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The Diffusion of Lithium in Lithium-Zinc Alloy

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Abstract

In a new type of secondary battery with a Li-Zn alloy as one electrode, chlorine as the other and a molten salt solution of LiCl-KCl, polarizations during charge and discharge at the Li-Zn alloy electrode may occur due to the slow diffusion of Li companying K in the alloy. This was examined by the use of chronoamperometric and chronopotentiometric methods. With a cathodic charge, the apparent diffusion coefficient of Li companying K was about 3.5×10^{-5} cm^2/sec at 500°C, whereas that of Li alone was about 6.0×10^{-5} cm^2/sec. Underan anodic discharge, the apparent diffusion coefficient was extremely large (the order of 10^{-4} cm^2/sec), and this may be caused by the existence of convection at the alloy-electrolyte interface. The optimum charging and discharging current densities of the battery were estimated to be 0.2 and 0.3 A/cm^2 respectively.

Introduction

The lithium-zinc alloy-chlorine secondary battery using a molten saltion of lithium chloride-potassium chloride as an electrolyte was proposed by the authors[1)] as an automotive and also a stand-by battery. In this battery, the rate determining step of charge and discharge reactions of the negative electrode composed of a lithium-zinc alloy may be a diffusion process of lithium of companying potassium in the alloy. Therefore, the diffusion coefficients of lithium companying potassium in the alloy during cathodic discharge and anodic charge were measured by the use of chronoamperonoamperometric and chronopotentiometric methods. From these data, optimum charge and discharge performances of the alloy electrode were estimated.

Theoretical equations for analysis

Polarization of the lithium-zinc alloy electrode grows so slowly as in more than a

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few msec during charge and discharge. For that reason, it is suggested that the rate determining step of the charge and discharge is the diffusion process of the alkali metals (both lithium and potassium) in the alloy. Therefore, we assume that the electrode is kept at the partial equilibrium expressed as follows

$$E = E_0' + \frac{2.303\,RT}{F} \log \frac{a_{Li^+}}{a_{Li}} \tag{1}$$

where E is the electrode potential, E_0' the standard electrode potential, a_{Li^+} the activity of Li^+ ion in the electrolyte and a_{Li} the activity of Li in the alloy. Consider the concentration of the Li^+ ion in the electrolyte constant, which was approximately valid in the polarization. Let C represent the concentration of Li in the alloy surface, f_E the activity coefficient of Li in the alloy at potential E and E_0 the potential at $C = 10^{-3}$ mol/ml, then the equation (1) can be expressed by

$$E = E_0 - \frac{2.303\,RT}{F} \log(f_E C \times 10^3) \tag{2}$$

We shall deduce the theoretical equation for the charge and discharge curves at a constant current or potential. Assuming the one-dimensional diffusion of Li from the electrode surface (x=0) into the interior of the alloy electrode and infinite diffusion, we get

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{3}$$

where D is the diffusion coefficient of Li in the alloy.

(1) Cathodic reduction (charge) at a constant current

Let the anodic current be positive, initial Li concentration in alloy C_0. When the constant current, i, is supplied to the electrode, initial and boundary conditions are

$$\begin{gathered} C(x, 0) = C_0,\ C(\infty, t) = C_0 \\ D\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{i}{F} \end{gathered} \tag{4}$$

By solving equation (3), the concentration of Li on the electrode surface (x=0) can be expressed as

$$C(0, t) = C_0 - \frac{2i\sqrt{t}}{F\sqrt{\pi D}} \tag{5}$$

Consider $C_0 = 0$ at $t = 0$. By combining equations (2) and (5), we get

$$y_1 = \log D - \log t \tag{6}$$

where

$$y_1 \equiv 2\left[\frac{(E-E_0)F}{2.303\,RT}+\log\left(\frac{-2f_E i}{F\sqrt{\pi}}\times 10^3\right)\right]$$

(2) Anodic oxidation (discharge) at a constant current

Consider that the *Li* concentration on the alloy surface is C_0 at t=0 and the concentration becomes zero at $t=\tau$. Equation (5) becomes

$$i\sqrt{\tau}=\frac{FC_0\sqrt{\pi D}}{2} \tag{7}$$

and

$$D=\frac{4\tau i^2}{\pi F^2 C_0^2} \tag{8}$$

by combining equations (2) and (7), we get

$$y_2=-\log\left[1-\left(\frac{t}{\tau}\right)^{1/2}\right] \tag{9}$$

where

$$y_2 \equiv \frac{(E-E_0)F}{2.303\,RT}+\log(f_E C_0\times 10^3)$$

(3) Polarization at a constant potential

Assuming infinite diffusion at a constant potential, equation (3) must be satisfied at the following initial and boundary conditions.

$$C(x,0)=C_0,\ C(\infty,t)=C_0,\ C(0,t)=C_s \tag{10}$$

where C_s is the *Li* concentration on the alloy surface at the potential of *E*. By solving equation (3) with the conditions (10) and substituting the following relation

$$i=FD\left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{11}$$

the following equation is obtained.

$$i=\frac{(C_s-C_0)F\sqrt{D}}{\sqrt{\pi t}} \tag{12}$$

Experimental technique

The values of E_0 and f_E and the polarization curves at a constant current were measured by using the cell as shown in Fig. 1(A). A molten lithium alloy was in the form of a pool consisting of pyrexglass on the bottom of the cell under the electrolyte of lithium chloride (58 mol%) and potassium chloride (42 mol%). The current was introduced to the molten alloy through the graphite lead with a ceramics coating.

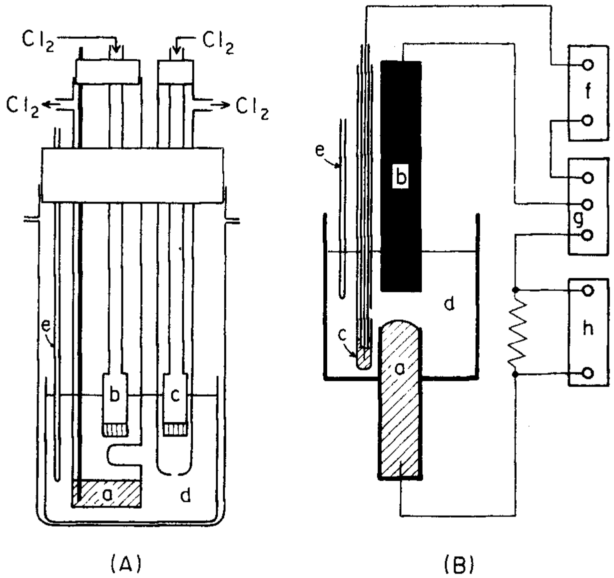

Fig. 1. Experimental cells. (A) for chronoamperometric method; (B) for chronopotentiometric method; a: Li(Zn)/Li$^+$ electrode; b: Cl_2/Cl^- electrode; c: reference electrode (Cl_2/Cl^- or Li(Zn)/Li$^+$); d: LiCl-KCl; e: thermocouple; f: function generator; g: potentiostat; h: oscilloscope.

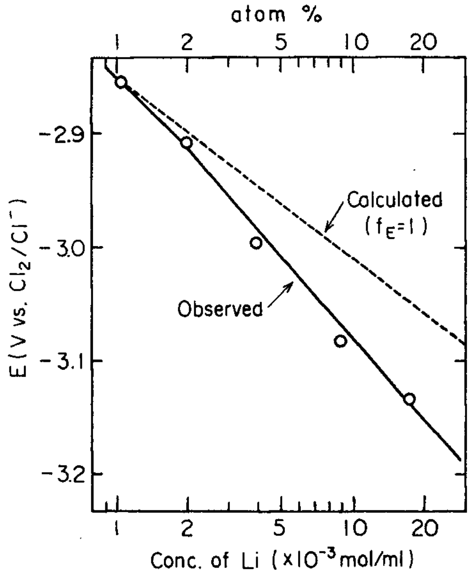

Fig. 2. Equilibrium potential of Li-Zn alloy in LiCl-KCl melt at 500°C.

A chlorine electrode was used as are counter and a reference electrode. A cylindrical graphite tube with porous carbon at the end was employed as the supporting material of the chlorine electrode. The electrolyte was purified by the introduction of hydrogen chloride and then argon. The electrode potentials of the lithium alloy were measured in reference to the chlorine electrode. At equation (2), the values of E_0 and f_E are not known, so these values were measured experimentally. The alloy formed by the charge was settled in the electrolyte for about a few hours at open circuit. Then, the potential of the alloy electrode and the concentration of alkali metal in the alloy by using chemical analysis were measured as shown by open circles in Fig. 2. By the comparison of the observed values and the theoretical dotted line by assuming $f_E=1$, the values of E_0 and f_E were determined.

The potential change during anodic or cathodic polarization under a constant current was measured, and the ohmic drops, at the supporting materials of the electrodes and the electrolyte included in the polarization measurements, were eliminated by the use of the current interruption technique.

The chronopotentiometric method, the elimination of ohmic drop at the electrolyte included in polarization, is the diffcult problem. In order to avoid this problem, the cell as shown in Fig. 1(B) was used for measuring the polarization curve at a constant potential.

Diffusion coefficient of lithium accompanying potassium in alloy

During the cathodic charge, lithium accompanying potassium may be deposited on the zinc alloy, so the depositing metal during the charge was analyzed by emission spectral analysis. Potassium of about 10% of lithium was observed in the alloy during the cathodic charge at 0.1 A/cm^2, 450°C; and after the anodic discharge at 0.01 A/cm^2, 450°C, lithium and potassium were not observed in the zinc. This shows that lithium and potassium are used as the electroactive metals.

The polarization curves under various conditions at a constant current or potential were measured. The applicabilities of equation (6), (9) and (12), by using the data from these curves, were examined as shown in Figs. 3, 4 and 5.

(1) Diffusion coefficient from the chronoamperometric method

Equation (6) shows a straight line in a y_1-t plot. This equation is satisfied only in the initial stage of cathodic polarization; and on further polarization, the relation deviates from the equation. Cespecially, at a low temperature, the deviation is remarkable as shown in Fig. 3. This phenomenon is due to the decrease of the diffusion coefficient of alkali metal in the alloy by increasing the viscosity of the alloy with the progress of charge. Equation (9) shows a straight line in a $y_2-[1[(t/\tau)^{1/2}]$ plot. This

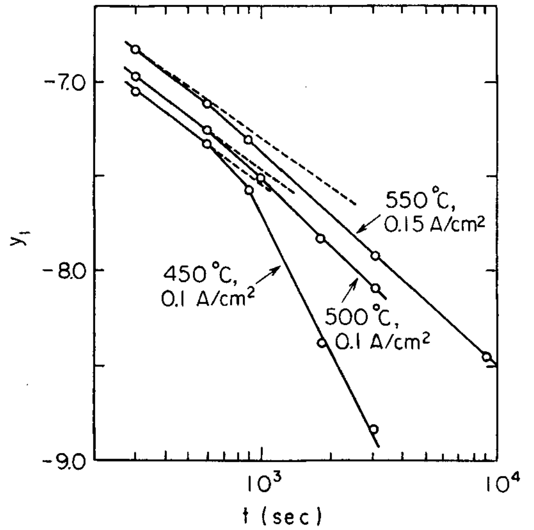

Fig. 3. Application of equation (6) to the cathodic polarization of Li-Zn electrode during constatn constant current density, when the polirization is started from pure zinc. (dotted lines are theoretical lines by assuming the constancy of D).

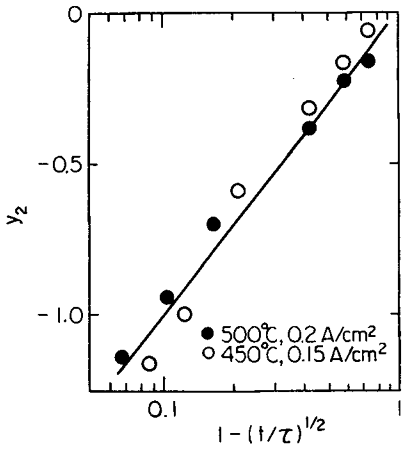

Fig. 4. Application of equation (9) to the anodic polarization of Li-Zn electrode durni during constant current density, when the polarization is started from the alloy containing 7 atomic % Li. (stright line is theoretical line by assuming the constancy of D).

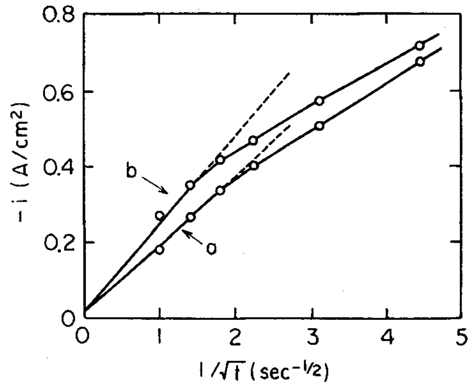

Fig. 5. Application of equation (12) to the charge of current density through Zn-Li electrode at constant cathodic polarization at 500°C in LiCl-KCl melt. a: Zn-Li alloy (Li, 1 atomic %), polarization −30 mV; b: Zn-Li alloy (Li, 5 atomic %), polarization −20 mV.

equation is satisfied during the charge as shown in Fig. 4. In this case, the initial lithium concentration is 7 atomic %, so the viscosity of the alloy during discharge may not be changed remarkably. From Figs. 3 and 4, the diffusion coefficients of lithium accompanying potassium in the alloy of various concentration during a cathodic charge or an anodic discharge can be calculated as shown in Table 1.

On a cathodic charge, the diffusion coefficients were increased with the increase of temperature and the decrease of the concentration of lithium in the alloy. The apparent diffusion coefficient was the same order of 10^{-5} cm^2/sec as thatob tained by

Table 1 Diffusion coefficient of Li (companying K) in Zn by using chronoamperometric method

Charge

Temperature (°C)	Diffusion Coeffidient ($\times 10^{-5}$ cm^2/sec)	Mean Concentration of Li in Alloy ($\times 10^{-3}$ mol/ml)
450	3.0	1.2
	0.7	3.6
	0.4	6.0
500	3.2	1.2
	2.6	3.6
	2.4	6.0
550	4.5	1.8
	3.5	9.4
	3.0	18

Discharge

450	ca. 12	0～7
500	ca. 19	0～7

Table 2 Diffusion coefficient at 500°C of Li in Zn by using chronopotentiometric method

By using LiCl-KCl melt (with codeposition of K)

Diffusion Coefficient ($\times 10^{-5}$ cm^2/sec)	Mean Concentration of Li in Alloy ($\times 10^{-3}$ mol/ml)	Polarization from Equilibrium Potential (mV)
3.9	1.0	−30
3.1	5.0	−20

By using LiCl-LiF melt

5.4	1.1	−20
6.3	1.1	−15

J. B. Edwards.2) On an anodic discharge, the apparent diffusion coefficient was extremely large and the order of 10^{-4} cm^2/sec. This high value may be explained by the existence of alloy-electrolyte interfacial convection. This phenomenon was directly observed during the discharge.

(2) Diffusion coefficient from the chronopoteniometric method

Equation (12) shows a straight line in a $i-1\sqrt{t}$ plot. Fig. 5 shows the results during the charge at a constan at cathodic polarization and satisfies equation (12) only at the value of a cathodic current lower than about 0.4 A/cm^2. At a higher value of cathodic current, the relation deviates from the equation due to the inclusion of ohmic drop at the electrolyte in polarization. The diffusion coefficients, calculated from the slops of the portion of the straight line in Fig. 5, are shown in Table 2 with the same order as those obtained from the chronoamperometric method.

In our case, lithium accompanying potassium diffuses in alloy. So, both the diffusion coefficient of lithium accompanying potassium and lithium alone were compared by using the chronopotentiometric method. In the latter case, the molten salt of lithium chloride (71 mol%)-lithium fluoride (29 mol%) was used as an electrolyte and the melting point of this salt was 485°C. The observed values of the diffusion coefficient in the latter case are also shown in Table 2. By a cathodic charging process, the apparent diffusion coefficient of lithium accompanying potassium waw about 3.5×10^{-5} cm^2/sec at 500°C, whereas that of lithium metal alone was about 6.0×10^{-5} cm^2/sec. This shows that the existence of potassium in the alloy causes some retardation of the diffusion process.

Estimation of optimum current density

By the increase of the concentration of lithium (accompanying potassium) at the alloy surface during a cathodic charge, the diffusion rate of lithium in alloy is decreased gradually. After the solidification of the surface of the liquid alloy, the diffusion process of lithium in alloy becomes very difficult. Moreover, the density of the alloy at the surface is decreased furing the charge; and if the density becomes lower than that of the electrolyte, the alloy disperses like a metal fog in the electrolyte. From these points, the chargeable coulombic capacity of the alloy is limited and the capacity is affected by the cathodic current density. On an anodic discharge, it is impossible to with-draw all the lithium from the alloy due to the limitation of the diffusion rate of the lithium in the alloy. After the anodic polarization becomes very large, the anodic dissolution of the zinc takes place as a main reaction.

When pure zinc as a starting material is charge cathodically at a current density of i for time of t, from equation (5) with the concentration of Li on the electrode surface, C is expressed as

$$C=\frac{2i\sqrt{t}}{F\sqrt{\pi D}} \tag{13}$$

When the alloy surface is just before its solidification, or the density of the alloy is 1.5 times larger than that of electro-we can sider that the *Li* concentration of alloy surface is

lyte, is C^*, so, $C=C^*$ at

$$i\tau^{1/2}=\frac{FC^*\sqrt{\pi D}}{2} \tag{14}$$

When the alloy of a constant *Li* concentration of *Co* is discharged at a constant current density of i (cathodic current, positive), and after the discharge of time of τ, the *Li* concentration of alloy surface becomes zero, from equation (13) we get

$$i\tau^{1/2}=\frac{FC_0\sqrt{\pi D}}{2} \tag{15}$$

The values of C^* at various temperatures can be obtained experimentally. At 450°C and 500°C, the observed values of C^* obtained from solidification concentration were 15 atomic % ($=1.5\times10^{-2}$ mol/ml) and 25 atomic % ($=2.2\times10^{-2}$ mol/ml). At 550°C, the density of the alloy becomes 1.5 times larger than that of the electrolyte before solidification of the alloy, so in this case, 63 atomic % ($=5.2\times10^{-2}$ mol/ml), was adopted as the value of C^*.

From equation (14), the values of $i\tau^{1/2}$ can be calculated for various current densities, and then the relation between the chargeable coulombic capacity and the charging current density is obtained as shown in Fig. 6. Equation (14) was derived

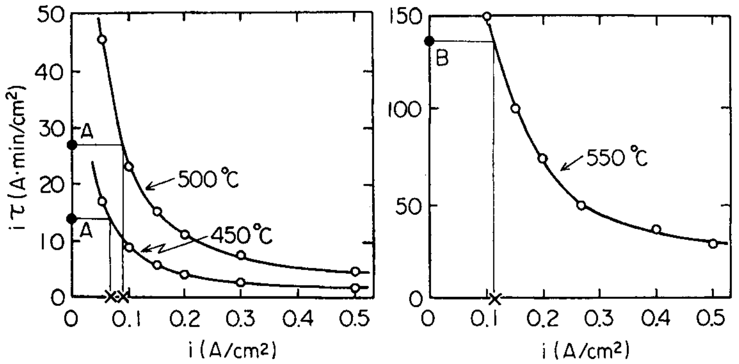

Fig. 6. Estimation of optimum current density of charge. (Zn: 0.05 mol; surface area: 1 cm²; thickness of electrode layer: ca 0.5 cm); A: coulombic capc capacity of Zn-Li electrode just before its solidification; B: coulombic capacity of Zn-Li electrode of which density is 1.5 times of that of Li-CKl melt; X: optimum current density.

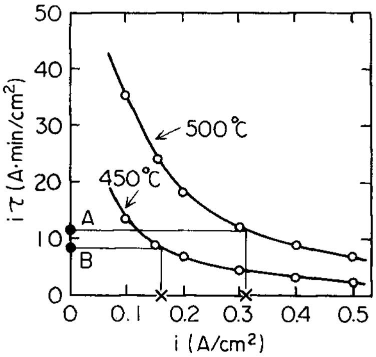

Fig. 7. Estimation of optimum current density of discharge (Zn: 0.05 mol; surface area: 1 cm^2; thickness of electrode layer: ca 0.5 cm); A: coulombic capacity which is chargeable at 450°C, 0.1 A/cm^2; B: coulombic capacity which is chargeable at 500°C, 0.2 A/cm^2; X: optimum current density.

by assuming an infinite diffusion. But the alloy thickness is finite in actual cell, so the value of $i\tau$ has a limitation. The maximum value of $i\tau$ may be calculated from the lithium concentration C^* in the alloy. This maximum value at the alloy thickness of 0.5 cm is plotted by the closed circle in Fig. 6. Here, the infinite diffusion is assumed in all stages of charge, although this approximation might not be sufficiently accurate. However, it can be applied without much error to the estimation of the optimum charging current density. From Fig. 6, the maximum charging current density with a maximum coulombic capacity at alloy thickness of 0.5 cm is estimated to be about 0.1 A/cm^2.

By the application of the same method as the estimation of the optimum charging current density to equation (15), the optimum discharging current density can be estimated as shown in Fig. 7.

In the case of the alloy thickness being 0.5 cm and the charging current density being 0.2 A/cm^2, the optimum discharging current density is estimated to be about 0.3 A/cm^2 at 500°C.

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