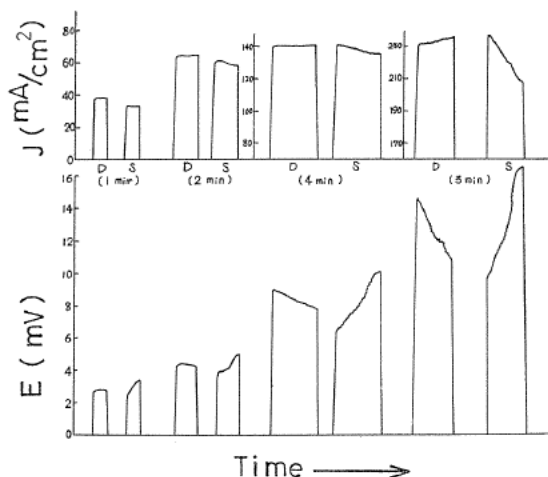


FIG. 8. Currents and potentials between a reference electrode and a working electrode during electrodeposition (D) and dissolution (S) of silver in AgCl-KCl (70 : 30) at 450°C in the case that the end surface of the reference electrode sticks 1 mm out of the plane of the end surface of the working electrode.

The coefficients α_0 and β_0 introduced above relation (4) mean proportional constants. These constants will be called "overpotential coefficients" and its numerical values depend on the reference electrode chosen.

For anodic process of reaction (1) a similar relation to (2) can be obtained as

$$J_a = J_0 \{ e^{nFA'\eta_a/RT} - e^{-nF(1-A')\eta_a/RT} \} \quad (2')$$

$$J_0 = nFa_R^0 \mathcal{M}_R k_b \quad (3')$$

where A' : transfer coefficients for anodic process, η_a : anodic overpotentials, a_R^0 : activity of a reductant in an equilibrium state, \mathcal{M}_R : number of moles of a reductant per cm² in a reference state of an activity, and k_b : a reaction rate constant for backward direction. Since relation (1) is reversible, thus

$$nFa^0 \mathcal{M}_0 k_f = nFa_R^0 \mathcal{M}_R k_b = J_0 \quad (8)$$

This is the criterion whether a cathodic and anodic process in a steady state is reversible or not. If the condition similar to (4) is satisfied for an anode, the following relations are obtained.

$$J_a = J_0 \{ e^{nF\alpha_0'\eta_{pa}} - e^{nF\beta_0'\eta_{pa}} \} \quad (5')$$

$$\eta_a = (\alpha_0' + \beta_0')\eta_{pa} \quad (6')$$

$$A' = \frac{\alpha_0'}{\alpha_0' + \beta_0'} \quad (7')$$

As usual in the relation (2) and (5) for cathode or (2') and (5') for anode in high overpotentials namely in high current densities the second terms can be neglected compared to large values of first terms. Consequently

$$J_c = J_0 e^{-nFA\eta_c/RT} \quad (8)$$

$$J_c = J_0 e^{-nF\alpha_0\eta_{pc}/RT} \quad (9)$$

$$J_a = J_0 e^{nFA'\eta_a/RT} \quad (8')$$

$$J_a = J_0 e^{nF\alpha_0'\eta_{pa}/RT} \quad (9')$$

in high current densities. Logarithm of these relations means well known Tafel's relation. In low current densities, due to the small values of overpotential in parenthesis of relation (2) and (2'), or (5) and (5') can fairly well be approximated two terms of the series. Therefore

$$J_c = J_0 (nF\eta_c/RT) \quad (10)$$

$$J_c = J_0 nF(\alpha_0 + \beta_0)\eta_{pc}/RT \quad (11)$$

$$J_a = J_0 (nF\eta_a/RT) \quad (10')$$

$$J_a = J_0 nF(\alpha_0' + \beta_0')\eta_{pa}/RT \quad (11')$$

The relations (5), (9) and (11) for cathode or (5'), (9') and (11') for anode are useful to criticize the results.

The relationship between logarithms of current densities and overpotentials

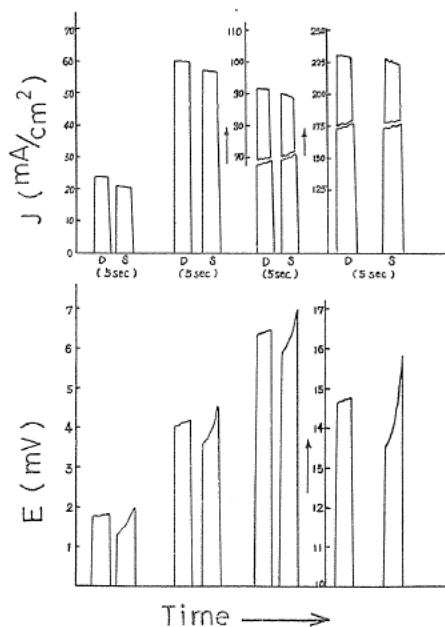


FIG. 9. Currents and potentials between a reference electrode and a working electrode during electrodeposition (D) and dissolution (S) of silver in AgCl-KCl (70 : 30) at 450°C in the case that the end surface of the reference electrode sticks 2 mm out of the plane of the end surface of the working electrode.

there were not much differences between cathodic and anodic one at each temperature. From the linear parts of the curves increments assumed to be α_0 or α_0' were calculated with the equation (9) or (9'). These values are represented on the column of α_0 and α_0' in Table 2 and 3. Then with these values of α_0 or α_0' the J_0 values were calculated according to the relation (9) or (9') in logarithmic form. The values of J_0 both cathodic and anodic thus obtained were consistent with each other within an error of ± 0.5 mA as shown in Table 4.

Another overpotential coefficients β_0 and β_0' were determined by two methods. (i) β_0 were obtained by the relation (11) with the value of J_0 and α_0 . The coefficient of β_0 thus calculated are shown as the numerical values in Fig. 11. (ii) These coefficients can be calculated according to equation (5) or (5') with current

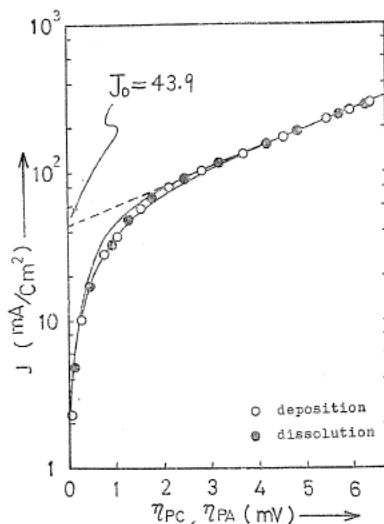


FIG. 10. Relationship between observed overpotentials and current density of silver in a AgCl-KCl (7 : 3 mole ratio) melt at 400°C.

from which ohmic overpotentials both cathodic and anodic were subtracted at 400°C are represented in Fig. 10. Similar curves were obtained at 370°, 450°, 500° and 550°C. In those curves

TABLE 2. Comparison of the results for working electrodes of different surface area at 400°C

Surface of working electrode (cm ²)	E_{po} (mV)	I (mA)	IR (mV)	J (mA/cm ²)	η_{po} (mV)	α_0	β_0	A	η_0
0.7	3.8	67	1.00	95.7	2.8	13.8	29	0.332	120
1.8	5.12	176.5	4.00	98.1	1.12	41.9	76.6	0.354	133

TABLE 3. Kinetic parameters for deposition and dissolution silver in a AgCl-KCl (70 : 30 mol. ratio) melt

Temp (°C)	370	400	450	500	550
α_0	47.5±1.5	41.9±1.5	36.9±1.0	31.4±1.0	26.4±1.2
$\beta_{0\text{mean}}^*$	83.0±4.3	76.6±2.8	75.5±2.1	59.4±1.3	53.1±0.9
$\alpha_0 + \beta_{0\text{mean}}^*$	130.8±5.8	118.5±4.0	112.4±3.1	90.8±2.3	79.5±2.1
A	0.365±0.014	0.354±0.011	0.328±0.009	0.346±0.010	0.332±0.012
$1/A$	2.74±0.17	2.83±0.09	3.05±0.08	2.89±0.09	3.01±0.10
α'	49.5±1.29	43.1±1.3	37.1±1.2	31.7±1.2	26.7±1.0
$\beta'_{0\text{mean}}^*$	2.0±3.5	81.4±2.6	71.9±2.1	59.2±1.5	51.0±0.9
$\alpha_0' + \beta'_{0\text{mean}}^*$	141.5±4.7	124.5±3.9	109.0±3.3	90.9±2.7	77.7±1.9
A'	0.350±0.010	0.346±0.010	0.340±0.010	0.349±0.012	0.348±0.012
$1/A'$	2.86±0.08	2.89±0.08	2.94±0.08	2.89±0.11	2.88±0.10

* Using probable error

TABLE 4. Exchange current density in a AgCl-KCl (70 : 30 mole ratio)

Temp. (°C)	370	400	450	500	550
J_0 (mA/cm ²)	41.1±0.5	44.0±0.5	48.5±0.5	52.8±0.5	57.1±0.5

densities around J_0 , and the mean value thus calculated is adopted. The coefficients by this method are represented by $\beta_{0\text{mean}}$ or $\beta'_{0\text{mean}}$, and these are shown in Table 3. For comparison calculated curve of equation (11) obtained by $\beta_{0\text{mean}}$ are represented also in Fig. 11. Experimental values are rather well consistent with the calculated values considering the experimental error.

Consequently it can be concluded that overpotentials measured with a backside reference electrode for the deposition and dissolution of silver in AgCl-KCl (70 : 30 mol) satisfy both equation (5) and (5'). Therefore, considering the context from equation (2) to (5), it is also evident that the overpotentials (η) and the current densities of silver deposition and dissolution at a steady state in a concentrated solution as this experiment satisfy the equation (2) and (2'), which is very popular relation in electrochemistry.

Concerning the method to obtain β_0 or β'_0 the second method mentioned was applied because of accuracy. With relation (7) and (7')

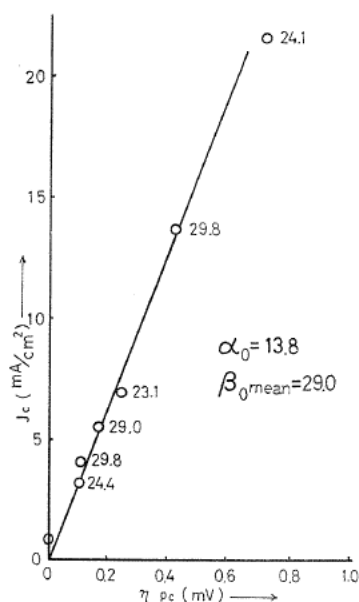


FIG. 11. Comparison of calculated values with experimental one at low current densities at 400°C.

the transfer coefficients A and

TABLE 5. Calculated values of transfer coefficient for deposition and dissolution of silver in a AgCl-KCl (70 : 30 mol. ratio) melt

500°C	J_o (mA/cm ²)	η_{pc} (mV)	β_0	$\alpha_0 + \beta_0$	A	$1/A$
$J_0 = 52.8 \pm 0.5$ mA/cm ² $\alpha_0 = 31.4 \pm 1.0$ $A = 0.346$	11.8 ± 0.5	0.17 ± 0.02	58.7 ± 3.2	90.1 ± 4.2	0.349 ± 0.014	2.86 ± 0.19
	20.6 ± 0.5	0.32 ± 0.02	54.4 ± 2.6	85.5 ± 3.6	0.366 ± 0.013	2.73 ± 0.10
	30.2 ± 0.5	0.46 ± 0.02	57.9 ± 2.4	89.3 ± 3.4	0.352 ± 0.012	2.84 ± 0.11
	41.7 ± 0.5	0.66 ± 0.02	56.0 ± 1.7	87.3 ± 2.7	0.359 ± 0.011	2.78 ± 0.10
	49.3 ± 1.3	0.77 ± 0.04	58.4 ± 2.5	89.7 ± 3.5	0.350 ± 0.072	2.86 ± 0.11
	54.2 ± 1.3	0.83 ± 0.04	63.7 ± 3.2	95.1 ± 4.2	0.330 ± 0.012	3.03 ± 0.12
	63.9 ± 1.3	0.97 ± 0.04	68.5 ± 6.9	99.8 ± 7.9	0.314 ± 0.016	3.18 ± 0.18
	70.1 ± 1.3	1.03 ± 0.04	79.9 ± 7.5	111.3 ± 8.9	0.282 ± 0.015	3.54 ± 0.17
500°C	J_a (mA/cm ²)	η_{pa} (mV)	β_0'	$\alpha_0' + \beta_0'$	A'	$1/A'$
$J_0 = 52.8 \pm 0.5$ mA/cm ² $\alpha_0' = 31.7 \pm 1.2$ $A' = 0.349$	17.2 ± 0.5	0.27 ± 0.02	52.5 ± 3.1	84.2 ± 4.3	0.377 ± 0.016	2.66 ± 0.12
	28.3 ± 0.5	0.44 ± 0.02	54.6 ± 2.2	86.3 ± 3.4	0.367 ± 0.014	2.72 ± 0.11
	36.5 ± 0.5	0.56 ± 0.02	57.3 ± 1.3	89.0 ± 2.5	0.356 ± 0.012	2.81 ± 0.10
	47.9 ± 1.3	0.74 ± 0.04	60.3 ± 2.6	92.0 ± 3.8	0.345 ± 0.013	2.90 ± 0.12
	52.5 ± 1.3	0.82 ± 0.04	60.1 ± 3.4	91.8 ± 4.6	0.345 ± 0.015	2.90 ± 0.13
	68.4 ± 1.3	1.05 ± 0.04	66.9 ± 3.8	98.5 ± 5.0	0.322 ± 0.014	3.11 ± 0.15
	83.6 ± 1.3	1.23 ± 0.04	83.9 ± 6.1	115.6 ± 7.3	0.274 ± 0.015	3.65 ± 0.19

TABLE 6. Overpotentials and overpotential coefficients of electrodeposition and dissolution of silver in AgCl-KCl (70 : 30 mol. ratio) melt. at 500°C

J_o (mA/cm ²)	η_{pc} (mV)	$\alpha_0 + \beta_0$	$\eta_c = \eta_{pc}(\alpha_0 + \beta_0)$ (mV)
9.3 ± 0.5	0.12 ± 0.02	110.6 ± 10.4	12.2 ± 3.3
11.8 ± 0.5	0.17 ± 0.02	90.1 ± 4.2	15.3 ± 2.5
20.6 ± 0.5	0.32 ± 0.02	85.5 ± 3.6	27.2 ± 2.8
30.2 ± 0.5	0.46 ± 0.02	89.3 ± 3.4	41.1 ± 3.3
41.7 ± 0.5	0.66 ± 0.02	87.3 ± 2.7	57.6 ± 3.5
49.3 ± 1.3	0.77 ± 0.04	89.7 ± 3.5	69.5 ± 6.3
54.2 ± 1.3	0.83 ± 0.04	95.1 ± 4.2	78.9 ± 7.3
63.9 ± 1.3	0.97 ± 0.04	99.8 ± 7.9	96.8 ± 11.6
70.1 ± 1.3	1.03 ± 0.04	111.3 ± 5.9	114.1 ± 10.5
J_a	η_{pa}	$\alpha_0' + \beta_0'$	$\eta = \eta_{pa}(\alpha_0' + \beta_0')$
9.4 ± 0.5	0.14 ± 0.02	87.9 ± 7.2	12.1 ± 2.7
17.2 ± 0.5	0.27 ± 0.02	84.2 ± 4.3	22.5 ± 2.8
28.3 ± 0.5	0.44 ± 0.02	86.3 ± 3.4	40.0 ± 3.2
36.5 ± 0.5	0.56 ± 0.02	89.0 ± 2.5	50.1 ± 3.2
47.9 ± 1.3	0.74 ± 0.04	92.0 ± 3.8	67.8 ± 6.4
52.5 ± 1.3	0.82 ± 0.04	91.8 ± 4.6	74.8 ± 7.4
68.4 ± 1.3	1.05 ± 0.04	98.5 ± 5.0	183.1 ± 9.2
83.6 ± 1.3	1.23 ± 0.04	115.6 ± 7.3	142.2 ± 13.7

A' were able to be calculated from overpotential coefficients as shown in Table 5 and 3. Those values were acceptable for the discussion of the following chapter. According to the relation (6) and (6') the overpotentials (η) were also calculated. The values obtained at 500°C are listed in Table 6. The values of $\log J$ vs. η are illustrated in Fig. 12-15. In these figures cathodic curves and anodic ones calculated by relation (2) and (2') are represented as C and D. Also in these figures the equation (2) or (2') with the same exchange current but a different transfer coefficient *i.e.* 1/2, 1/3, and 1/4 are illustrated. It is apparent from these curves that at a constant temperature in the range from 400°C to 500°C the transfer coefficients in a steady state are almost the same both on the deposition

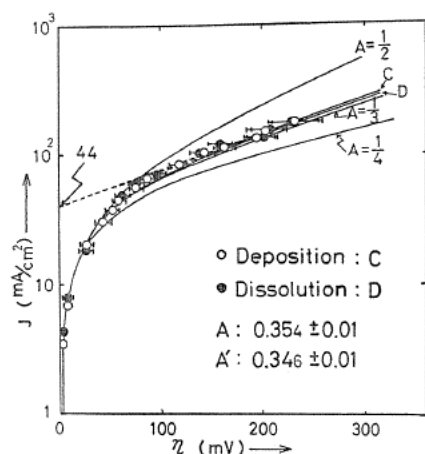


FIG. 12. Overpotentials and current densities of deposition and dissolution of silver in AgCl-KCl (70 : 30 mol) at 400°C.

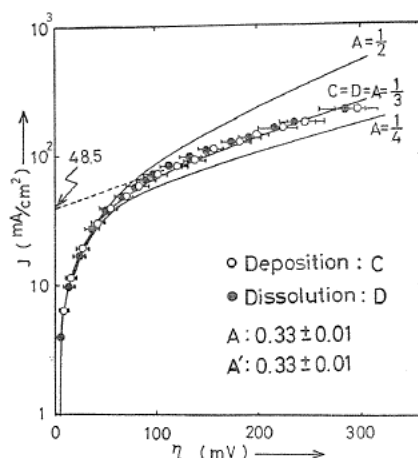


FIG. 13. Overpotentials and current densities of deposition and dissolution of silver in AgCl-KCl (70 : 30 mol) at 450°C.

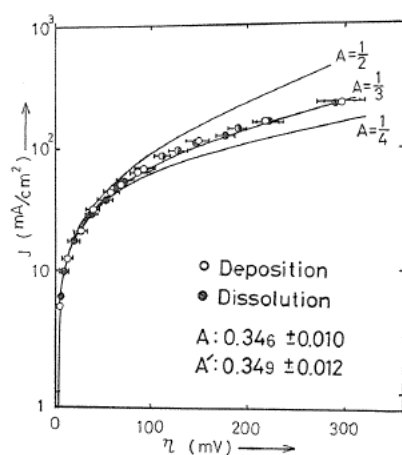


FIG. 14. Overpotentials and current densities of deposition and dissolution of silver in AgCl-KCl (70 : 30 mol) at 500°C.

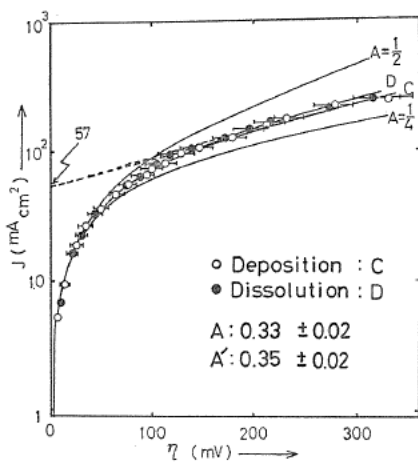


FIG. 15. Overpotentials and current densities of deposition and dissolution of silver in AgCl-KCl (70 : 30 mol) at 550°C.

and the dissolution of silver in a concentrated chloride fused salt, and the values of the coefficient are nearly equal to 1/3.

3.2. Miscellaneous results

It should be pointed out here that the overpotential coefficient β_0 changes with current densities as shown in Table 5. The influence of the current densities on β_0 will be discussed in the next chapter. Considering the relation (6) or (6') and $\alpha_0 + \beta_0$ values it is apparent that there is much overpotential between a reference electrode and an equilibrium state. Since η_{pc} and $\alpha_0 + \beta_0$ increase with current densities, the overpotentials above described *i.e.* $\eta_{pc}(\alpha_0 + \beta_0 - 1)$ increase with current densities, generally the equilibrium potential of the reference electrode shifts to higher one. This means that in higher current densities the concentration of oxidant on the surface of the reference electrode becomes lower. It is apparent that for dissolution opposite situations occur on the reference electrode.

It seems contradicting the common-sense of electro-chemistry. However, the context of relation (2) to (6) or (2') to (6') the change of the reference state in a different run of experiment gives no effects on the results.

The surface area of electrode also have an influence on the overpotential coefficients. The results obtained with different areas are listed in the Table 2. The exchange current densities, the transfer coefficients, and overpotentials of two electrodes are consistent with each other within the experimental errors.

3.3. The activation energy of electro-deposition and dissolution of AgCl in KCl

Since the exchange current densities of electro-deposition and dissolution coincide well with each other, the activation energies and the activated states of these processes should be equal. The relationship of $\log J_0$ vs. $1/T$ is illustrated in Fig. 16. From the liner relationship of those plots the activation energy was obtained as 1.95 ± 0.03 Kcal. This rather small value will be explained in the next chapter.

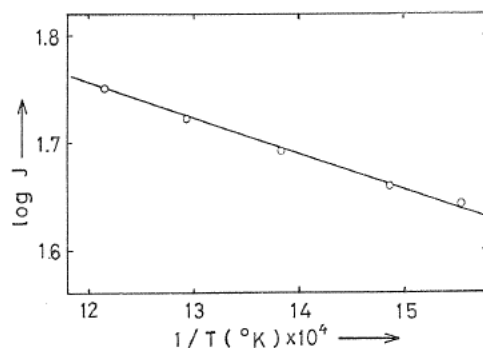


FIG. 16. Relationship between exchange current density and $1/T$ in AgCl-KCl (7:3 mole ratio) melt.

Chapter II. Theoretical Consideration of Electro-deposition and Dissolution of Silver in AgCl-KCl (70:30 mol)

1. Theoretical consideration of electro-deposition and dissolution of simple processes

1.1. Preliminary consideration⁴⁾

Simple process mentioned in heading of this section means that in solution there is one kind of simple ions such as Ag^+ , which is the main oxidant for the electrochemical reaction or the electrodeposition of this metal in a stationary state. Usually such a reaction are represented as $\text{M}^{n+} + ne \rightarrow \text{M}$. For this reaction early workes⁷⁾ proposed several equations for current densities in a steady state.

They deduced the equation in the view that there had no reverse reaction in electro-deposition. As we know Mattson⁷⁾ applied usual equation for an activation control process to copper deposition in sulfuric acid. The one of the authors of this paper applied this equation to electro-deposition and dissolution in a fused salt and proposed the some relation between the transfer coefficient and the number of the oxidant ions. These procedure will be briefly discussed below.

It was assumed in a steady state of electrodeposition of metal for example $n=1$, $M^+ + e \rightarrow M$ that (1) M^+ ions have a sufficient concentration to overcome the diffusion process, (2) some activated ion species, which are mobile equilibrium with $p'M^+$, and (3) the electron transfer process is $M^+ + e \rightarrow M$. Then the following relation will be obtained.

$$nF\eta_c = E_o + RT \ln \left(\frac{a_M^{\circ+}}{a_{M_{ac}}^{\circ+}} \right)^{p'} \quad (1)$$

Therefore

$$a_{M_{ac}}^{\circ+} = a_M^{\circ+} e^{-nF(1/p')(\eta_c - E_o)/RT} \quad (2)$$

From the assumption (3)

$$a_{M_{ac}}^{\circ+} k_c^{\circ} / k_a = e^{-nF\eta_c/RT} \quad (3)$$

It was assumed the cathodic rate constant does not change with overpotentials. Consequently

$$\begin{aligned} J_c &= nF(a_{M_{ac}}^{\circ+} k_c^{\circ} - k_a) \\ &= nF a_M^{\circ+} e^{nF(1/p') E_o/RT} k_c^{\circ} \{ e^{-nF(1/p') \eta_c/RT} - e^{nF(1-1/p') \eta_c/RT} \} \\ &= J_o \{ e^{-nF a \eta_c/RT} - e^{n(1-a) \eta_c/RT} \} \end{aligned} \quad (4)$$

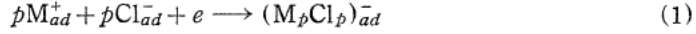
where $a_M^{\circ+}$, $a_{M_{ac}}^{\circ+}$ are an activity of M^+ and $M_{ac}^{\circ+}$ ions respectively, and $a_M^{\circ+}$ denotes in an equilibrium concentration. Other nomenclatures represent usual meaning. As a consequence of this treatment the transfer coefficient was connected with the numbers of the ions to be deposited as $\alpha = \frac{1}{p'}$. In this treatment, however, the assumption (2), (3) and procedures seem to be artificial. Refined treatment will be described in the next section.

1.2. Mobile equilibrium treatment¹⁰⁾

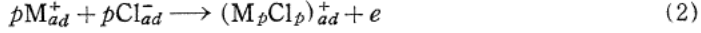
Mobile equilibrium concepts were introduced to the electrodeposition and dissolution of silver and zirconium in fused salt solutions by one of the authors. In this paper only the simple process as silver deposition and dissolution have been treated. In a fused salt solution as in chloride the ions with a single valency are reasonably assumed not to make a complex ions. And it is not necessary to consider the solvation which usually occurs in aqueous solutions. Therefore there is a possibility that the essential features of metal deposition are revealed by investigation of these processes.

In the following monovalent chloride was adopted as an example. It was assumed as follows:

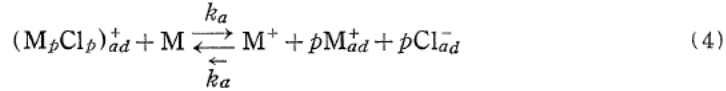
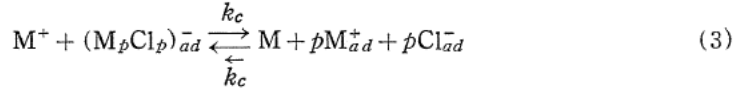
[1] Activated ions of negative charge and positive charge on the electrode are in a mobile equilibrium with overpotentials applied, *i.e.* in a cathode



and in an anode



[2] Deposition and dissolution proceed according to the following reaction,



What are the activated complexes above described will be discussed in the next section. The ion M_{ad}^+ is also activated one which is a different species of metal ions. If the existence of the activated complex were verified, the logic mentioned above is reasonable from thermodynamical points. It should be noticed that the rate constant of deposition or dissolution reaction *i.e.* the reaction of (3) or (4) is usual one used in chemical reactions, which do not depend on the electrical potential applied but only on temperatures.

In this way the whole electrode process obtained from (1) and (3) as for deposition is



and similarly from (2) and (4) for dissolution



For brevity here after activated complexes are denoted by M_p^- and M_p^+ . Then the reaction (1) and (2) are written briefly as



It should be noticed that the relations (5) and (6) are representations for convenience on the following treatments. When standard potentials of (5) and (6) are denoted E_c° and E_a° , at an arbitrary potential (5) and (6) have the potentials,

$$E_c = E_c^\circ + \frac{RT}{F} \ln \frac{(a_M^+)^p}{a_{M_p^-}}$$

$$E_a = E_a^\circ - \frac{RT}{F} \ln \frac{(a_M^+)^p}{a_{M_p^+}}$$

Since in equilibrium $E_c = 0 = E_a$,

$$\eta_c = \frac{RT}{F} \left\{ \ln \frac{a_{M_p^-}^\circ}{(a_M^+)^\circ} + \ln \frac{(a_M^+)^\circ}{a_{M_p^-}} \right\}$$

$$= \frac{RT}{F} \left\{ \ln \frac{a_{M_p}^{\circ-}}{a_{M_p}^-} + \ln \left(\frac{a_M^+}{a_M^{\circ+}} \right)^p \right\} \quad (7)$$

$$\begin{aligned} \eta_a &= \frac{RT}{F} \left\{ \ln \frac{(a_M^+)^p}{a_{M_p}^{\circ+}} - \ln \frac{(a_M^+)^p}{a_{M_p}^+} \right\} \\ &= \frac{RT}{F} \left\{ \ln \frac{a_{M_p}^+}{a_{M_p}^{\circ+}} + \ln \left(\frac{a_M^+}{a_M^{\circ+}} \right)^p \right\} \end{aligned} \quad (8)$$

where a_{M^+} means the activity of M^+ ions adsorbed on the electrode to which an overpotential has been applied, and $a_M^{\circ+}$ means the activity of the same ion on the equilibrium electrode, which is in equilibrium with the activity of M^+ ions in solution. Similar notations were adopted for M_p^+ ions. Usual convention was accepted for the signs of overpotentials *i.e.* negative for η_c and positive for η_a . Since

$$\eta_c = A\eta_c + (1-A)\eta_c \quad (9)$$

$$\eta_a = A'\eta_a + (1-A')\eta_a \quad (10),$$

comparing (7) and (8) with (9) and (10), on a cathode

$$A\eta_c = \frac{RT}{F} \ln \frac{a_{M_p}^{\circ-}}{a_{M_p}^-} \quad (11)$$

$$(1-A)\eta_c = \frac{RT}{F} \ln \left(\frac{a_M^+}{a_M^{\circ+}} \right)^p \quad (12)$$

and on an anode

$$A'\eta_a = \frac{RT}{F} \ln \frac{a_{M_p}^+}{a_{M_p}^{\circ+}} \quad (13)$$

$$(1-A')\eta_a = \frac{RT}{F} \ln \left(\frac{a_M^+}{a_M^{\circ+}} \right)^p \quad (14).$$

In the case

$$\frac{a_{M_p}^{\circ-}}{a_{M_p}^-} \simeq \frac{a_M^+}{a_M^{\circ+}} \quad \text{or} \quad \frac{a_{M_p}^+}{a_{M_p}^{\circ+}} \simeq \frac{a_M^+}{a_M^{\circ+}} \quad (15)$$

equation (7) and (8) becomes

$$\eta \simeq \eta_1 + p\eta_1 \simeq (p+1)\eta_1 \quad (16)$$

where $\eta_1 = \frac{RT}{F} \ln \left(\frac{a_M^+}{a_M^{\circ+}} \right)$ or $\frac{RT}{F} \ln \left(\frac{a_M^{\circ+}}{a_M^+} \right)$

then with equation (11)

$$A \simeq \frac{1}{p+1} \quad (17).$$

Similarly

$$A' \simeq \frac{1}{p+1} \quad (18).$$

If the number of p in A and A' are equal then $A \simeq A'$, if not $A \neq A'$. The condition of (15) could well be fulfilled in a steady state.

From the relation of (17) and (18) the transfer coefficients of electro-deposition and dissolution of the simple process can be approximately calculated as $1/2=0.5$, $1/3=0.333$, $1/4=0.25$, $1/5=0.2$, $1/6=0.166$ and etc. It is also evident from equation (11) to (14) that the transfer coefficients depend on the temperature and the concentration of solution, because an activity depends on them.

It is evident in this point p' described in 1.1 equals to $p+1$ and $p'M^+$ means the left side of the rate determining equation of (3).

In the treatment above described it can occur that the activated ion of dissolution process may be the divalent ion *i.e.* in the reaction of (2) and (4) $p=1$.* Then dissolution process becomes



Then anodic overpotentials are expressed in the equation:

$$F\eta_a = RT \ln \left(\frac{a_{M_{ad}^{2+}}}{a_{M_{ad}^+}} \right) + RT \ln \left(\frac{a_{M^+}}{a_{M^+}} \right) \quad (21)$$

Since first term and second term will be represented by the potentials, (21) becomes

$$\begin{aligned} F\eta_a &= 2F\eta_2 + F\eta_1 \\ &\simeq 3F\eta_2 \end{aligned} \quad (22)$$

where $\eta_2 \simeq \eta_1$

Consequently $\eta_2 \simeq \frac{1}{3}\eta_a \simeq \eta_1$

Therefore (21) becomes

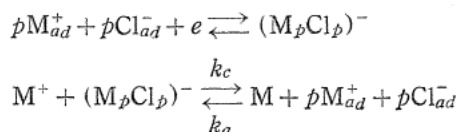
$$\eta_a = A'\eta_a + (1 - A')\eta_a \simeq \frac{2}{3}\eta_a + \frac{1}{3}\eta_a \quad (23)$$

Thus $A' \simeq \frac{2}{3} = 0.66$

In any case as shown in equation (11), (13) and (21) the transfer coefficients are expressed as the ratio of the concentration overpotentials to the total overpotential referred to an equilibrium state. It has been clarified that the relation between the transfer coefficient of electro-deposition and that of dissolution *i.e.* $A'=1-A$, which is generally accepted, is not valid all the time. This relation is approximately realized only in the case where the activated ion of dissolution process is a divalent metal ion* or $p=1$ in (17) and (18), *i.e.* $A \simeq A' \simeq \frac{1}{2}$.

In the treatment above mentioned the rate determining steps of deposition and dissolution were different. If the rate determining steps of deposition and dissolution were the forward and the backward of the same reaction, only one

species of activated complex exist. This assumption might be in the case where $(M_pCl_p)^-$ complex ion is very stable. In this way the following relation can be obtained.



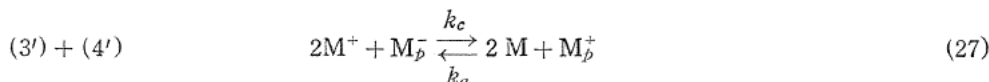
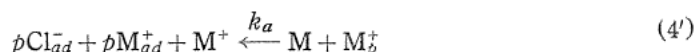
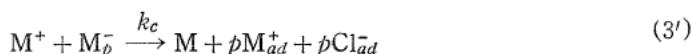
Since for the cathode processes the equation between an overpotential and a transfer coefficient is the same to (7), (9), (11) and (12), the next relations are obtained.

$$A'\eta_a = \frac{RT}{F} \ln \left(\frac{a_M^+}{a_{M^+}^{\circ+}} \right)^p = (1-A)\eta_c \quad (24)$$

$$(1-A')\eta_a = \frac{RT}{F} \ln \frac{a_{M_p}^{\circ-}}{a_{M_p}^-} = A\eta_c \quad (25)$$

then
$$A' = (1-A) \quad (26)$$

This generally accepted relation in electrochemistry is only valid in this case. Turning to the beginning of this section the assumption [2] about the rate determining reaction will be discussed more detail. The reaction (3) and (4) should be written in another way to consider the whole system.



If this equilibrium (27) is extremely in the left side, then the deposition and dissolution occur in one rate determining relation (3).

Hence the procedure to get the equation for a current density will be described. When the rate constants of the forward reactions of (3) and (4) have been written by k_c and k_a respectively, and those of backward reactions by \tilde{k}_c and \tilde{k}_a , the current densities can be expressed

$$J_c = F\mathcal{M}_0 a_{M_p}^- k_c - F\mathcal{M}_0 (a_M^+)^p \tilde{k}_c \quad (28)$$

where \mathcal{M}_0 is the concentration of a reference state of activities in mol/cm²

$$J_a = F\mathcal{M}_0 a_{M_p}^+ k_a - F\mathcal{M}_0 (a_{M_p}^+)^p \tilde{k}_a \quad (29)$$

From (11) and (12) for cathode

$$a_{M_p}^- = a_{M_p}^{\circ-} e^{-FA\eta_c/RT} \quad (30)$$

$$(a_M^+)^p = (a_{M_p}^{\circ+})^p e^{F(1-A)\eta_c/RT} \quad (31)$$

and in equilibrium

$$a_{M^+}^{\circ-} k_c = (a_M^{\circ+})^p \tilde{k}_c \quad (32)$$

therefore with (30), (31) and (32), (28) becomes

$$J_c = nF \mathcal{M}_0 (a_M^{\circ+})^p \tilde{k}_c \{e^{-FA\eta_c/RT} - e^{F(1-A)\eta_c/RT}\} \quad (33)$$

Similarly (29) becomes

$$J_a = nF \mathcal{M}_0 (a_M^{\circ+})^p \tilde{k}_a \{e^{FA'\eta_a/RT} - e^{-F(1-A')\eta_a/RT}\} \quad (34)$$

When $\tilde{k}_c = \tilde{k}_a$

$$F \mathcal{M}_0 (a_M^{\circ+})^p \tilde{k}_c = F \mathcal{M}_0 (a_M^{\circ+})^p \tilde{k}_a = J_0 \quad (35)$$

In the case $\tilde{k}_c \neq \tilde{k}_a$ exchange currents do not coincide each other. In definition $a_M^{\circ+}$ is the activity of M^+ ions on the electrode in equilibrium state, those ions are usually called ad-ions. Between the activity of ad-ions and that of ions in solution there is the relation in equilibrium state

$$a_M^{\circ+} = a_{M(s)}^{\circ+} e^{-\Delta G_{ad}^{\circ}/RT} \quad (36)$$

where $a_{M(s)}^{\circ+}$ means the activity of M^+ ions in the solution with which an electrode is in equilibrium, and ΔG_{ad}° means the free energy of formation of ad-ions in the standard state. The values of ΔG_{ad}° usually have negative signs. Accordingly exchange currents are indicated

$$J_0^c = F \mathcal{M}_0 a_{M(s)}^{\circ+} e^{-p(\Delta G_{ad}^{\circ})/RT} \nu_c e^{-E_c^*/RT} \quad (37)$$

$$J_0^a = F \mathcal{M}_0 a_{M(s)}^{\circ+} e^{-p(\Delta G_{ad}^{\circ})/RT} \nu_a e^{-E_a^*/RT} \quad (38)$$

where $\tilde{k}_c = \nu_c e^{-E_c^*/RT}$, $\tilde{k}_a = \nu_a e^{-E_a^*/RT}$ and E_c^* and E_a^* are the respective activation energies.

In the range of temperatures where the temperature dependence of the activity of metal ions in solution is almost constant activation energy E_{AC} obtained by an increment of $\log J_0$ vs. $1/T$ is expressed

$$E_{AC} = p(\Delta H_{ad}^{\circ}) + E_c^* \quad (39)$$

or
$$E_{AC} = p(\Delta H_{ad}^{\circ}) + E_a^* \quad (40).$$

Since ΔH_{ad}° usually have negative value, E_{AC} is less than E_c^* or E_a^* .

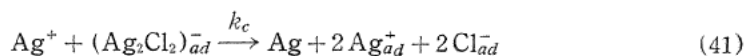
2. Electro-deposition and dissolution of AgCl in fused salt solutions

As has been stated in Chapter I for silver the transfer coefficients of cathodic and anodic process were almost the same values from 400°C to 500°C in KCl melt. Since the values of the coefficient were around 0.33=1/3, p is obtained as 2 according to the equations (17) and (18) of 1.2 in Ch. II. Therefore the activated complex can be assigned as $(Ag_2Cl_2)^-$, and $(Ag_2Cl_2)^+$ adsorbed on the electrode. According to the preliminary work on the absorption spectrum of AgCl melt described in the next chapter confirmed the existence of colloidal band of Ag° . The species of Ag° have been considered as apparent mono-valent

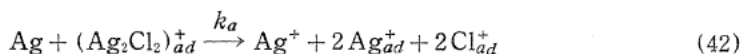
ion loosely connected with electron¹¹). Therefore there must be negative sign defect ions which loosely bind or trap the electron. Then it may be considered as $(Ag_2Cl_2)^-$ or $(AgAg^\circ Cl_2)^-$. Absorption bands of negative defects also have been observed. It is assumed in this stage that $(Ag_2Cl_2)^+$ include Cl_2^- ion.

As a consequence the rate determining reaction could be considered as follows:

for cathode



for anode



Since exchange currents of deposition and dissolution coincided well as shown in the figure in Chapter I, the rate constant, $\bar{k}_c = \bar{k}_a$ from equation (35). The activation energy obtained interpreted from equation (39) and (40) as

$$E_{Ac} = 2\Delta H_{ad} + E_c^* = 1.95 \pm 0.03 \text{ Kcal/mol and } E_c^* = E_a^*$$

If ΔH_{ad} was assumed about -2 Kcal/mol, then the activation energy of deposition and dissolution are estimated as 6 Kcal/mol.

3. Summary

For the end of this chapter it will be useful to present a summary. In section 1.1 the electro-deposition of metals which usually have a single metal ion was treated by electrochemical kinetic method. In this way it was assumed that the activated state was produced by p' number of metal ions and only the charge (n) of a single activated metal ion was transferred to the electrode. As the result of this treatment the transfer coefficient (α) appeared, which we call electrochemical transfer coefficient, was connected with p' as $= \frac{1}{p'}$. It was possible to apply the similar treatment to electro-dissolution of metals¹¹, procedures, however, were omitted in this paper.

In section 1.2 usual chemical kinetic method was introduced to electrochemical processes. This method was named in this paper mobile equilibrium treatment. It may be more preferable to call thermodynamical treatment or chemical kinetic method. It has been clarified in this treatment that the transfer coefficient means a proportion of the partition of a overpotential to the concentration polarization of a reactant in a rate determining reaction. The transfer coefficients in this treatment *i.e.* A and A' was distinguished in notation from that of electrochemical treatment.

Another important results of this treatment as follows;

(1) There are two cases of the processes in electro-deposition and dissolution of metals. One has the same rate determining reaction for deposition and dissolution processes in which the transfer coefficients of deposition, A and dissolution, A' have the relation, $A=1-A'$, and the other has the different rate determining reaction for each process. In the latter case there are another two cases in which $A \simeq A'$ or $A \approx A'$. It has been concluded that all the cases are included in this treatment.

(2) The existence and the composition of an activated complex were elucidated by this treatment. A clear account was also given to p' in section 1.1.

(3) Application of this treatment to electro-deposition and dissolution of silver in AgCl-KCl fused salt has been described in Section 2. It has been suggested in this case that Ag° and Cl_2^- ions on the electrodes play a main role in deposition and dissolution respectively.

(4) This concept will be applied to electro-deposition and dissolution of metals not only in a fused salt but also in an aqueous solution. In aqueous solution the dehydration process of a metal ion should be considered before adsorption.

Chapter III. Absorption Spectra of Molten Silver Chloride

1. Introduction

It was reported by early Workers¹²⁾ that the absorption spectra of pure silver chloride melt consists of a broad intense absorption band which obscures the ultraviolet end of the spectrum and a region of complete transparency. However, the absorption spectra of molten silver chloride was not simple spectrum which described previously¹³⁾. It changes markedly in color with chlorine pressure. Then we suggested from the quasi-crystalline model that a defect with negative or positive charge are formed by chlorine pressure¹³⁾.

In this chapter we describe at first the absorption spectra of pure silver chloride from solid to molten state and secondly those of the molten salts when silver chloride was dissolved in a eutectic mixture of sodium and potassium chloride as a solvent at 700°C.

2. Experimental

2.1. Experimental procedure

The technique for obtaining absorption spectra of molten salt has been described previously¹³⁾.

The instrument used for this studies consists of the monochromator of a Model CT-50 JASCO spectrophotometer. The measurement was performed in the spectral region from 400 to 800 $m\mu$, keeping the furnace at a constant temperature in the range from room temperature to 700°C. The furnace has a cylindrical ceramic cell-holder which is wound by a nichrom wire for heating, and has a small window (ϕ 10 mm) for an optical path of the light beam. The cell were made of quartz with 1 mm optical path for pure silver chloride and 10 mm optical path for diluted silver chloride, and the empty cell was used for a reference. These cells were loaded on one hand with pure silver chloride under the vacuum of 10^{-4} mmHg and on the other with the mixture of silver chloride, sodium and potassium chloride under pure argon atmosphere, and then these cells were heated to suitable temperature for experiment. In the case where the temperatures of measurement were varied, step-descending or ascending was applied to melt or solid respectively.

2.2. Specimens

Chemicals of analytical grade were purified as follow; Silver chloride was heated to melt in an atmosphere of dry argon and purified by passing dry purified chlorine gas for one hour at 500°C.

Sodium and potassium chloride were also treated with chlorine for one hour

at 800°C.

Solid silver chloride sample was prepared from pure silver metal (99.999%), analytical grade nitric acid and hydrochloric acid. Final purification was carried out in high vacuum at 500°C. A purified salt was solidified on a thin quartz plate under a dry argon, and then covered with a similar plate. After one more cycle of heating and cooling the specimen was removed from the plates.

3. Results and Discussion

3.1. The spectrum of pure silver chloride

The temperature dependencies on the wavelength of the absorption spectra for solid and liquid silver chloride are shown in Fig. 17 to 18.

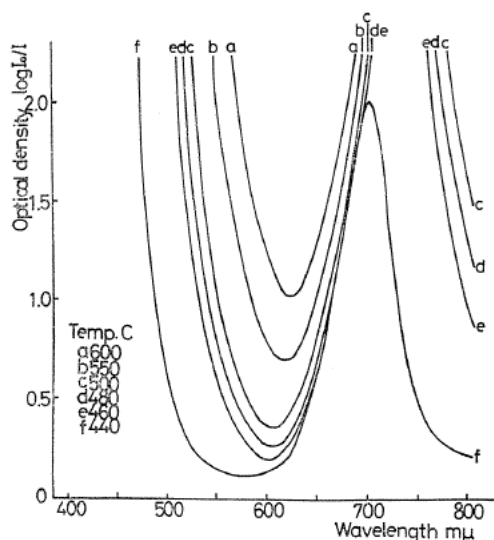


FIG. 17. Absorption spectra of AgCl.

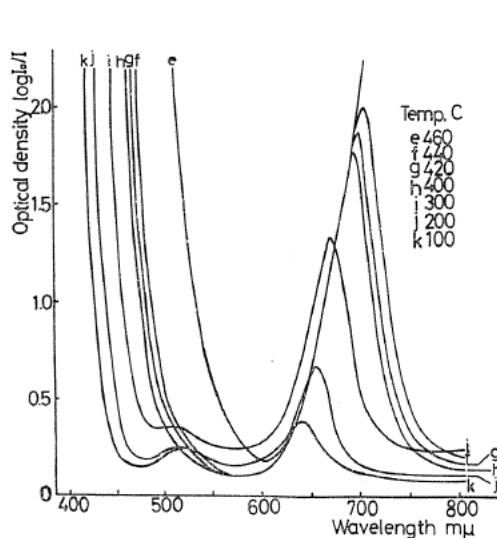


FIG. 18. Absorption spectra of AgCl.

The observed spectra of liquid silver chloride in Fig. 17 were divided in the wavelength scale to two parts, *i.e.* one of a complete absorption band and the other of a transmission part except one band *e.g.* 710 m μ at 460°C. The absorption band edge moved to shorter wavelength with decreasing temperature.

The temperature dependency of the wavelength on the peak shifted linearly from 500°C to 460°C in the melts. At melting point these peak shifted to a shorter wavelength but the same increment to the temperature were also observed for solid to 400°C. Therefore these bands might be caused by the same species. On the other hand, at 300°C the band appeared at 530 m μ as shown in Fig. 18 and its intensity decreased slowly with decreasing temperature. It may be considered that for melt this band was hidden in absorption edge. Simultaneously, at 300°C the broad bands appeared at 650 m μ and the intensity rapidly decreasing temperature.

Those changes of optical absorption were further studied by thin solid silver chloride plate. In this case the temperature was ascended. There was no absorption band from 600 m μ to 650 m μ at room temperature, but with increasing

temperature there appeared a band at 100°C. Then the peak was shifted to a longer wavelength. It was confirmed that the band observed around 650 m μ below 300°C in Fig. 18 corresponded to the results above mentioned. Consequently, it is suggested that these band caused by some defects in AgCl.

These observation can be interpreted in the following way;

(1) The 530 m μ band correspond to a well known colloid band of solid (Ag $^{\circ}$) around 550 m μ reported by others¹⁴⁾.

(2) The 630-650 m μ band below 400°C differ from that of 680-720 m μ band. The former may be a F' type center (Cl $^{2-}$).

(3) The 680-720 m μ band above 400°C had not been found and explained. We propose this band to be associated with electrons trapped on Cl $^-$ or any defect on the bases of previous paper¹³⁾¹⁵⁾. Negative defects considered are Cl $^{2-}$ and Cl $_2^-$. It was observed in previous paper that the electromotive force of AgCl depended linearly on chlorine pressure in the deep color region. This result predicts the existence of Cl $_2$ or Cl $_2^-$ ions in the melt. Therefore it was considered that these bands were caused by Cl $_2^-$ ions.

The discussion for other band observed in solid is not important for this paper. It will be discussed in elsewhere.

3.2. The absorption spectra of silver chloride dissolved in NaCl-KCl (1:1) melts

In this section, we have discussed the spectrum of molten sodium and potassium chlorides with various concentration of silver chloride.

The absorption spectra for the melts, in which silver metal was inserted, and silver chloride was added in mole fraction from 5.35×10^{-4} to 1.08×10^{-1} mole fraction at 700°C are shown in Fig. 19.

The band for silver chloride appeared at 430, 530, 620, 640, and over 700 m μ , and their intensity increased with increasing silver chloride concentration except for 620 m μ . The 620 m μ band disappeared at concentration just above 5.08×10^{-3} mole fraction silver chloride, and then the 640 m μ band began to grow. The 530 and 640 m μ bands perfectly coincide with those of pure silver chloride, as discussed in preceding section. Therefore, it is considered that former is due to silver colloidal band (Ag $^{\circ}$) and the latter might be due to Cl $^{2-}$. The absorption band over 700 m μ corresponds to 680-710 m μ band of pure silver chloride melt. Therefore, it might be considered that this absorption caused by Cl $_2^-$ ions. The height of 430 m μ band increased rapidly with concentrations above 2×10^{-3} mole fractions. It might be caused by a positive charge defects because energy is high compared to Ag $^{\circ}$ band. This band was supposed due to Ag $^{2+**}$. Further investigation is necessary to determine of this band and others. It should be noticed here that in AgCl-KCl-NaCl melts there exist the species Ag $^{\circ}$, Cl $_2^-$ and probably Ag $^{2+}$ ions.

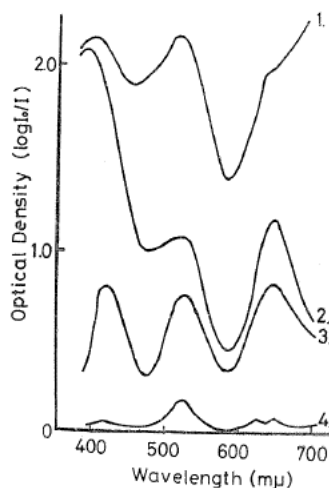


FIG. 19. Absorption spectra of AgCl in NaCl-KCl (1:1) melt at 700°

Concentration of AgCl (mole fraction)

- 1: 1.08×10^{-1} , 2: 4.92×10^{-2}
3: 2.01×10^{-3} , 4: 5.08×10^{-3}

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* Main deposition process is $M^+ + e \rightarrow M$ and $p=2$.

** Ag^{2+} was supposed to be in the field of the ligand.

Nomenclature

- A : thermodynamical cathodic transfer coefficients [cf. Eq. (7)-(10) Ch. II]
 A' : thermodynamical anodic transfer coefficients [cf. Eq. (7)-(10) Ch. II]
 a^o : activities of an oxidant in an equilibrium state
 a_R^o : activities of a reductant in an equilibrium state
 a_M^+ : activities of a monovalent metal ions on the electrode
 $a_{M_{ac}}^+$: activities of M_{ac}^+ ion species cf. Eq. (2) Ch. II 1.1
 a_M^+ : activities of M^+ ion of equilibrium
 $a_{M_p^+}$: activities of $(M_pCl_p)^+$ on the cathode cf. Ch. II. 2.1
 $a_{M_p^-}$: activities of $(M_pCl_p)^-$ on the anode cf. Ch. II. 2.1
 $a_{M_p}^o$: $a_{M_p^+}$ on equilibrium electrode

- $a_{M_p}^{\circ-}$: $a_{M_p}^-$ on equilibrium electrode
 $\hat{a}_{M(s)}^{\circ-}$: activities of M^+ ion in equilibrium solution with a metal electrode
 E_a : anode potentials
 E_a° : standard potentials of anode
 E_c : cathode potentials
 E_c° : standard potentials of cathode
 E_{AC} : activation energies for cathode or anode
 E_a^* : activation energies for anodic rate determining reaction
 E_c^* : activation energies for cathodic rate determining reaction
 \vec{i} : kinetic cathodic currents in cathodic processes per cm^2
 \overleftarrow{i} : kinetic anodic currents in cathode processes per cm^2
 J : current densities ($/\text{cm}^2$)
 J_a : anodic current densities
 J_c : cathodic current densities
 J_0 : exchange current densities
 J_0^a : anodic exchange current densities
 J_0^c : cathodic current densities
 k_a : forward rate constants for rate determining reaction of anodic processes
 \overleftarrow{k}_a : backward rate constants for rate determining reaction of anodic processes
 k_c : forward rate constants for rate determining reaction of cathodic processes
 \overleftarrow{k}_c : backward rate constants for rate determining reaction of cathodic processes
 k_c° : electrochemical rate constants for cathode processes at equilibrium
 k_b : electrochemical rate constants for anode processes
 k_f : reaction rate constants for a forward direction cf. Eq. (3) Ch. I
 M : metals
 M^+ : monovalent ions of metals
 M^{n+} : n valent ions of metals
 M_{ac} : activated states of electro-deposition or electro-dissolution of metals (cf. Ch. II 1.1)
 M_{ac}^+ : activated ion species in cathodic processes
 M_{ad}^+ : metal ions on the electrode
 M_p^+ : activated complexes of anodic processes *i.e.* $(M_pCl_p)^+$ cf. Ch. II 1.2
 M_p^- : activated complexes of cathodic processes *i.e.* $(M_pCl_p)^-$ cf. Ch. II 1.2
 \mathcal{M}_0 : number of moles of an oxidant per cm^2 in a reference state of the activity
 \mathcal{M}_R : number of moles of a reductant per cm^2 in a reference state of the activity
 p : number of metal ions to produce an activated complexes Ch. II 1.2
 p' : number of metal ions in activated state Ch. I 1.1
 ΔG_{ad}° : free energies of adsorption of metal ions on the electrode
 ΔH_{ad}° : heat contents of adsorption of metal ions on the electrode
 α : transfer coefficients electrochemically obtained cf. Eq. (4) Ch. II 1.1
 α_0 : cathodic overpotential coefficients cf. Eq. (5) Ch. I
 α'_0 : anodic overpotentials coefficients cf. Eq. (6') Ch. I
 β_0 : cathodic overpotential coefficients cf. Eq. (5) Ch. I
 β'_0 : anodic overpotential coefficients cf. Eq. (5') Ch. I
 η : overpotentials of a cathodic process or an anodic process
 η_a : anodic overpotentials

η_c : cathodic overpotentials

η_{pa} : anodic overpotentials measured with a reference electrode without ohmic overpotentials

η_{pc} : cathodic overpotentials measured with a reference electrode without ohmic overpotentials

ν_a : frequency factors in the rate constant of \tilde{k}_a^{\leftarrow}

ν_c : frequency factors in the rate constant of \tilde{k}_c^{\leftarrow}