Studies on the Lithium Alloys-Chlorine Secondary Battery

By

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Abstract

A new type of lithium alloys-chlorine secondary battery, by using molten salt of LiCl and KCl as an electrolyte, was constructed as an automobile and a stand-by battery. In this kind of battery, the electromotive force is somewhat less than that of a conventional lithium-chlorine battery; but the cell structure is much simpler and the operating temperature much lower. Also, the self discharge rate is much lower. The output coulombic capacity, output power and output energy were calculated to be 55 Ahr, 260 W and 150 Whr respectively, when zinc of 1 kg was used as the substratum metal. From these data it may be concluded that this type of secondary battery is very promising for automotive and stand-by uses.

Introduction

A new type of secondary battery composed of

$\ominus$ *Li*-Metal (*Zn, Sn or Pb*)|*LiCl-KCl*   molten salt/Carbon-Chlorine $\oplus$

was constructed to determine its feasibility as an automobile and stand-by battery. A liquid alloy of lithium with other metals was used instead of using pure metallic lithium as the active mass for the anode. Because of its high density, it occupied a position beneath the molten salt. The polarization characteristics of both the lithium alloy and chlorine electrodes were measured in a molten salt solution of lithium chloride potassium chloride mixture. From these results, the output coulombic capacity, power and energy of this battery were caluculated. In this kind of battery, the electromotive force is somewhat less than that of a conventional lithium-chlorine battery,[1]

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but the cell structure may become much simpler, and the operating temperature is much lower (450°C as compared to 614°C of lithium-chlorine battery using a molten salt solution lithium chloride as an electrolyte). Furthermore, the self discharge rate is much lower.
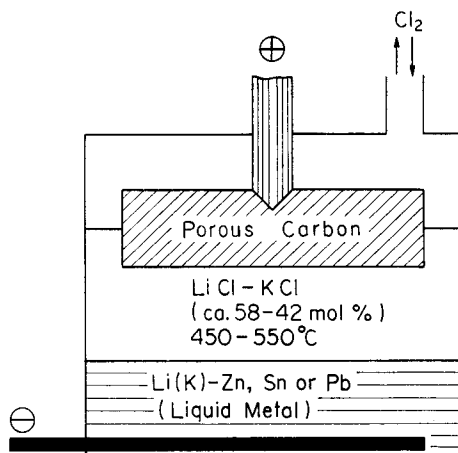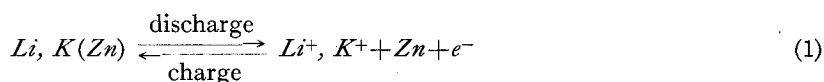
Reaction on charge and discharge

Fig. 1. Shema of lithium alloy-chlorine secondary battery.

As an example, when a lithium-zinc alloy as shown in Fig. 1 is used, the following electrochemical reactions occur;
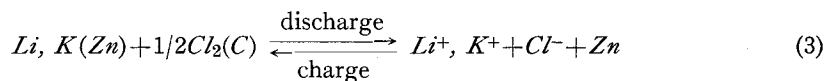
anode (negative electrode)

$$Li, K(Zn) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Li^+, K^+ + Zn + e^- \tag{1}$$

cathode (positive electrode)

$$1/2 \ Cl_2(C) + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Cl^- \tag{2}$$

overall reaction is then

$$Li, K(Zn) + 1/2Cl_2(C) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Li^+, K^+ + Cl^- + Zn \tag{3}$$

On charge, lithium and potassium are deposited on molten zinc which is in the form of a pool at the bottom of the cell under the molten salt of lithium chloride (ca. 58 mol%)-potassium chloride (ca. 42 mol%). They then diffuse into the bulk of the

molten zinc. On discharge, lithium and potassium diffuse to the interface of zinc-electrolyte, and then are discharged to form lithium and potassium ions. The porous carbon is used as the cathode, the absorbed chlorine gas is discharged, and the chloride ion is charged on the porous carbon.

Table 1 Weight % of Li in liquid alloy

Liquid alloy	450°C	500°C
Li-Zn	1.9	4.1
Li-Sn	3.7	7.4
Li-Pb	2.6	5.4

The phase diagrams of the alloys of lithium and other metals are shown by M. Hansen.[2] When zinc, tin and lead are used as the substratum metals, the alloys are liquid till the concentration as shown in Table 1.

Polarization characteristics

Polarizations of both the lithium-metal and chlorine-carbon electrodes were measured in lithium chloride (58 mol%)—potassium chloride (42 mol%) melt, using an experimental cell as shown in Fig. 2.

Typical time dependences of various lithium alloys on potentials during charge and discharge at constant current density are shown in Fig. 3. On charge or dis-
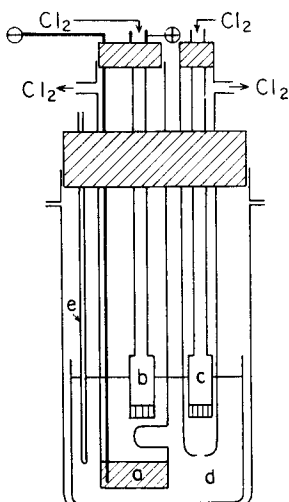

Fig. 2. Experimental cells. a: Li(Me)/Li$^+$ negative electrode; b: Cl_2/Cl$^-$ positive electrode; c: Cl_2/Cl$^-$ reference electrode; d: LiCl-KCl electrolyte; e: thermocouple.
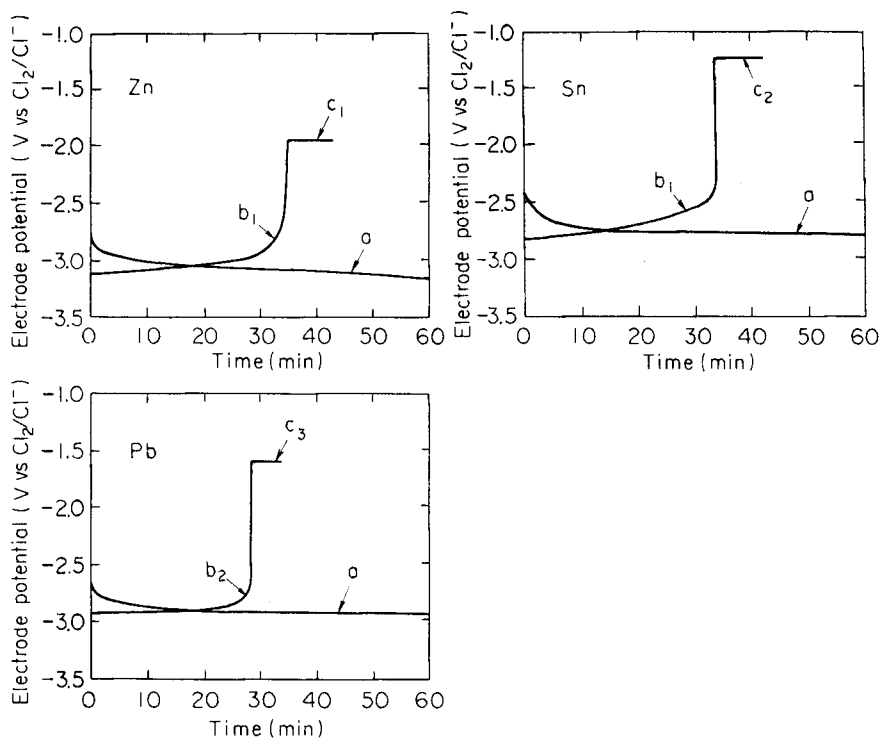
Fig. 3. Polarization characteristics at constant current charge and discharge of the negative electrode in LiCl-KCl melt at 450°C. a: charge at 0.08 A/cm² from metal (Zn, Sn, Pb); b: discharge frommetal-Li, K alloy after charge of 0.08 A/cm², 60 min. (b₁: current density 0.12 A/cm², b₂: 0.16 A/cm²); c: polarization for ionization of metal (C₁: Zn, C₂: Sn, C₃: Pb).

charge, the polarization was not so large, though the equilibrium potential was changed due to the change of the lithium concentration in alloys. After the end of discharge, the potential shifted sharply to a positive direction, and the dissolution of the substratum metal took place. Before this dissolution, lithium of 90~95% deposited on the sub-stratum metal during charge was discharged effectively at the discharge of 0.1~0.2 A/cm².

On charge, lithium accompanying potassium was found to be deposited on the substratum metal(*Zn, Pb* and *Sn*) by emission spectral analysis. Hence, both lithium and potassium were used as the electroactive metals.

Typical current-potential relations of both electrodes during charge and discharge are shown in Figs. 4 and 5. At the chlorine electrode, polarization during discharge was much higher than that during charge. For example, on discharge of 0.5 A/cm², polarization was about 0.15 V. At the alloy electrode, when the concentration of the alkali metals is lower, the polarization is higher during discharge. So, better
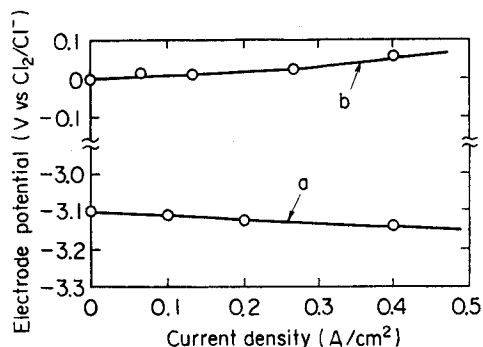
Fig. 4. Current-potential relation during charge at steady state of negative and positive electrode in LiCl-KCl melt at 450°C. a: at negative electrode of Zn-Li, K alloy (Li, K 10 atomic %); b: at positive electrode of Cl₂ on carbon.
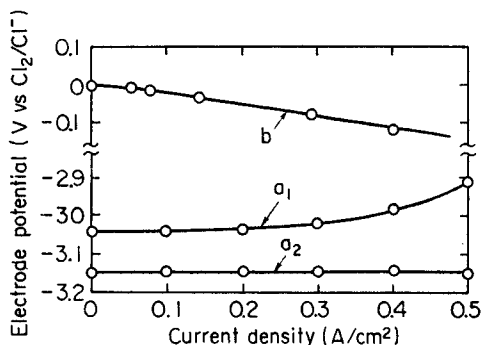

Fig. 5. Current-potential relation during discharge at steady state of negative and positive electrode in LiCl-KCl melt at 450°C. a: at negative electrode of Zn-Li, K alloy (a₁: Li, K 5 atomic %, a₂: Li, K 15 atomic %); b: at positive electrode of Cl₂ on carbon.

polarization characteristics may be expected by the development of a chlorine electrode with a better discharge performance, and also by the use of an alloy of higher concentration of alkali metals. From Figs. 4 and 5, the voltage of unit cell was estimated as shown in Fig. 6. When the ohmic drop at the electrolyte is negligible, high voltage of about 2.18 V is obtained at the discharge of 0.5 A/cm².

At the actual cell, this ohmic drop is not negligible. Specific electrical conductivity and density of the molten salt of lithium chloride (58 mol %) and potassium chloride (42 mol%) at 500°C are about 1.9 Ω^{-1} cm^{-1} and 1.6, respectively. When the electrode interval is 0.5 cm, the ohmic loss at the electrolyte during charge or discharge of 0.5 A/cm² is about 0.13 V. Hence, the cell voltage is reduced to 2.68 V in the case of assuming the electrode interval to be 0.5 cm. The reduction of this ohmic drop is also a problem to obtain a high performance.
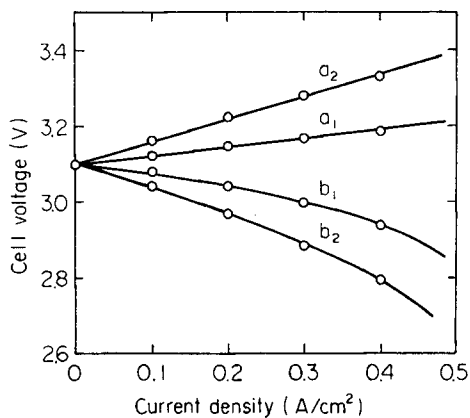
Fig. 6. Estimation of cell voltage of battery Li, K(Zn)/LiCl-KCl/C·Cl₂ at 450°C. 1 a_1, b_1: in the case of neglecting ohmic loss in LiCl-KCl melt; a_2, b_2: in the case of assuming 0.5 cm interval between electrodes; a_1, a_2: in the case of charge; b_1, b_2: in the case of discharge.

The self discharge rates of lithium alloy in a molten salt of lithium chloride-potassium chloride under chlorine atmosphere were measured from the time dependences of alloy potential after immersion. For example, in the case of using lithium (10 atomic %)-lead alloy at 500°C, the self discharge rate was about 1.2×10^{-5} A/cm². This rate is considered to be a negligible value.

Estimation of cell performance

The performances of lithium-metal alloy electrodes in a lithium-chlorine battery are summarized in Table 2. The output energy per unit weight of such an electrode is less than that of a pure lithium electrode, but it may be similar to that of a matrix type electrode.

Table 2 shows the maximum output energy in the case of very slow charge and discharge. At the actual cell, many energy losses, $e.g.$, polarizations of both electrodes, ohmic loss in the electrolyte, decrease of usability of lithium at a high current discharge, self discharge etc., must be considered. According to out data,[3] apparent diffusion coefficients of lithium accompanying potassium in a lithium-zinc alloy at 500°C are about 3.5×10^{-5} cm²/sec at charge and about 10^{-4} cm²/sec at discharge. Therefore, the optimum charging and discharging current density at 500°C are estimated to be 0.2 and 0.3 A/cm² respectively, when the alloy thickness is 0.5 cm.

From Figs. 6 and 7 in the previous paper,[3] usabilities of lithium as an active mass in the case of alloy thickness of 0.5 cm, and voltage losses in the case of electrode interval of 0.5 cm can be determined at various charge and discharge conditions, res-

Table 2 Performance of Li-metal alloy electrode in lithium-chlorine battery

Alloy	Concentration of Li		Coulombic Capacity (Ahr/kg(Li-Me))	Electromotive Force at 450°C (V)	Output Energy (Whr/kg(Li-Me))
	(atomic %)	(wt %)			
Li	100	100	3890	3.6	14000
Li-Zn	10	1.2	47	3.1	146
	15(a)	1.9	74	3.1	230
	28(b)	4.1	159	3.2	510
Li-Sn	10	0.6	23	2.8	64
	40(a)	3.7	144	2.9	417
	58(b)	7.4	288	3.0	864
Li-Pb	10	0.4	15	3.0	45
	45(a)	2.6	101	3.1	313
	63(b)	5.4	210	3.2	671

(a) just befor its solidification at 450°C
(b) just befor its solidification at 500°C

Table 3 Estimation of the cell performances of the type of Li, K(Zn)/LiCl·KCl/C·Cl$_2$
at 500°C (alloy thickness and electrode interval are both 0.5 cm)

Current Density		Output Coulombic Capacity		Output Power Density		Output Energy Density	
Charge (A/cm²)	Discharge (A/cm²)	(Ahr/Zn-1kg)	(Ahr/cm²)	(W/Zn-1kg)	(W/cm²)	(Whr/Zn-1kg)	(Whr/cm²)
0.1	0.1	126	0.42	91	0.31	384	1.3
0.2	0.3	55	0.18	260	0.87	160	0.52
0.2	0.5	33	0.11	385	1.3	86	0.29
0.5	0.5	18	0.06	385	1.3	47	0.15

pectively. Various performances at the actual cell were calculated from the data of these usabilities of lithium and voltage losses, when liquid zinc of 1 kg was used as the substratum metal and the alloy thickness and electrode interval were both supposed to be 0.5 cm. At the charging current desnity of 0.2 A/cm² and discharging current density of 0.3 A/cm², the output coulombic capacity, output power and output energy were calculated to be 55 Ahr, 260 W and 160 Whr respectively. At the various charging and discharging current densities, cell performance are summarized as shown in Table 3.

With a lower charging current density of 0.09 A/cm², calculation shows that 140 Ahr would be retained for 1 kg-*Zn*. When the discharging current density is increased to 0.5 A/cm², it shows a high output power 385 W. From these estimations it may be concluded that this type of secondary battery is very promising for automotive and

stand-by uses, especially for applications involving low rate charge and high rate discharge.

If the mass transfer rate of the alkali metals in the alloy is increased, better cell performance will be obtained.

Acknowledgements

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