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D.R. Vissers, K.E. Anderson and F.C. Mrazek

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D. R. Vissers, K. E. Anderson and F. C. Mrazek
Chemical Engineering Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

ABSTRACT

Solid lithium-aluminum alloy electrodes have shown a great deal of promise for meeting the performance requirements of negative electrodes in lithium/metal sulfide batteries for stationary energy storage and for electric vehicle propulsion. In an effort to improve the performance of the lithium-aluminum alloy electrode, investigations were conducted to determine the effect of various metal additives (tin, lead, copper and indium) on the performance and cycle life (capacity retention) of these lithium-metal alloys. The electrodes were characterized by measuring the achievable capacity densities as a function of current density and number of cycles. The addition of 5 wt % copper, 5 wt % tin or 10 wt % lead did not markedly improve the cycle life of the lithium-metal alloy electrode, however, the tin additive improved the performance of the electrode during its first 100 cycles. In contrast, the addition of indium at the 3.9 wt % level markedly improved the cycle life. The capacity decline of the Li-Al-3.9 wt % In alloy was <0.01% per deep cycle, which compares with about 0.06% per deep cycle for the binary Li-Al alloy electrode. Preliminary studies of the indium additive at the 1 wt % level also look very promising. Postoperative photomicrographic examinations of the active material in the lithium-metal alloy electrodes suggest that the indium additive results in a more dendritic-like material than that in the binary Li-Al alloy electrodes.

INTRODUCTION

The interest in the development of high-performance secondary batteries has increased markedly in recent years throughout the industrialized world. Batteries of this type are being developed at Argonne National Laboratory (ANL) for stationary energy storage applications and for vehicle propulsion. The present cells utilize positive electrodes of either iron sulfide (FeS) or iron pyrite (FeS_2),[1-5] negative electrodes of lithium-aluminum alloy,[6-11] and a molten salt electrolyte such as LiCl-KCl eutectic (mp, 352°C), and are operated at temperatures between approximately 400-450°C.

A 48 at. % lithium-aluminum alloy has shown excellent promise of meeting the performance requirements for negative electrodes in these cells.[12-14] Previous attempts to develop a negative electrode using liquid lithium as the active material for high-energy secondary cells have been extensive[15-17] but generally unsuccessful. The primary problem in these cells has been cell shorting. This problem results from the high rates of corrosion of the ceramic separators and feedthroughs by liquid lithium and from the movement of liquid lithium from the negative electrode structure into the ceramic separator, with consequent decline in cell capacity with time. The problem can be avoided or alleviated by the use of a solid lithium-aluminum alloy as the negative electrode material.

The present electrodes utilize that portion of the lithium-aluminum phase diagram wherein both the β-phase LiAl and the lithium-saturated α-phase of aluminum are present. In going from this region, which at 425°C has a potential of +0.3 V relative to liquid lithium, into the single-phase region of β-phase LiAl, the potential decreases very rapidly as the lithium content increases, as shown by the studies of Selman *et al.*[9] These studies also indicated that the use of Li-Al electrodes containing more than 50 at. % lithium is not practical because of the high lithium activity at these concentrations.

The work described herein is an investigation of the effects of various metal additives on the electrochemical perofmrnace and cycle life of the lithium-aluminum alloy electrode. The electrodes are also being examined to determine whether a correlation exists between electrode performance and the morphology of the alloy after repeated cycling. The alloy systems investigated were Li-Al-3.9 wt % In, Li-Al-10 wt % Pb, Li-Al-4.9 wt % Sn and Li-Al-5 wt % Cu.

A liquid lithium electrode was chosen as the counter electrode because this electrode is unpolarized at high current densities.[15] Thus, the liquid lithium electrode serves both as a counter electrode and as a near-perfect reference electrode. Consequently, for measurements made during normal cycling, the electrochemical potential of the Li-Al electrode can be easily monitored.

EXPERIMENTAL

The general design of the cells is illustrated in Fig. 1. The lithium counter-electrodes consisted of 5-cm-dia by 0.64-cm-thick disks of Type 302 stainless steel Feltmetal (90% porosity; 27 μm, ave. pore dia) that contained ∿6 g (23 A-hr) of lithium. Approximately 25 wt % copper was added to the liquid lithium to improve the lithium retention in the Feltmetal.

The Li-Al-M (M = metal additive) alloys were prepared by melting mixtures of the desired composition at about 800-900°C in tantalum crucibles. Each alloy was ground to a powder and vibratorily loaded

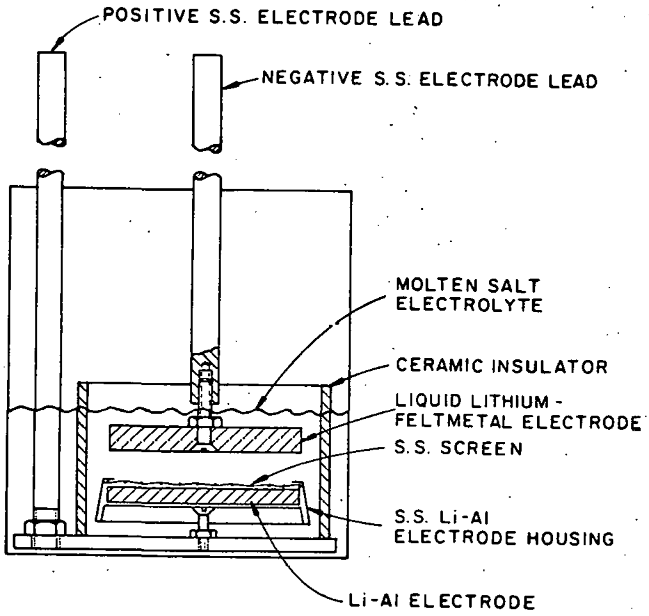

Fig. 1. Cell Design

into a porous iron Retimet* disk, which was then inserted in a housing of Type 304 stainless steel to form the working electrode. Two screens (16 and 24 mesh) across the face of the housing provided support for the electrodes, and a sheet of zirconia fabric was inserted between the disk and the screen to retain the Li-Al particles. The Li-Al electrodes had areas of 15.6 cm^2.

The cell electrolyte was LiCl-KCl eutectic (mp, 352°C) obtained from the Anderson Physics Laboratories Inc., Urbana, Illinois, where it was prepared by a procedure outlined by Laitinen, Tischer, and Roe.[18] The cell interelectrode spacing was ∿0.6 cm; a BeO cylinder served to prevent shorting. In all experiments, the cells were operated in sealed furnace wells attached to a high-purity helium-atmosphere glove box.

The following cutoff potentials were used during cell cycling: 0.15 V during Li-Al electrode charge and 0.70 V during Li-Al electrode discharge (all cutoff potentials cited are IR-free voltages *vs.* lithium). These cutoff potentials are believed to be quite conservative. In the normal operation of a Li-Al/LiCl-KCl/FeS_2 cell having electrodes of matched capacity, the potential of the Li-Al electrode during cell charge may reach 0.05 V, and during discharge, 0.67 V. If a large excess of FeS_2 is used, the potential of the Li-Al electrode during cell discharge may reach as high as 0.97 V, whereas during cell charge it will remain essentially unchanged from that of a cell with equal-capacity electrodes.

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*The Retimet was obtained from the Hydro-Jet Corp., Rancho Santa Fe, CA.

The cells were cycled in a constant-current mode with the aid of a regulated DC power supply. A meter relay automatically reversed the direction of cell current when a preset cutoff voltage for either charge or discharge was attained. In this way, the cells could be automatically charged and discharged at selected current densities. The total capacity (A-hr) for the charge and discharge half-cycles was measured electronically and the data were provided in print-out form.

The capacity density of a Li-Al-M electrode was used as a measure of its electrochemical performance. Capacity-density measurements were carried out at current densities of 0.05 to 0.10 A/cm^2 during charge and 0.05 to 0.30 A/cm^2 during discharge. The effect of the additive on cycle life was assessed by measuring the rate of decline of capacity density at 0.05 A/cm^2 (C/12 rate) with repeated deep cycling.

RESULTS AND DISCUSSION

The performance and the capacity retention with cycling of a Li-Al electrode without a metal additive was investigated initially to establish baseline data for the Li-Al electrode. The baseline Li-Al electrode had a theoretical capacity density of 0.65 A-hr/cm^2 (10.14 A-hr). The performance of the electrode, as measured by the achievable capacity density at 435°C during early cell cycling, is presented in Table 1. These results indicate excellent lithium utilization even at high discharge rates. For example at the C/10 charge rate the C/1.8 discharge rate the lithium utilization is near 82% of theoretical; at the higher charge rates, the achievable capacity density declines markedly. After 100 deep cycles, the lithium utilization at the C/12 rate was 87% thereafter, it declined at a rate of ∿0.06% per cycle for the next 100 cycles.

Table 1. Capacity Density of Li-Al Baseline Electrode at 435°C

Charge Rate, A/cm^2	Discharge Rate, A/cm^2	Capacity Density, A-hr/cm^2	Lithium Utilization, % of theor.
0.050	0.050	0.60	92.3
0.050	0.100	0.58	89.2
0.050	0.200	0.55	84.6
0.050	0.300	0.53	81.9
0.100	0.050	0.52	80.2
0.100	0.100	0.50	76.6
0.100	0.200	0.50	76.6
0.100	0.300	0.43	65.6

The performance of the Li-Al-5 wt % Sn electrode, which contained 0.574 A-hr/cm^2 of lithium, was superior to that of the baseline electrode during early cycling (see Table 2). The addition of tin to the Li-Al alloy appeared to improve the charging characteristics of the alloy. After 100 deep cycles, the lithium utilization at the C/12 rate was 82.8%, it declined at the rate of 0.14% per cycle over the next 35 cycles, at which point the cell operation was terminated. The addition of tin at the 5 wt % level did not appear to improve the cycle life of the Li-Al electrode.

Table 2. Capacity Density of LiAl-5 wt % Sn Electrode at 435°C

Charge Rate, A/cm^2	Discharge Rate, A/cm^2	Capacity Density, A-hr/cm^2	Lithium Utilization, % of theor.
0.050	0.050	0.54	94.1
0.050	0.100	0.53	92.4
0.050	0.200	0.52	90.6
0.050	0.300	0.48	83.7
0.100	0.050	0.47	81.9
0.100	0.100	0.47	81.9
0.100	0.200	0.47	81.9
0.100	0.300	0.45	78.4

The performance of the Li-Al-10 wt % Pb alloy electrode, which had a theoretical capacity density of 0.499 A-hr/cm^2, is shown in Table 3. During early cycling the achievable capacity density of this

Table 3. Capacity Density of Li-Al-10 wt % Pb Electrode at 435°C

Charge Rate, A/cm^2	Discharge Rate, A/cm^2	Capacity Density, A-hr/cm^2	Lithium Utilization, % of theor.
0.050	0.050	0.46	92.2
0.050	0.100	0.45	90.2
0.050	0.200	0.43	86.2
0.050	0.300	0.42	84.2
0.100	0.050	0.41	82.2
0.100	0.100	0.37	74.1
0.100	0.200	0.37	74.1
0.100	0.300	0.36	72.1

electrode system was quite similar to that of the baseline Li-Al electrode. After 100 cycles, the lithium utilization at the C/12 rate was 77% of theoretical and it declined at a rate of 0.30% per cycle. Cell operation was terminated after 116 cycles. These results indicated the 10 wt % lead additive did not improve either the performance or cycle life of the Li-Al electrode.

The addition of 5 wt % copper to the Li-Al alloy produced an electrode material that had poorer charging characteristics than the baseline Li-Al electrode (see Table 4). The achievable capacity of this electrode, which contained 0.544 A-hr/cm^2, was greatly reduced at the higher charge rates. The lithium utilization at the C/12 rate after 100 cycles was 83% of theoretical and it declined at a rate of ∿0.06% per cycle during the next 100 cycles.

Table 4. Capacity Density of Li-Al-5 wt % Cu Electrode at 435°C

Charge Rate, A/cm^2	Discharge Rate, A/cm^2	Capacity Density, A-hr/cm^2	Lithium Utilization, % of theor.
0.050	0.050	0.54	98.6
0.050	0.100	0.53	96.6
0.050	0.200	0.46	83.7
0.050	0.300	0.44	80.9
0.100	0.050	0.36	66.7
0.100	0.100	0.36	65.9
0.100	0.200	0.36	65.3
0.100	0.300	0.35	63.5

The performance of the Li-Al-3.9 wt % In alloy system was next investigated using an electrode with a capacity density of 0.658 A-hr/cm^2 (see Table 5). The cell data was quite similar to the data for the baseline cell. The lithium utilization after 100 cycles was 89.2% and declined at a rate of 0.01% per cycle over the next 35 cycles, at which time cell operation was terminated. These results (see Table 6) indicate that the addition of indium to the Li-Al alloy electrode is indeed beneficial, and confirm observations made earlier by Buzzelli.[19] Unpublished engineering-scale studies at ANL with Li-Al-In/FeS cells have also confirmed the beneficial effect of the indium additive.[20] The use of the indium additive at the 1 wt % level is currently being evaluated. Preliminary results suggest that, even at this level, the indium additive is very beneficial.

Postoperative photomicrographic examinations of the cross-sectioned Li-Al-M alloy electrodes clearly showed that the additives

Table 5. Capacity Density of Li-Al-3.9 wt % In Electrode at 435°C

Charge Rate, A/cm^2	Discharge Rate, A/cm^2	Capacity Density, A-hr/cm^2	Lithium Utilization, % of theor.
0.050	0.50	0.61	92.7
0.050	0.100	0.60	90.5
0.050	0.200	0.58	88.6
0.050	0.300	0.55	83.2
0.100	0.050	0.46	70.0
0.100	0.100	0.46	70.0
0.100	0.200	0.46	70.0
0.100	0.300	0.43	65.4

Table 6. Performance of Li-Al-M Electrodes After 100 Cycles

Additive	Utilization[a] (%)	Capacity Decline (%/cycle)
None	87.0	0.06
3.9 wt % In	89.2	<0.01
5 wt % Sn	82.8	0.14
10 wt % Pb	77.0	0.30
5 wt % Cu	83.0	0.06

affect the morphology of the Li-Al particles. The indium additive appears to generate high surface area Li-Al particles which are more dendritic in nature than particles generated in the binary Li-Al electrode. The lithium-alloy particles in the electrodes that contained the lead, tin and copper additives are much smaller and more uniform than those found in either the baseline electrode or in the electrode which utilized the indium additive. These observations suggest that the electrodes containing the high-surface-area dendritic Li-Al particles have improved cycle life.

The study of additives to solid Li-Al alloy electrodes may be briefly summarized as follows. Additions of lead (10 wt %), tin (5 wt %), or copper (5 wt %) did not improve the lithium retention characteristics of the electrodes, but the tin addition improved the capacity density during early cycling. In contrast, the addition of indium, at a level of 3.9 wt %, greatly improved the lithium retention; the rate of capacity decline per cycle was <0.01%, as compared with a rate of 0.06% for a Li-Al electrode with no additive. Preliminary performance results for a cell with a Li-Al-1 wt % In electrode are also promising. Photomicrographic examination of the test electrodes showed that the major morphological difference exhibited by the Li-Al-In electrode was the presence of dendritic high-surface-area particles. Studies are being continued with additives of antimony and zinc.

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