

## STUDIES ON THE ALKALI METAL ALLOY-CHLORINE SECONDARY BATTERY

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### Summary

This paper is concerned with an alkali metal-chlorine secondary battery for a load levelling device, and especially with the negative electrode. An alkali metal alloy is a promising negative electrode material for a high performance battery. The energy density and power density of such alloy electrodes can be discussed in relation to the phase diagram. A liquid alloy is preferable when long cycle life is required, and a solid alloy is preferable from the cell design aspect. Experimental data and theoretical considerations to support such conclusions are given.

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### Introduction

A high temperature battery using a molten salt electrolyte is very promising for a load levelling device. One of the reasons is its low polarization, and the other is that we can use an alkali metal, which shows high electromotive force, for the negative electrode material, but when we try to use alkali metals some technical difficulties occur, such as metal fog formation and corrosion of the cell materials. A further difficulty is their low density. Because of this, alkali metals float up to the upper part of the cell, and hence, the cell construction has to be rather complex. To avoid such difficulties, the use of a solid electrolyte or a paste type electrolyte, or the wick electrode etc. has been proposed and developed elsewhere.

Another possible solution to such difficulties is to use an alkali metal alloy, by which we can avoid the metal fog formation and can design a simple cell construction. This paper is concerned with a detailed study of the alkali metal alloy electrode, from which a basic concept for selecting a high performance alloy electrode can be established. As an example, an alkali metal-chlorine battery using such an alkali metal alloy electrode, whose reaction can be written as follows, is discussed here.

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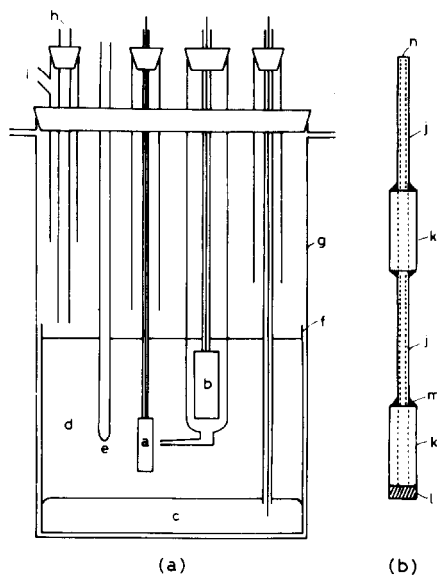
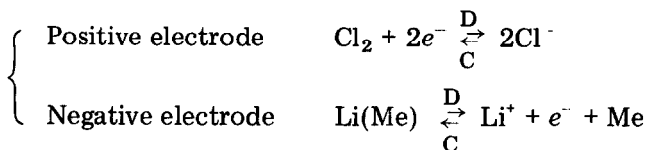


Fig. 1. (a) Experimental cell for solid alloy electrodes. a, Solid Li-Zn/Li<sup>+</sup> electrode (W.E.); b, liquid Li-Sn-Zn/Li<sup>+</sup> electrode (C.E.); c, solid Li-Al/Li<sup>+</sup> electrode (R.E.); d, electrolyte; e, thermocouple; f, corundum crucible; g, Pyrex holder; h, argon inlet; i, argon outlet. (b) Detail of a chlorine electrode. j, Graphite pipe, k, graphite joint; l, porous carbon; m, carbon cement; n, chlorine inlet.



## Experimental

Figure 1(a) shows an experimental cell used to examine solid alloy electrodes. For liquid alloy electrodes, a similar arrangement was used. Cell and cell holder are made of Pyrex glass, and a corundum crucible cell was used for long term operation. As electrolytes, either LiCl-KCl eutectic or LiCl-KCl-NaCl molten mixtures were used. All reagents used were of chemically pure grade, and were dehydrated before use in a conventional manner [1]. If necessary, further pre-electrolysis was done to eliminate residual water and other unknown contaminants. All experiments were carried out in a dried argon atmosphere. As a substrate metal for the working electrode, zinc or aluminium plate was used for a solid electrode and lead or tin for a liquid electrode. To insulate the molybdenum lead of the negative electrode, it was covered with an alumina pipe. As a counter electrode, a Sn-Zn-Li liquid alloy or a chlorine electrode was used depending on the circumstances. As a reference electrode, a Al-Li alloy, reported by Yao [2], or a chlorine electrode was used, also depending on the circumstances. The Sn-Zn-Li and Al-Li electrodes were prepared by the electrolysis of a LiCl-KCl eutectic

melt. As shown in Fig. 1(b), the chlorine electrode was made of a porous carbon disc and graphite pipes which were connected by graphite joints.

### Classification of alloy electrodes

Alloy electrodes are divided into two categories, *i.e.* liquid and solid. As an example, let us consider the Zn-Li alloy for which a phase diagram was given by Hansen [3]. When we start charging from pure zinc at 400 °C, a solid state is maintained until the concentration of lithium is 47 atomic %; and when we start at 450 °C, a liquid state is maintained until 10 atomic %. In this way, various alloys can be classified by phase diagrams. For example, Sn-Li, Pb-Li, Zn-Li and Pb-Na work as liquid electrodes at 450 °C. On the other hand, Zn-Li and Al-Li work as solid electrodes at 400 °C, and Sn-Li and Pb-Li containing higher lithium concentrations can also be used as solid electrodes.

## Results and Discussion

### *Solid alloy electrodes*

#### *Effect of the number of charge-discharge cycles*

Figure 2 shows typical behaviour of the negative electrode when a zinc plate was used as a substrate. After charging at 100 mA/cm<sup>2</sup> for a certain time, this electrode was discharged at 100 mA/cm<sup>2</sup> until an abrupt rise in potential was observed. After that, the discharge current was decreased to 50 mA/cm<sup>2</sup>, which caused the potential to return to its former value. When an abrupt potential rise appeared again at this current density, the discharge current was decreased further. This procedure was continued until the discharge current was some hundreds of  $\mu$ A/cm<sup>2</sup>. During this procedure, care was taken to keep the potential more negative than the dissolution potential of the zinc plate itself. During the repetition of this procedure, charge-discharge current efficiencies and charge-discharge curves changed with the number of charge-discharge cycles.

Figure 3 shows current efficiencies as a function of the number of cycles. In this experiment, a 20 atomic % (Li and K) alloy prepared by charging at 50 mA/cm<sup>2</sup> was discharged in the same way as above. The change of the charge curve and of the discharge curve obtained at a maximum current density with number of cycles are shown in Figs. 4 and 5, respectively. In Fig. 3, total current efficiency rises from 50% to 90% after several charge-discharge cycles. At the same time, the quantity of electricity obtained on discharge at 50 mA/cm<sup>2</sup> increased from 15% to 85%, too. On the other hand, the quantity obtained on discharge at 20 mA/cm<sup>2</sup> decreases from the third run and becomes only a few % on the last. In Fig. 4, as the number of cycles increases, the potential plateaux at +0.27 V, +0.05 V, and -0.06 V (*vs.* Li<sup>+</sup>/Li-Al) are more clearly defined and the shape of curves becomes more smooth. In the discharge curve of Fig. 5, a similar tendency can be observed. This might be explained by a slow mass transfer from the bulk to the surface of

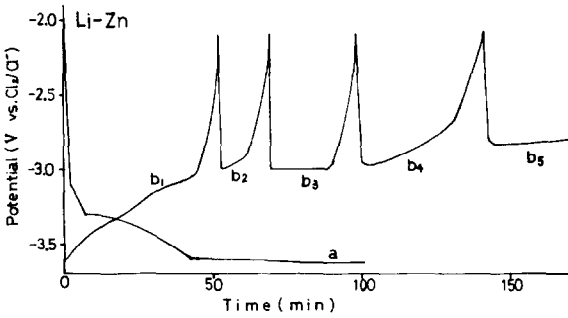


Fig. 2. Charge-discharge curves of a solid Li-Zn alloy electrode in LiCl-KCl at 390 °C. a, Charge, 100 mA/cm<sup>2</sup>; b, discharge, b<sub>1</sub> 100, b<sub>2</sub> 50, b<sub>3</sub> 20, b<sub>4</sub> 10, b<sub>5</sub> 5, mA/cm<sup>2</sup>.

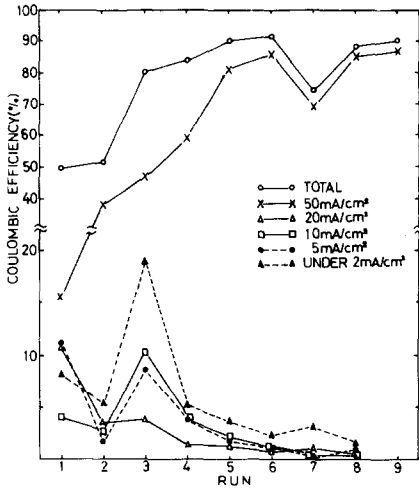


Fig. 3. Change of coulombic efficiency with number of charge-discharge cycles.

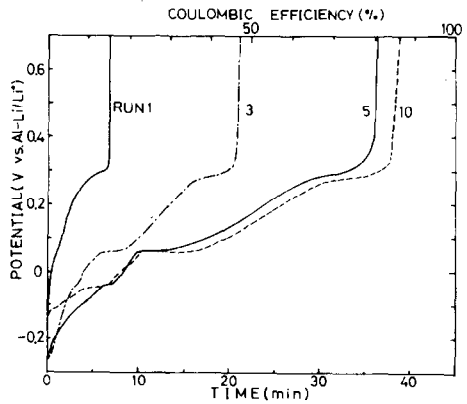
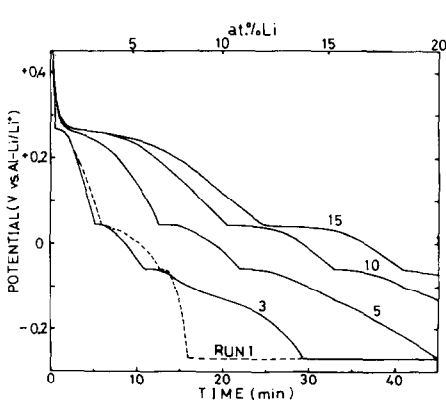


Fig. 4. Change of charge curve at 380 °C with number of cycles (current density, 50 mA/cm<sup>2</sup>). Fig. 5. Change of discharge curve at 380 °C with number of cycles (initial concentration of alloy, 20 atomic % lithium; current density, 50 mA/cm<sup>2</sup>).

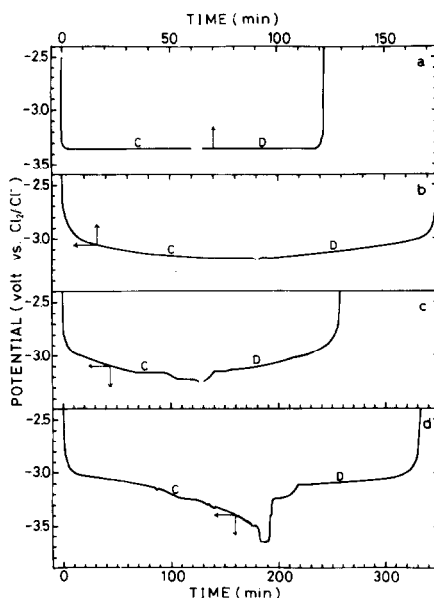
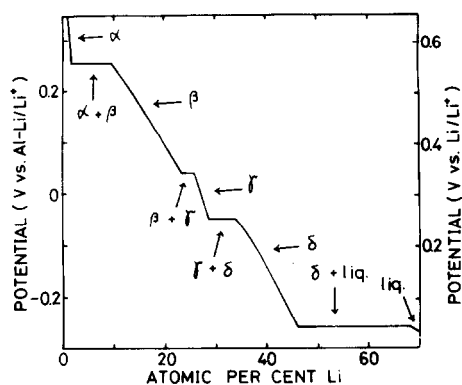


Fig. 6. Relationship between potential and concentration of solid Li-Zn alloy at 390 °C. Fig. 7. Various charge-discharge curves at 100 mA/cm<sup>2</sup>. (a) Solid Li-Al alloy at 390 °C; (b) liquid Li, K-Pb alloy at 450 °C; (c) liquid Li, K, Na-Pb alloy at 450 °C, LiCl-KCl-NaCl electrolyte; (d) solid and liquid Li, K-Sn alloy at 400 °C.

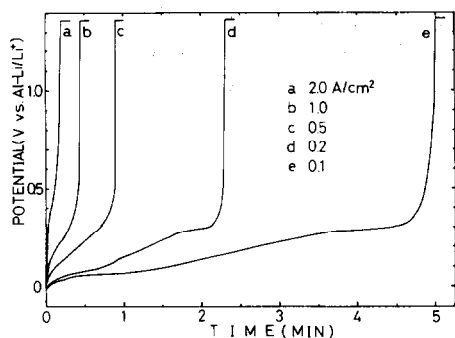


Fig. 8. Discharge curves at various current densities at 380 °C (initial concentration of Li-Zn alloy, 10 atomic % lithium).

the solid electrode, or *vice versa*, which is accelerated by the structure change caused by repetition of the charge-discharge cycles. After more than three cycles, the remarkable current efficiency change was not observed any more, and it stayed around 90% as can be seen in Fig. 3. As an explanation for this, recombination with chlorine of the alkali metal produced, redissolution of the deposited potassium into the electrolyte, and/or trapping of alkali metal inside the electrode etc. might be possible. But the third one cannot be regarded as a main reason, because Fig. 4 cannot be explained by it. As mentioned above, repetition of the charge-discharge cycle makes an electrode

TABLE 1

Operating characteristics of solid Li-Zn alloy electrode at 380 °C.  
(Power density is for the electrode only.)

Current density (A/cm <sup>2</sup> )	Potential range (V)	Duration (min)	Power density (kW/kg)	Utilization (%)
2.000	-3.35 ~ -2.70	0.16	19.1	47.1
1.000	-3.35 ~ -2.95	0.36	9.88	55.9
0.500	-3.35 ~ -3.02	0.80	5.00	58.8
0.200	-3.36 ~ -3.05	2.15	2.02	63.2
0.100	-3.38 ~ -3.05	4.60	1.01	67.6

active, and this is caused by an electrode structure change. But this accelerates expansion or degradation of the electrode, which is not desirable from the viewpoint of cycle life. In a practical cell, therefore, it might be necessary to use some kind of matrix to buffer this structure change.

As can be seen in Figs. 4 and 5, four stable potential regions are observed, which can be explained in relation to the phase diagram of the Li-Zn system, *i.e.*, a stable potential corresponds to the concentration region where two phases coexist. Comparing the stable potential with the phase diagram of the Li-Zn system, the relation between potential and concentration of the alloy can be drawn as in Fig. 6. For comparison, charge-discharge curves of the solid Li-Al electrode are shown in Fig. 7(a). This result agrees with that obtained by Yao [2]. Stable potential corresponds to the region where  $\alpha$ -phase and  $\beta$ -phase coexist. One merit of a solid electrode is to show such a stable potential over a wide concentration range.

#### *Fast discharge of the solid electrode*

Figure 8 shows discharge curves obtained at various current densities. The electrode used was pre-treated by repeating several charge-discharge cycles before obtaining these curves. The initial Li concentration of this electrode was 10 atomic %. Current efficiency stayed within 50 - 70% on each discharge and this means a rapid mass transfer rate in the electrode, as had been expected. At 2 A/cm<sup>2</sup>, however, an abrupt potential change was observed even at the beginning. But for example, with an initial Li concentration of 40 atomic %, 10 min discharge at 1 A/cm<sup>2</sup> was possible. Table 1 summarizes the data obtained from Fig. 8. Power density was calculated assuming an electrode thickness of 1 mm, and refers only to a single electrode.

This result shows the high feasibility of this type of cell.

#### *Liquid alloy electrodes*

On a cycle life basis, a liquid alloy electrode seems preferable, because it does not change its structure at all during charge-discharge cycles. Hence, it is worth while examining liquid alloy electrodes in more detail in a practical sense.

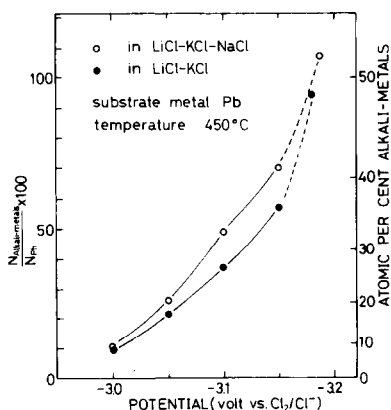


Fig. 9. Relationship between potential and concentration of alloy electrodes in two electrolytes.

#### *Behaviour of liquid alloy electrodes in LiCl-KCl*

As mentioned above, the concentration range to be used in a liquid state can be selected from the phase diagram. For example, the Li-Zn system can be used as a liquid up to 10 atomic % Li at 450 °C, but this liquid phase region is rather narrow. It is, therefore, necessary to seek for another system that has a wide liquid phase region. Li-Sn and Li-Pb systems are interesting in this sense [3]. Figure 7(b) shows charge-discharge curves obtained with the Li-Pb system in LiCl-KCl. As can be seen in this Figure, the behaviour of the liquid alloy differs from that of solid alloy electrode, *i.e.*, in the case of the liquid alloy, the electrode potential shifts gradually towards a more negative value as the quantity of charge increases, up to -3.18 V. This final potential of -3.18 V corresponds to the region where liquid and solid phases coexist. The current efficiency of the liquid electrode is usually more than 95% and the effect of the repetition of charge-discharge cycles was not observed in this case. Hence the liquid alloy electrode suggested is preferable from the cycle life viewpoint as suggested at the beginning of this section.

#### *Behaviour of liquid electrodes in LiCl-KCl-NaCl*

From an economic viewpoint, possible only small amounts of LiCl should be used, because it is rather expensive. Therefore, we tried the addition of NaCl to the LiCl-KCl system. Figure 7(c) shows charge-discharge curves obtained with a LiCl-KCl-NaCl electrolyte and a liquid lead substrate. The reason for using lead as a substrate is its ability to form a liquid phase both with lithium and potassium over a fairly wide concentration range, and with sodium over the whole concentration range. From Fig. 7(c), solid formation at this alloy electrode is suggested at a potential of -3.16 V, *i.e.*, this potential suggests solid-liquid equilibrium. Comparing this result with that of Fig. 7(b), an increase of charge capacity by the addition of NaCl is confirmed. Both liquid and liquid-solid equilibrium phases are included in the discussion. Figure 9 shows a more remarkable effect of NaCl addition, which was obtained by a potentiostatic charge and subsequent constant current discharge. Detailed study of this effect is necessary in the future.

TABLE 2

Operating characteristics of Li, K-Sn alloy electrode at 400 °C.  
(Power density is for the electrode only.)

Current density (A/cm <sup>2</sup> )	Potential range (V)	Power density (kW/kg Sn)	Utilization (%)
1.000	-3.47 ~ -2.55	0.907	83.9
0.400	-3.47 ~ -2.90	0.369	72.8
0.100	-3.50 ~ -2.90	0.092	80.2

#### *Utilization of both liquid and solid phase as an alloy electrode*

If we can use both liquid and solid phase as an active mass, the capacity of this electrode will increase very much. For example, with the Li-Sn system, the quantity of electricity obtained from the alloy containing 80 atomic % lithium is four times more than that obtained from the liquid alloy containing a maximum lithium concentration of 50 atomic %. To confirm such an idea, the Li-Sn system was examined in LiCl-KCl. Figure 7(d) shows charge and discharge curves for this electrode. Unfortunately, the maximum charge capacity obtained on charge at 100 mA/cm<sup>2</sup> was only 50% of the theoretically expected value, which is probably due to the slow mass transfer in the solid electrode. On discharge, a potential plateau at -3.24 V was observed. This is probably due to the discharge in a region where two solid phases coexist. Figure 10 shows discharge curves obtained from the same electrode at different current densities. The initial concentration was 67 atomic %. Violent potential disturbance was observed at a current density of 1 A/cm<sup>2</sup>, but otherwise, fairly high current efficiency was obtained. Table 2 summarizes the results obtained from Fig. 10. In this Table, power density refers only to a single electrode, and not to a complete cell.

Its power density is only about 10% of that of the Li-Zn system. This comes mainly from the fact that a thickness of at least 3 mm was necessary, instead of 1 mm for the solid electrode, to keep the liquid electrode on the substrate. The current efficiency was more than 90% in each case.

#### Conclusion

For high current density and stable potential, a solid electrode is preferable, whereas for long cycle life, a liquid alloy electrode is better. Utilization of both liquid and solid phases is also possible. Addition of NaCl to the eutectic LiCl-KCl electrolyte is effective for lowering its cost and increasing the concentration of alkali metals.



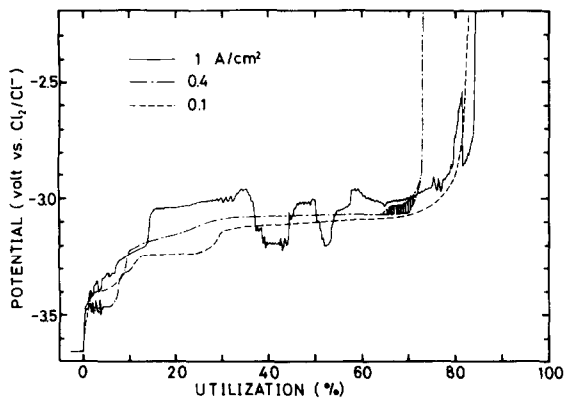


Fig. 10. Discharge curves at various current densities at 400 °C. Li, K-Sn alloy electrode.

### Acknowledgment

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