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Development of a High-Power and High-Energy Thermal Battery

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Abstract

The Li(Si)/FeS_2 and Li(Si)/CoS_2 couples were evaluated with a low-melting LiBr-KBr-LiF eutectic and all-Li LiCl-LiBr-LiF electrolyte for a battery application that required both high energy and high power for short duration. Screening studies were carried out with 1.25"-dia. triple cells and with 10-cell batteries. The Li(Si)/LiCl-LiBr-LiF/CoS_2 couple performed the best under the power load and the Li(Si)/LiCl-LiBr-LiF/FeS_2 was better under the energy load. The former system was selected as the best overall performer for the wide range of temperatures for both loads, because of the higher thermal stability of CoS_2.

Introduction

We were asked to develop a thermal battery for a unique application that required both high power as well as a reasonably high energy density. These tend to be mutually exclusive, as the energy requirements will drive the ultimate size of the battery. The minimum mass required for the anodes and cathode pellets in the stack will be dictated by the application. Because of the range in current densities and capacities for such an application, it was necessary to first screen a number of electrochemical couples and electrolytes, to determine which was best suited for such an application. The difference in the load requirements also make thermal balancing a concern. What might work fine in the high-energy-mode could result in a thermal runaway under a high-power mode, due to internal Joule (I^2R) heating.

We examined the Li(Si)/FeS_2 as well as the Li(Si)/CoS_2 couple in the all-Li LiCl-LiBr-LiF minimum-melting electrolyte as well as the low-melting LiBr-KBr-LiF eutectic for this application. We had previously evaluated the Li(Si)/LiCl-LiBr-LiF/CoS_2 system for a related high-power application.[1] Screening studies were carried out using 1.25"-dia. triple cells discharged at the equivalent current densities expected for the final application. In addition, 10-cell tests built with 1.25"-dia. stacks were carried out to validate the results and recommendations resulting from the single-cell tests. This paper presents the results of the screening study and the battery tests.

Experimental

<u>Materials</u> – Flooded anodes of 25% electrolyte and 75% active anode (44% Li/56% Si) were used for all tests. The final anode pellet weight was 0.99 g. The presence of electrolyte aids in pelletizing and improves the electrochemical performance. The LiBr-KBr-LiF eutectic electrolyte has a melting point of 324.5°C, while the LiCl-LiBr-LiF electrolyte has a melting point of 436°C. The low-melting electrolyte has a larger liquidus range than does the all-Li electrolyte. This can result in longer functioning times for batteries activated under cold conditions. The all-Li electrolyte, on the other hand, has a much higher ionic conductivity, since it contains only Li cations. This avoids the concentration gradients that occur under high-rate conditions.

The separators formulated with the low-melting electrolyte contained 25% Maglite 'S' MgO, while the separators with the all-Li electrolyte contained 35% MgO. The FeS_2 catholyte pellet contained 73.5% FeS_2/25% separator/1.5% Li_2O and weighed 1.47 g. The CoS_2 catholye contained 78.5% CoS_2/20% electrolyte/1.5% Li_2O and weighed 1.59 g. (A heavier pellet is needed for the CoS_2 cathodes because of the lower gravimetric coulombic capacity for this material.) The heat powder composition for battery tests was 84/16 Fe/$KClO_4$ (by weight). All processing of powders and materials for battery construction was conducted in a dry room maintained at <3% relative humidity.

<u>Apparatus and Testing</u> – Batteries were constructed using a reusable test fixture that used an O-ring seal to protect the stack components from ambient conditions. Electrical feedthroughs at the header (base) end provided power output as well as allowed connection to an internal thermocouple that was inserted between the end and next-to-the-end cells at the header end.

DISCLAIMER

The batteries and triple cells were tested using an HP6060B programmable electronic load under control by an HP9836 computer running Rocky Mountain BASIC. Readings were taken once a second with an HP3456A 6-1/2 digit digital voltmeter (DVM), interfaced to an HP3497A data acquisition unit which mutiplexed several channels. One channel was used for recording voltage and a second was used to monitor the current through a calibrated shunt. A third channel was used to record stack temperature.

The load profiles used are shown in Figure 1. Load #1 is the Power Load. Load #2 is the Energy Load. This is equivalent to current densities of 0.36 A/cm^2 for the steady state and 1.64 A/cm^2 for the pulse load. The cells and batteries were discharged for 300 s under Load #1 and for longer times under Load #2. Triple cells were tested at temperatures of 450°C and 500°C. The 10-cell batteries were activated at temperatures of -54°C and +71°C.

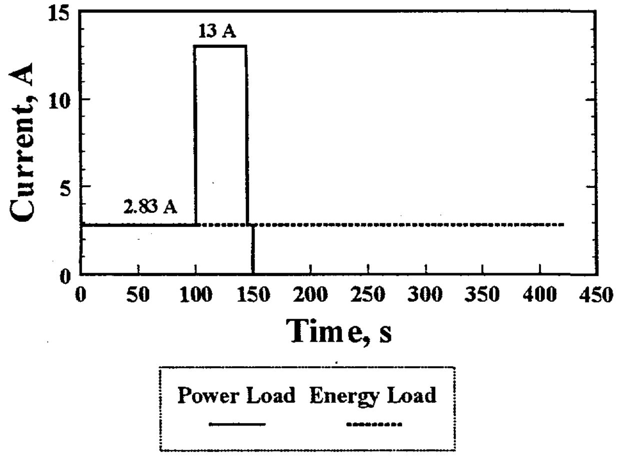

Figure 1. Load Profile used for 1.25"-Dia. Cells and Batteries.

Results and Discussion

Triple-Cell Tests – Normally, screening tests would have been conducted using single cells. However, the high currents used in this study resulted in unacceptably low cell voltages so that the electronic load did not regulate properly. Consequently, it was necessary to use three-cells in series instead. (Triple cells were not tested under the Load #2 regime, which was a much less severe load. The batteries, however, were subjected to both load profiles.)

I^{2}R heating during the pulse was quite evident for all chemistries, but more so for the FeS$_2$-based cells. The corresponding voltage for Li(Si)/FeS$_2$ triple cells under Load #1 is shown in Figure 2, along with related data for the low-melting system. The voltage drop during the pulse was much more severe at 450°C than at 500°C and was greater for the low-melting electrolyte. This indicates that the combination of FeS$_2$ with the low-melting electrolyte or the all-Li electrolyte could have inadequate performance under cold-activation conditions. Even at 500°C, the performance of FeS$_2$ using the low-melting electrolyte was not much improved over that at 450°C. The results of the tests done at 450°C for the all-Li system are not surprising, as the cells are only 14°C above the melting point of the electrolyte.

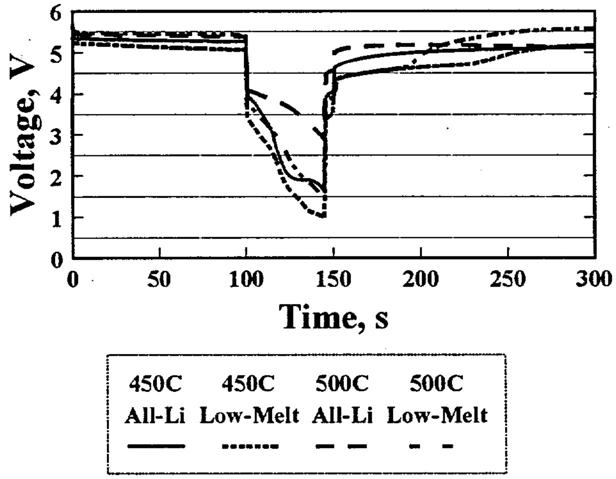

Figure 2. Response of Li(Si)/FeS$_2$ Cells at 450°C and 500°C for LiCl-LiBr-LiF and LiBr-KBr-LiF Electrolytes to Load #1.

Similar data for the Li(Si)/CoS$_2$ couple for the two electrolytes and same temperatures are presented in Figure 3. There was an expected severe voltage drop for the CoS$_2$ cell when used with the low-melting electrolyte, especially at the lower temperature. In contrast, the temperature effects were not pronounced for the Li(Si)/CoS$_2$ couple when discharged in the all-Li electrolyte. This makes this combination the most attractive from a battery-performance perspective.

The rapid drop in voltage during the pulse for the cells with the low-melting electrolyte is due to a somewhat lower ionic conductivity than the all-Li system and, more importantly, to severe concentration polarization. Under high-current discharge, Li ions are generated at a high rate at the anode-separator interface. If there is not enough time for diffusion into the bulk of the separator, a large concentration gradient of Li ions is created. The consequence of this is that the localized composition of the electrolyte at the interface is moved off the eutectic with a concomitant increase in the melting point. This results in precipitation of solid which rapidly raises the resistance of the separator, with a corresponding drop in potential.

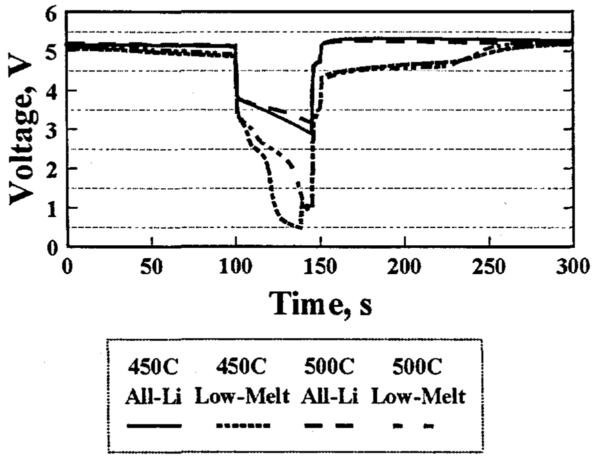

Figure 3. Response of Li(Si)/CoS_2 Cells at 450°C and 500°C for LiCl-LiBr-LiF and LiBr-KBr-LiF Electrolytes to Load #1.

The results of the triple-cell tests are summarized in Table 1. The all-Li electrolyte was superior to the low-melting electrolyte and CoS_2 outperformed FeS_2 overall. The CoS_2 has a lower electronic resistance that reduced voltage losses under high-current discharge. The worst combination was CoS_2 with the low-melting electrolyte. Apparently, under deep discharge conditions, severe polarization occurs that is normally not observed for short pulses or for lower power levels. The combination of CoS_2 with the all-Li electrolyte provided the best overall performance under these discharge conditions. Based on these test results, one would expect similar behavior in the battery tests.

10-Cell Battery Tests – The four electrolyte-cathode combinations were tested under the same load conditions, as were the triple cells. The optimum heat balances (heat output per total cell mass) are summarized in Table 2. Representative voltage traces under Load #1 are shown in Figure 4 for 10-cell batteries built using CoS_2 and the low-melting electrolyte. The voltage loss during the pulse under the cold condition was much greater than that under the hot conditions. This reflects the triple-cell test results with this combination.

Table 2. Heat Balance for 10-Cell Batteries.

Electrolyte	Cathode	Heat Balance, cal/g cell
Low-melting	FeS_2	96.1
All-Li	FeS_2	100.9
Low-melting	CoS_2	105.8
All-Li	CoS_2	109.1

The corresponding performance of the FeS_2 cathode is shown in Figure 5. The voltage loss during the pulse for the cold battery was slightly more than for the hot one. The gradient-relaxation process that takes place when the cell was placed on open circuit was slow in this case, as evidenced by the slow return to the background voltage level that existed just before the pulse.

Table 1. Summary of Results of Triple-Cell Tests with Various Cathode and Electrolyte Combinations.

Temp., C	Cathode	Electrolyte	R @ Start of Pulse, ohms	R @ End of Pulse, ohms	Min. Pulse Voltage, V	Power @ End, W
450	FeS_2	Low-melting	0.161	0.268	1.041	13.5
		All-Li	0.133	0.229	1.600	20.8
	CoS_2	Low-melting	0.150	0.267	0.583	7.60
		All-Li	0.126	0.182	2.748	35.2
500	FeS_2	Low-melting	0.154	0.217	1.399	17.7
		All-Li	0.125	0.164	3.068	39.9
	CoS_2	Low-melting	0.150	0.296	0.690	7.80
		All-Li	0.121	0.145	3.266	40.1

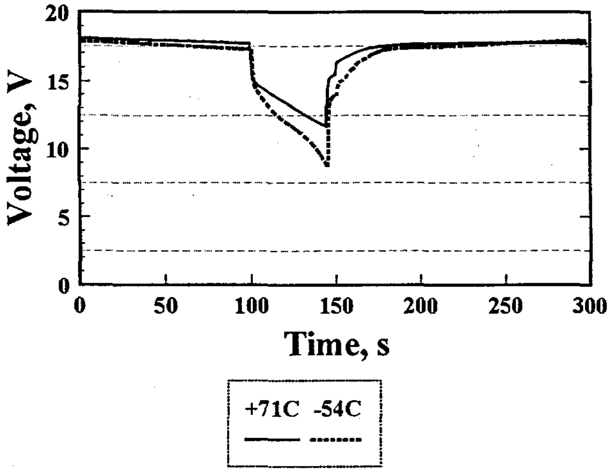

Figure 4. Response under Load #1 of 10-Cell Batteries using CoS_2 and LiBr-KBr-LiF Eutectic.

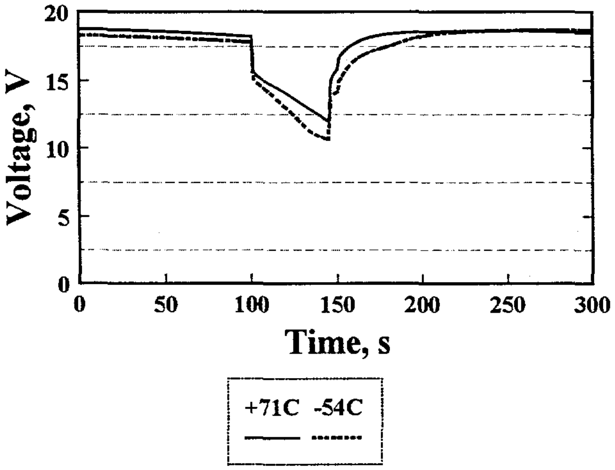

Figure 5. Response under Load #1 of 10-Cell Batteries using FeS_2 and LiBr-KBr-LiF Eutectic.

This is characteristic of such processes in multi-cation melts under high-rate discharge.

The discharges of the 10-cell batteries under Load #1 with CoS_2 and FeS_2 cathodes and the all-Li electrolyte are shown in Figures 6 and 7, respectively. The voltage response during the pulse was very similar in the case of the CoS_2 cathode for both the hot and cold batteries (Figure 6). In contrast, there was a severe voltage droop for the cold battery for the FeS_2 counterpart (Figure 7). These data corroborate the results of the isothermal triple-cell tests: the best overall combination is the Li(Si)/LiCl-LiBr-LiF/CoS_2 electrochemical system.

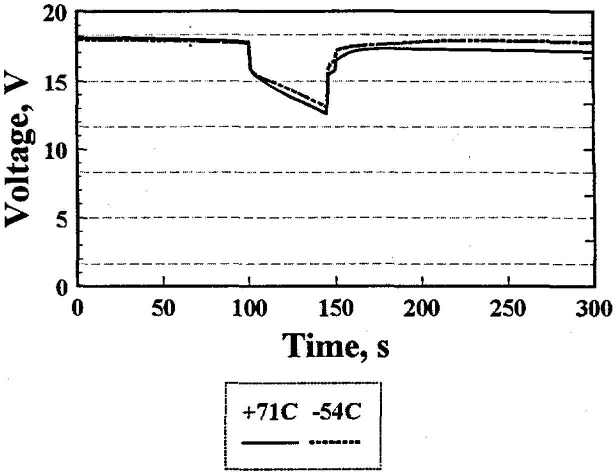

Figure 6. Response under Load #1 of 10-Cell Batteries using CoS_2 and LiCl-LiBr-LiF Eutectic.

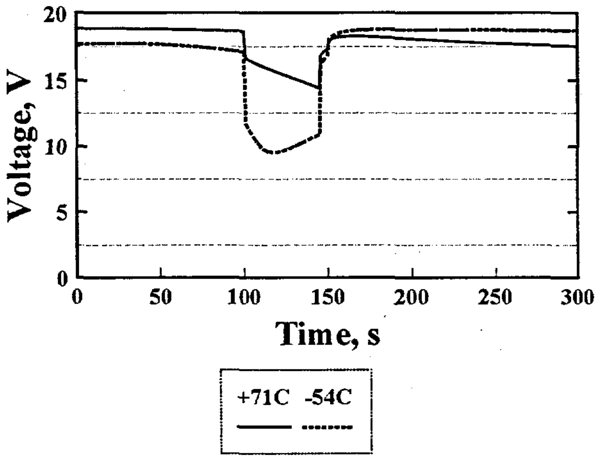

Figure 7. Response under Load #1 of 10-Cell Batteries using FeS_2 and LiCl-LiBr-LiF Eutectic.

It is also noteworthy that the voltage response to open circuit after the pulse was markedly faster with the all-Li system than for the multi-cation low-melting electrolyte, due to the lack of severe Li^+ concentration gradients.

The electrochemical response of the four electrolyte-cathode combinations is summarized in Figure 8 under the Load #2 discharge for 10-cell batteries built with the optimum heat balance and activated at –54°C. In this case, the best overall results were observed for the battery with the all-Li electrolyte and the FeS_2 cathode. Under these lower-power discharge conditions, overheating problems encountered by the FeS_2 cathode under the Load #1 discharge conditions were absent.

The results of the Load #2 tests with the 10-cell

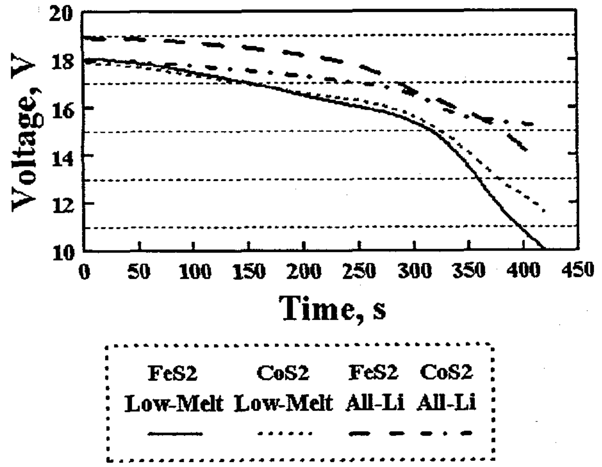

Figure 8. Discharge at –54°C under Load #2 of 10-Cell Li(Si)/FeS_2 and Li(Si)/CoS_2 Batteries with Low-Melting and All-Li Electrolyte.

batteries are summarized in Table 3. The open-circuit voltage of the Li(Si)/CoS_2 couple is about 100 mV less than that of the Li(Si)/CoS_2 at the same temperature. For a 10-cell battery, that amounts to a 1-V difference. However, the intrinsic higher conductivity of the CoS_2 cathode and its lower-resistance discharge product resulted in the voltage of this couple being slightly higher than that of the corresponding FeS_2 couple after 350 s for the all-Li electrolyte.

Table 3. Performance Summary of Various Systems Tested in 10-Cell Batteries under Load #2.

System	Temp., C	Power @ End, W	Volt. @ End, V
FeS_2/LM	-54	28.3	10.0
FeS_2/all-Li	-54	24.6	8.7
CoS_2/LM	-54	32.6	11.6
CoS_2/all-Li	-54	42.9	15.2
FeS_2/LM	+71	N.A.	N.A.
FeS_2/all-Li	+71	38.6	13.7
CoS_2/LM	+71	N.A.	N.A.
CoS_2/all-Li	+71	38.3	13.6

In the case of the low-melting electrolyte, the performance of the Li(Si)/CoS_2 couple was comparable to that of the Li(Si)/FeS_2 and actually surpassed it after ~325 s. These data illustrate that one cathode-electrolyte system will not necessarily perform the same under widely varying conditions. This makes designing one battery to do the job of two challenging.

Because of the much higher thermal stability of CoS_2 relative to FeS_2, the Li(Si)/LiCl-LiBr-LiF/CoS_2 couple was chosen as best suited for this study.

Conclusions

The Li(Si)/FeS_2 and Li(Si)/CoS_2 couples were screened with LiBr-KBr-LiF and LiCl-LiBr-LiF electrolytes for a battery application requiring both high power and high energy. The results of 1.25"-dia. triple-cell tests showed that the Li(Si)/LiCl-LiBr-LiF/CoS_2 couple performs the best overall. Follow-up 10-cell tests with 1.25"-dia. stacks show that the Li(Si)/LiCl-LiBr-LiF/CoS_2 couple is best for the high-power condition and that the Li(Si)/LiCl-LiBr-LiF/FeS_2 couple is somewhat better for the high-energy condition. The former couple was selected as best overall because of the higher thermal stability of CoS_2.

References

1. Ronald A. Guidotti, Gregory L. Scharrer, Edward Binasiewicz, and Frederick W. Reinhardt, *Proc. 38th Power Sources Conf.*, 240 (1998).

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