Summary

- 1) The electromotive force of the cell $\text{Th(S)}/\text{ThCl}_4\text{-NaCl(L)}/\text{Cl}_2\text{(g)}$ was measured in the ranges of 0.2 mole fraction of ThCl_4 at $630^\circ\text{C} \sim 720^\circ\text{C}$ and $0.3 \sim 0.7$ at $600^\circ\text{C} \sim 700^\circ\text{C}$.
- 2) The cell reaction can be regarded as $\text{Th(S)} + 2\text{Cl}_2\text{(g)} = \text{ThCl}_4\text{(L)}$ by the fact that the extrapolated value from the measured curve is not very much different from the values calculated from thermodynamic data, and that the Th^{4+} ion is more stable than that of other valences of thorium.
- 3) The excess stability shows the existence of a compounds, the structure of which is in accordance with that indicated by thermal analysis, that is Na_2ThCl_6 .
- 4) The large deviation from ideal state

may be due to the formation of a complex ion such as $[\text{ThCl}_6]^{2-}$ in the melt.

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Studies on the Anodic Dissolution of Silver in a LiCl-KCl Eutectic Melt*

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- 1) Theoretical treatments are made on the anodic dissolution of silver in the LiCl-KCl eutectic melt. The main results are:
 - i) When anodic polarization is small, electrode process is controlled by diffu-

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sion or convective diffusion in a nonsteady and a steady state, respectively.

ii) When the polarization is very intense, migration controls the process in a steady state and current (i) obeys the following equations.

$$i = k(V - \psi_s)$$

where k , V and ψ_s are a constant, the applied potential and E.M.F. of the cell, Ag/AgCl/LiCl-KCl-AgCl/Ag, respectively.

2) The experiments were performed as follows. The mixture of LiCl, KCl and AgCl was dehydrated by passing dry HCl gas. The electrode system consisted of a microelectrode (Ag point), a reference electrode (Ag wire) and a counter electrode (Ag plate). The potentiostat, which responds to 50 kc/sec., was employed and the response was recorded by a high speed pen recorder or a synroscope.

3) The experimental results coincided with theoretical presumptions. The classification of dissolution mechanism at a constant potential was made on the potential-time plane.

1. Introduction

Elucidation of the electrode processes in molten salts has begun recently.¹⁾ According to the results obtained so far, electrode processes in halide melts have the following characteristics.

- i) The activation overpotential is small.
- ii) When a metal is dissolved anodically, it is possible that the electrode surface is covered with its pure halide.

Piontelli and his coworkers^{2~4)} and Sternberg et al.^{5,6)} investigated anodic and cathodic behaviors of various metals in their molten halides. Takahashi et al.⁷⁾ studied anodic behaviors of metals in the LiCl-KCl eutectic melt.

In the present paper, as the initial step, theoretical analysis are made on the anodic behaviors of Ag electrode in the LiCl-KCl eutectic melt.

As the next step, the above theories are ascertained by means of rapid methods which eliminate the change of electrode condition. Especially, two kinds of measuring method, "Two-points method" and "Differential method", are employed.

2. Theory

2.1 Assumptions and Conditions

Theoretical treatments are carried out on the following assumptions and conditions.

- i) The concentrations of Cl^- , Ag^+ , K^+ and Li^+ are represented by C_n ($n = 0, 1, 2, 3$). C_0 , the concentration of Cl^- , is uniform even in the vicinity of electrode.

There is no flow of Cl^- in the direction perpendicular to the electrode ($j_0 = 0$).

- ii) Experimental temperature is above the melting point of AgCl.
- iii) Activation overpotential is neglected.
- iv) Ag equilibrated with Ag^+ in bulk solution is used as the reference electrode, whose potential is defined as zero. Therefore, "Electrode potential" means the potential difference between the microelectrode and the reference electrode.

2.2 Derivations of equations for the steady-state condition

Under steady-state condition, C_n is assumed to be the bulk concentration C_n^b at the distance δ from electrode surface. The flux of charged species is expressed

by Nernst-Planck's equation.

$$j_n = FD_n C_n E / RT - D_n \partial C_n / \partial x \quad (1)$$

(n=1,2,3)

Where, x ; distance from electrode surface,
 D_n ; diffusion coefficient of n 'th ions,
 j_n ; flux per unit area of n 'th ions,
 E . strength of electric field which is assumed to be constant through the region $0 < x < \delta$

Under the steady-state condition, only Ag^+ flows and ions of K^+ or Li^+ do not. Accordingly,

$$j_n = 0 \quad (n=2,3) \quad (2)$$

The solution of Eq.(1) and (2) is

$$C_n(x) = C_n^b \exp \{ FE(x-\delta)/RT \} \quad (3)$$

where C_n^b is the bulk concentration of K^+ or Li^+ . The condition of Electro-neutrality leads to the relation.

$$\sum_{n=1}^3 C_n(x) = C_0(x) = C_0^b = \sum_{n=1}^3 C_n^b \quad (4)$$

Thus the distribution of Ag^+ is expressed by the equation

$$C_1(x) = C_1^b - (C_0^b - C_1^b) \exp FE(x-\delta)/RT \quad (5)$$

On the other hand, applied potential V is equal to the sum of the concentration overpotential ψ and the ohmic drop ϕ .

$$V = \psi + \phi \quad (6)$$

ψ and ϕ are represented as follows.

$$\psi = \frac{RT}{F} \ln \gamma^0 C_1(o) / \gamma^b C_1^b \quad (7)$$

$$\phi = E\delta + iR \quad (8)$$

where γ is the activity coefficient of Ag^+ , R is the resistance of solution between $x=\delta$ and reference electrode and i is the current. Therefore, R depends on the position of reference electrode. Combining the relations of (1) and (5), i is expressed by Eq. (9).

$$i = F^2 D_1 C_0^b A E / RT = K_1 A E \quad (9)$$

where A is the surface area of electrode and $K_1 = F^2 D_1 C_0^b / RT$.

-From Eqs.(8) and (9),

$$\phi = (\delta + K_1 R A) E = r E \quad (10)$$

r means the effective thickness of layer

through which potential drops.

Fig. 1 Relation of E , ϕ , ψ and V .

Fig. 1 shows the relations between E or i and ψ , ϕ and V , when $r=0.05$ cm, $\delta=0.01$ cm, $C_0^b/C_1^b=100$, $\gamma^0/\gamma^b=1$ and $T=723^\circ K$.

a) Cases where V is sufficiently large. $C_1(o)$ and ψ approach C_0^b and ψ_s respectively, as V becomes larger.

$$\psi_s = RT/F \ln \gamma^0 C_0^b / \gamma^b C_1^b \quad (11)$$

The open-circuit potential (V_p) immediately after the cutting-off of current tends to ψ_s as V_0 increases. The V - i relation is

$$i = K_1 A (V - \psi_s) / r \quad (12)$$

It is difficult to ascertain Eq.(12) directly from the measurements because r varies as the dissolution proceeds. However, two kinds of method described below make it possible to confirm Eq.(12) indirectly.

Two points of (V, i) in steady-states are measured in succession and a straight line passing through these two points is extrapolated to $i=0$. From the intersection with x -axis, ψ_s is obtained. We call this method as "Two-points method". The other is "Differential method". First, a constant potential V_0 is added to the

electrode. After the current reaches a stationary value, a sweep voltage (dV) is superimposed on V_0 . The di/dV gives the differential conductance. Thus the extrapolation of the tangent to $i=0$ yields ψ_s (see Fig. 7(b) and (c)).

(b) The cases where V is small.

In this case the relation of $\psi \approx V$ and $\gamma^0 \approx \gamma^b$ holds. If the limitation of $E \ll RT/F$ and $C_0^b \gg C_1^b$ are added to the above relation, i is given by Eq. (13) approximately.

$$i = FAD_1 C_1^b \delta^{-1} [\exp(FV/RT) - 1] \quad (13)$$

Eq. (13) agrees with the equation derived from the assumption that ions move near an electrode by only diffusion.⁸⁾

2.3 Non-steady state

In order to obtain C_n as a function of x and t , the partial differential equation (14) must be solved with the condition of Eq. (15).

$$\partial C_n / \partial t = D_n \frac{\partial}{\partial x} (FEC_n / RT - \partial C_n / \partial x) \quad (14)$$

$$V = \frac{RT}{F} \ln \{ \gamma^0 C_1(o, t) / \gamma^b C_1^b \} + r'E \quad (15)$$

Where r' means the effective thickness of layer through which potential drops at a certain instance. Although it is difficult to obtain the general solution of Eq. (14), it is possible to get the relations between V , i and t in some limiting cases.

a) i at an instance of imposition of V_0

Initial conditions in this case are

$$V=0 \text{ and } C_n(x, t) = C_n^b \text{ for } t < 0.$$

$$V=V_0 \text{ and } C_n(x, t) = C_n^b \text{ for } t=0.$$

Thus, the first term of (15) is eliminated.

$$V_0 = \kappa AR E = iR \quad (16)$$

Where κ and R are the specific conductivity and the resistance of the solution, respectively,

b) The case where migration is negligible

In this case, the diffusion equation with regard to C_1 well describes the movement of Ag^+

$$\partial C_1 / \partial t = D_1 \partial^2 C_1 / \partial x^2 \quad (17)$$

Since the second term of Eq. (15) can be eliminated and the relation $\gamma^0 \approx \gamma^b$ holds when V is much smaller than ψ_s , the initial conditions are;

$$C_1(x, t) = C_1^b \text{ for } t < 0, \quad (18)$$

$$C_1(0, t) = C_1^b \exp(FV_0/RT) \text{ for } t \geq 0$$

The boundary condition is;

$$C_1(\infty, t) = C_1^b \quad (19)$$

The solution of Eq. (17) is given by Eq. (20).

$$C_1(x, t) = C_1^b [1 + \frac{1}{2} \exp(FV_0/RT) - 1] \operatorname{erfc} x / 2\sqrt{D_1 t}] \quad (20)$$

Application of Fick's first law to (20) gives the equation for current response.

$$i = FA\sqrt{D_1} C_1^b \{ \exp(FV_0/RT) - 1 \} / \sqrt{\pi t} \quad (21)$$

3. Experimental

The electrolyte is composed of the LiCl-KCl eutectic melt containing 1.0 mol% AgCl. Because LiCl can not be desiccated completely only by means of heating and evacuation, the bath was treated by the following procedure.

LiCl, KCl and AgCl were weighed and mixed in the air. The mixture was put in the cell made of Telex glass and dried by heating in vacuum up to 200°C.

Between 200°C and the melting

point, dry HCl gas was passed through the system.

After the mixture was melted, the system was evacuated again for a few hours in order to remove HCl gas dissolved in the bath. After these treatments, dry N_2 gas was introduced into the system and measurements were carried out.

The electrode system consisted of a microelectrode, a reference electrode and a counter electrode. The microelectrode was a 0.5mm ϕ Ag wire sealed in a glass tube and polished so that a section of Ag wire was exposed. The Ag wire and Ag plate were used as a reference and a counter electrode, respectively. The potentiostat, which responds to 50 kc/sec was employed to set the voltage between the reference electrode and the microelectrode. The response was recorded by a high speed pen recorder or a synroscope. The electrical furnace was on-off controlled to maintain the temperature within $\pm 2^\circ\text{C}$. The distance between the microelectrode and the reference electrode was about 1cm but not fixed precisely because the accurate distance was not required.

4. Results

4.1 Anodic Dissolution at a Constant Potential

4.1.1 Outline of current response In order to obtain the outline of the dissolution mechanism, the current change with time was measured at a constant potential V_0 of the microelectrode. The plot of $(\log t, \log i)$ is given in Fig. 2, where i_p is the current at $t=0$.

The relationship between i_p and V_0 is shown in Fig. 3. i_p was measured in such a short period as the electrode did not change so much. Fig. 3 proves that the relation (16), i. e. ohmic relation, is

Fig. 2 Schematic current-time curve.

Fig. 3 Relation between V_0 and i_p .

fulfilled. In the interval of $0 < t < t_1$, the system behaves pseudo-capacitive. In other words, current decays exponentially with time from i_p and its amplitude is proportional to V_0 . For the interval $t_1 < t < t_2$, i is expressed by (22) experimentally.

$$i = K \cdot t \quad (22)$$

K is determined by the position and condition of the electrode and is not constant in the course of the experiments because the electrode surface goes on dissolving.

However, t_1 , t_2 and f in Fig. 2 depend not on the electrode condition but on V_0 only. Thus, t_1 , t_2 and f are given

Fig. 4 Dependence of f , t_1 , t_2 on V .

in Fig. 4 as the function of V_0 . It is seen in Fig. 2 that f approaches 0.5 as V_0 becomes small. The value of 0.5 for f means that diffusion controls the electrode process.

t_1 and t_2 were about 1 msec. and 1 sec., respectively and both decreased with V_0 . i_s decayed slowly as the dissolution of electrode proceeded.

4.1.2 Two-points method for high potential As shown in Fig. 4, above 500mV i reached a steady value within 1 sec. So the current at 1 sec. was adopted as a steady value. Measurements were made for the two sets of potentials; 500mV~1000mV and 700mV~1500mV. This fact accords with the theory derived in 2.1.

4.1.3 The current response to low potential $i \propto t^{1/2}$ was already proved for a small potential step in a nonsteady state. Then, the dependence of i on V_0

Fig. 5 Two-points method.

at a constant time was observed.

According to Fig. 4, the response is in a transient state within 1 sec. below 200mV. Thus, $\log(i)_{t=1 \text{ sec.}}$ is plotted against $\log [\exp(FV_0/RT) - 1]$ in Fig. 6 ① and ②.

Fig. 6 shows that $(i)_{t=1 \text{ sec.}}$ is proportional to $[\exp(FV_0/RT)-1]$ and Eq. (25) well holds. The values of D_1 , which was yielded by inserting the experimental data into Eq. (25), were $1.5 \times 10^{-5} \text{ cm}^2/\text{sec.}$ at 465°C and $2.9 \times 10^{-5} \text{ cm}^2/\text{sec.}$ at 515°C.

These values agree fairly well with the data obtained by the chronopotentiometric measurements (for example, $2.7 \times 10^{-5} \text{ cm}^2/\text{sec.}$ at 450°C). In a steady state, when V_0 was small, fairly reproducible results were obtained since the surface area of the electrode did not change so much because of the small dissolution rate. Line (3) in Fig. 6 shows an example of the plot of $\log i$ vs $\log [\exp(FV_0/RT) - 1]$.

Fig. 6 Plot of $\log i$ vs. $\log \{ \exp(FV/RT) - 1 \}$ for small electrode potential.

The steady current is proportional to $[\exp(FV_0/RT) - 1]$ and obeys Eq. (13).

Insertion of experimental values to Eq. (13) gives the value of δ of about 10^{-2} cm.

This thickness is considered to be about the same order as the thickness of diffusion layer.

4.2 Potential Sweep Experiments

The sweep signal (60mV/sec.) generated by means of a simple C-R integrator was fed to the potentiostat to control the electrode potential.

4.2.1 The case where potential sweep was started from zero A schematic current-time or a current-potential diagram is presented in Fig. 7(a).

The curve becomes straight when potential exceeds 300mV and its slope becomes smaller again as the potential increases still more because the dissolu-

Fig. 7 Illustration of potential sweep experiment.

tion of the electrode changes its state. The linear portion of the curve, which is presumed to represent Eq. (12), is extrapolated to $i=0$ in order to obtain ψ_s .

The actual values of ψ_s are 180~190 mV at 465°C and 195~200 mV at 515°C. These values well agree with those obtained by the two-points method.

4.2.2 Differential method After current reached a steady value at a constant potential V_0 , the positive or negative sweep voltage were superposed on V_0 . The current varied as is shown in Fig. 7(b) and (c). ψ_s , derived in the manner similar to 4.2.1 and plotted in Fig. 8, has the limiting values which are 210~220 mV at 515°C and 195~205 mV at 465°C.

4.3 Electrode Potential (V_p) Immediately after the Cutting off of Current

Fig. 8 Open circuit potential (V_p) and ψ_s obtained from differential method.

V_p was measured after the current responding to a step potential reached a steady value. Fig. 8 shows the data. V_p approaches the constant values about 210 mV at 515°C and 180~190 mV at 465°C as V_0 increases.

4.4 Application of the Potential having Alternating Component

The potential consisting of D.C. component V_0 and A.C. component ΔV was given to the electrode for the purpose of investigating the phase difference between ΔV and the alternating component of responding current Δi . ΔV was given in the form of sine wave having the frequency of 1000 c/sec and the amplitude of 100 mV. It was observed that the phase shift became zero and ohmic property appeared in cases where V_0 exceeded 200 mV both at 465°C and at 515°C.

This fact suggests that Eq. (12) well

holds for the large value of V_0 .

5. Discussion

5.1 Dissolution Mechanism when a Large Potential was Applied

The values of ψ_s obtained by these various experiments and the theoretical values calculated are listed in Table 1. Though the observed values appear slightly smaller than the calculated ones, agreements are fairly good.

Table 1. ψ_s Obtained by Various Methods

Method of Measurement	Temperature	
	515°C	465°C
Theoretical value	236mV	222mV
Open circuit potential	210	180~190
Two-points method	220~230	180~190
Potential sweep method	195~200	180~190
Differential method	210~220	190~205

The reason for the deviation from the theoretical values is considered to be the increase in the concentration of Ag^+ due to the corrosion of Ag, because it is assumed in the theoretical treatments that the bulk concentration of Ag^+ is always constant. Actually, chemical analysis of the bath after the experiment showed the increase of Ag^+ to some extent. It is concluded that, when the electrode potential exceeds ψ_s , its surface is covered with pure AgCl and the current obeys Eq. (12).

Accordingly, $(\partial C_1 / \partial x)_{x=0}$ is nearly zero owing to Eq. (5). These conclusions were further confirmed by the experiments in 4.4.

5.2 Dissolution Mechanism when Small Potential is applied

Current obeys Eq. (13) in nonsteady

state and Eq. (21) in steady state. The respective state may be mentioned as diffusion control or convective diffusion control.

5.3 Classification of Dissolution Mechanism

The dissolution mechanism of Ag at constant potentials can be classified as in Fig. 9. Domain ① in Fig. 9 is the one

Fig. 9 Classification of dissolution mechanism at constant potential electrolysis.

where the system is pseudo-capacitive and is electrically equivalent to a C-R series circuit. In domain ②, diffusion and migration take place in a nonsteady and complicated manner.

In domains ③, ④ and ⑤, the electrode processes are controlled by diffusion, migration and convective diffusion, respectively. Domain ③ corres-

ponds to Eq. (21), ④ to Eq. (12) and ⑤ to Eq. (13).

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