Technical Paper

Theoretical Analysis of Anode Effect in Chloride Melts (V)- Interpretation of Critical Current Density in Potentiodynamic, Potentiostatic and Galvanostatic Methods*

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On the assumption of Langmuir-type adsorption and kinetic balance between electrochemical formation and thermal decomposition reactions of inert carbon chloride, critical current density and critical potential of anode effect were expressed by the reaction parameters and their physical meaning was elucidated. The relationship between critical values and characteristic curves obtained under potentiodynamic, potentiostatic and galvanostatic conditions was discussed.

1 Introduction

In the electrolysis of halide melt with use of carbon anode, the so called anode effect phenomenon is observed and cell operation in high current density is remarkably restricted. Anode effect is characterized by a sudden decrease in current accompanied with increase in cell voltage, non-wetting at the anode/melt interface and arc discharge, which causes the loss of electrical energy. As an indicator showing the tendency to the occurrence of anode effect, critical current density has been most widely adopted (Table 1), but its physical meaning has not yet been discussed in detail.

Table 1 Critical and practical current density in various molten salt systems

Molten salt systems	Temperature (°C)	Anode material	Critical c.d. (A/cm ²)	Practical c.d. ¹⁾ (A/cm ²)
KF-2HF	100	carbon	0.5 ¹⁾	0.15~0.25
LiCl-KCl	420~450	graphite	30 ²⁾	1.4
NaCl-CaCl ₂	590	graphite	20~24 ³⁾	1
MgCl ₂ -NaCl-CaCl ₂ -KCl	700	graphite	20 ³⁾	0.7
CaCl ₂ -KCl	800	graphite	7 ³⁾	0.3
Na ₃ AlF ₆ -Al ₂ O ₃	960	carbon	4~14 ⁶⁾	0.6~1.2

Anode effect in chloride melt is induced by the non-wettability of an inert carbon chloride compound formed on the anode surface and critical current

density is determined by the kinetic balance between electrochemical formation and thermal decomposition reaction of carbon chloride^{8),9)}.

In the present work, an attention was focussed on the physical meaning of critical current density and its correlation with characteristic curves obtained under potentiodynamic, potentiostatic and galvanostatic conditions.

2 Theoretical

The electrode reaction is considered to consist of three elementary processes: i) the electrochemical formation of carbon chloride from metal chloride MCl and carbon,

ii) the thermal decomposition of carbon chloride, $4\text{C-Cl} \longrightarrow 3\text{C} + \text{CCl}_4$ (2)

and iii) the chlorine evolution,

On the assumption of Langmuir-type adsorption and Tafel I - V relationship, the rate of surface coverage by carbon chloride $d\theta/dt$ and the current density I , are obtained as follows:

$$Kd\theta/dt = k_1(1-\theta) \exp \{(V-V_1)/b_1\} - k_2\theta \quad (4)$$

$$I = k_0(1-\theta) \exp \{(V-V_0)/b_0\} + k_1(1-\theta) \exp \{(V-V_1)/b_1\} \quad (5)$$

$$\approx k_0(1-\theta) \exp \{(V-V_0)/b_0\} \quad (6)$$

where θ is the coverage by carbon chloride compound, K is the charge required to form an inert layer (coul/cm²), k_2 is the reduced rate constant of decomposition for reaction (2), (A/cm²) and the other symbols denote their usual meanings. In accordance with the conclusion of the preceding paper^{8),9)}, hereinafter

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the case of $b_0 > b_1$ is considered as example.

Under potentiodynamic condition, the anode potential V is represented as the linear function of time as follows

$$V = V_i + vt \quad (7)$$

where V_i is an initial potential and v the scan rate in volt/sec.

In the case of negligibly small k_2 , following equations are obtained:

$$I_p = k_0 \cdot \exp(k_1 b_1 / Kv) \cdot (Kv / b_0 k_1 e) b_1 / b_0 \quad (8)$$

$$V_p = b_1 \ln(Kv / b_0 k_1) \quad (9)$$

$$\theta_p = 1 - \exp(k_1 b_1 / Kv - b_1 / b_0) \quad (10)$$

where I_p is the peak current density (A/cm^2), and V_p (volt) and θ_p are the values corresponding to I_p .

The values of I for $V \rightarrow \infty$ (the limiting current density, I_l) is a characteristic value and equals to the decomposition rate of C-Cl:

$$I_l = k_2 (b_0 > b_1) \quad (11)$$

Critical current density, *i.e.* the peak value of I corresponding to the case of $d\theta/dt = 0$, is as follows:

$$I_c = k_0 (k_2 b_1 / k_1 b_0) b_1 / b_0 (1 - b_1 / b_0) (1 - b_1 / b_0) \quad (12)$$

I_c increases with the increase of k_0 and k_2 , and decreases with the increase of b_1 / b_0 (in the range of $0 < b_1 / b_0 < 0.5$) and k_1 .

Critical potential and critical surface coverage is obtained as follows:

$$V_c = b_1 \ln\{k_2 k_1 \cdot b_1 / (b_0 - b_1)\} \quad (13)$$

$$\theta_c = b_1 / b_0 \quad (14)$$

Under galvanostatic condition, two types of $V-t$ and $\theta-t$ curves are obtained according to the relation of $I \gtrless I_c$. In the case of $I > I_c$ and $k_2 \approx 0$, following equation is obtained:

$$I b_0 / b_1, t = \text{const.} \quad (15)$$

Under potentiostatic condition, following relationship is obtained:

$$I = k_0 \exp\{(V - V_0)/b_0\} / [k_1 \exp\{(V - V_1)/b_1\} + k_2] [k_2 + k_1 \exp\{(V - V_1)/b_1 - k_1/K [\exp\{(V - V_1)/b_1\} + k_2/K] t]\} \quad (16)$$

$$I_{t=\infty} = \lim I = k_0 k_2 \exp\{(V - V_0)/b_0\} / [k_1 \exp\{(V - V_1)/b_1\} + k_2] \quad (17)$$

3 Results and Discussion

In all subsequent calculations, the condition of $V_0 \approx V_1$, $b_1/b_0 = 0.5$, $b_0 = 0.065$, $k_0 = 0.25$, $k_1/K = 1.64 \times 10^{-5}$ was held.

3.1 Potentiodynamic method

Under potentiodynamic condition, as shown in Fig. 1, the current shows maximum value I_p and converges to a constant value I_l . I_l corresponds to the rate constant of the thermal decomposition reaction and does not depend upon the scan rate. I_l as well as I_c is very important value for the elucidation of the anode effect¹⁰⁾. The peak point on the $I-V$ curve at

Fig. 1 Calculated $V-\theta$ and $V-I$ plots for scan rate v . v as indicated

Fig. 2 Plots of $\log I_p$ and V_p vs. $\log v$. k_2/K as indicated

scan rate $v=0$, corresponds to the critical point (V_c , I_c). The value of θ_p is shown by closed circle. Furthermore, the variation of the deactivation current density I_d , corresponding to the 1st term of the R.H.S. of equation (4), with anode potential is shown in Fig. 1. At $k_2=0$, I_p is proportional to $v b_1/b_0$ ($k_1 b_1/Kv \approx 0$), while at $k_2 \neq 0$ the less dependence of I_p on v is observed and I_p converges to I_c with the decrease of v . Likewise, V_p converges to V_c with the decrease of v (Fig. 2). From eqs. (12), (13) and (14), the values of I_c , V_c and θ_c are obtained as 19.5A/cm², 0.328 volt and 0.5 respectively.

3.2 Galvanostatic method

Under galvanostatic condition, V - t curve shows two different behaviours according as the current density is larger than I_c or not (Fig. 3). At $I \leq I_c$, V inc-

Fig. 3 Calculated galvanostatic θ - t and V - t curves. I as indicated

reases with time, showing upwards convex curve, and converges to a finite constant value. At $I > I_c$, V increases with time, showing upwards convex curve at first and then downwards convex curve, and finally V tends to infinity ($\theta=1$). In the case of $I > I_c$, the product $I b_0/b_1 \cdot t$ is constant at $k_2=0$, while at $k_2 \neq 0$ the product decreases with the increase of I . Critical potential V_c appears in Fig.3 as the value corresponding

to about a half of the time elapsed to the onset of anode effect. This behaviour differs from that under diffusion control where the half-wave potential in chronopotentiometry corresponds to a quarter of the transition time¹¹.

3.3 Potentiostatic method

Under potentiostatic condition, at $V < V_c$ two I - t curves arbitrarily chosen don't cross with each other, while at $V > V_c$ two curves cross with each other. The steady state value of I ($I_{t=\infty}$) is equal or less than I_c (Fig.4). With the increase of V , $I_{t=\infty}$ shows maximum, which corresponds to the critical point (V_c, I_c), as shown in Fig. 5. This conclusion, of course, refers to the case where the contribution of the capacity current is negligible¹².

3.4 Measurements of critical current density

By the analysis developed above, the interpretation of the critical current density under three electrochemical conditions was confirmed.

The peak current density I_p under potentiodynamic method has very often been substituted for the critical current density as reviewed in the preceding papers^{13, 14}. In this case attention should be directed to the

Fig. 4 Calculated potentiostatic θ - t and I - t curves. V as indicated

Fig. 5 Relationship between V and $I_{t=0}$, $I_{t=\infty}$ under potentiostatic condition

scan rate ($I_p \geq I_c$), but for the purpose to know the relative change of I_c , the peak current density I_p with appropriate scan rate may be practically adopted instead of I_c .

Approximate measurement of critical current density from the asymptote on the current density-time (elapsed to the onset of anode effect) curve under galvanostatic condition has been adopted by some authors^{15), 16)}.

4 Summary

(1) The expressions for critical current density and critical potential in terms of reaction parameters

were obtained from the kinetic balance equations between electrochemical formation and thermal decomposition reactions of inert carbon chloride compound.

(2) The relationship between the critical values (current density and potential) and characteristic curves obtained under potentiodynamic, potentiostatic and galvanostatic conditions was thoroughly elucidated and interpreted.

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