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ELECTROLYTE EFFECTS IN Li(Si)/FeS_2 THERMAL BATTERIES

Ronald A. Guidotti and Frederick W. Reinhardt
Sandia National Laboratory
Battery Development Department
Albuquerque, NM 87185-0614

INTRODUCTION

The most common electrochemical couple for thermally activated ("thermal") batteries is the Li-alloy/FeS_2 system. The most common Li-alloys used for anodes are 20% Li-80% Al and 44% Li-56% Si (by weight); liquid Li immobilized with iron powder has also been used. Thermal batteries developed at Sandia National Laboratories/Albuquerque (SNLA) for the Department of Energy (DOE) are designed with the Li(Si)/FeS_2 couple.

The standard electrolyte that has been used in thermal batteries over the years is the LiCl-KCl eutectic that melts at 352°C. We evaluated several electrolytes in earlier ramp-cooled single-cell screening tests as alternatives to the LiCl-KCl eutectic electrolyte (Guidotti and Reinhardt, 1988). The LiCl-LiBr-LiF eutectic---the so-called "all-lithium" electrolyte--had the best rate and power characteristics. This electrolyte melts at 436°C and shows very low polarization because of the absence of Li^+ gradients common with the LiCl-KCl eutectic; the all-Li electrolyte appears ideally suited for pulse-power applications.
The low-melting electrolytes examined included a KBr-LiBr-LiCl eutectic used by Argonne National Laboratory (ANL) (melting at 321°C), a LiBr-KBr-LiF eutectic developed at SNLA (melting at 313°C), and a CsBr-LiBr-KBr eutectic (melting at 238°C). The CsBr-based salt had poor conductivity and was not studied further; similar results were noted with a number of Rb-halide-based electrolytes in earlier work (Searcy, 1984). The LiBr-KBr-LiF eutectic outperformed the KBr-LiBr-LiCl eutectic and was selected for more extensive testing. Because of their lower melting points and larger liquidi relative to the LiCl-KCl eutectic, the low-melting electrolytes are prime candidates for long-life applications (*i.e.*, for activated lives of one hour or more).

This paper will detail the relative performance of the Li(Si)/FeS_2 couple using primarily the LiCl-KCl (standard) eutectic, the LiCl-LiBr-LiF (all-Li) eutectic, and the LiBr-KBr-LiF (low-melting) eutectic electrolytes. Most of the tests were conducted with 5-cell batteries; validation tests were also carried out with appropriate full-sized batteries.

EXPERIMENTAL PROCEDURES

MASTER

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Materials

The catholyte used in the study contained 73.5% FeS_2, 25% electrolyte-binder (EB), and 1.5% Li_2O. (All compositions are in weight percent.) The catholytes containing the standard and low-melting electrolytes were fused at 400°C for 16 hours under an argon atmosphere before granulating and pelletizing. The fusion temperature for the catholyte based on the all-Li electrolyte was 500°C. The EBs used in the separator were also used in the catholytes. The LiCl-KCl and all-Li EBs contained 35% Maglite S MgO (Calgon, Pittsburgh, PA), the ANL low-melting EB contained 30% MgO, and the SNLA low-melting EB contained 25% MgO. [The results of earlier EB-characterization work (Guidotti and Reinhardt, 1988) were used to define the optimum composition for the separators used.] The EBs were prepared by blending with Freon® TF and fusing at 400°C (for the standard and low-melting EBs) or 500°C (for the all-Li EB) for 16 hours. The anode was 44% Li-Si and the heat source was 88% Fe/12% $KClO_4$.

The anode, separator, and catholyte powders were pressed into pellets to 72-75% of theoretical density (TD); the heat powder was pressed to 55% TD. The cathode mass was 1.05 g, which corresponds to 931 coulombs for a charge transfer of 1.5 eq mol^{-1} of FeS_2, as shown in Eqn. 1 for the first-discharge plateau:

$$2FeS_2 + 3Li^+ + 3e^- \text{----->} Li_3Fe_2S_4 \qquad [1]$$

The mass of the anode was 0.70 g, which corresponds to 1,223 coulombs for the $Li_{13}Si_4$--->Li_7S_{13} anode transition. The mass of the separator was 1.00 g.

The battery stack for the evaluation tests contained five cells and was 31.8 mm in diameter. It was insulated with a single wrap of 1-mm Fiberfrax® blanket (Carborundum Co., Niagara Falls, NY) and a 10.2-mm-thick sleeve of Min-K® TE1400 (Schuller Specialty Insulations, Denver, CO). The ends of the stack were insulated with 12.7-mm-thick Min-K discs. A 10-cell long-life thermal battery (LLTB) with a 50.8-mm-dia. stack was used for validation of the low-melting electrolyte. A 16-cell pulse battery with a 16-mm-dia. stack was used for validation of the all-Li electrolyte.

Testing

Single cells were discharged under a constant-current load of 125 mA cm^{-2} for 55 s followed by a pulse load of 250 mA cm^{-2} for 5 s each 60-s cycle.

The evaluation batteries were discharged under a constant-resistance load. A background load of 50 ohms was applied for 55 s and then a 1.05 ohms load was applied for 5 s for each 60-s cycle. (This corresponds to nominal current densities of 25 and 1,170 mA cm^{-2} respectively, at a battery voltage of 9.7 V.) The cycle was repeated until the battery voltage dropped to below 6.25 V (1.25 V $cell^{-1}$) at which point the test was ended. Batteries were tested at activation temperatures of -54° and 74°C. The tester consisted of a Hewlett-Packard Series 200 computer interfaced with a HP3456A DVM and HP3497A data acquisition unit. The stack temperature was monitored by a thermocouple placed between the heat pellet and the Grafoil® backing of the cathode pelllet of the cell adjacent to the header end of the battery.

The background load for the 10-cell LLTB was 13.5 mA cm^{-2} constant current, with a 6-ohm pulse applied for 4 s at 240 s and a 10-ohm pulse applied for 15 ms at 3,580 s. The 16-cell pulse battery was discharged under a constant 12-ohm resistive load.

RESULTS AND DISCUSSION

Single-cell Tests

The kinetics of the discharge process are influenced by the composition of the electrolyte as well as the temperature, as shown in Fig. 1 for six electrolytes (Guidotti *et al.*, 1990).
[Figure 1 here]

The all-Li system was generally superior at temperatures above 450°C. The loss in capacity at 550°C was observed for all of the electrolytes and results from the thermal decomposition of FeS_2. The somewhat lower capacity of the all-Li system at this temperature is a result of increased self-discharge (Hash *et al.*, 1992, Guidotti *et al.*, 1990). At temperatures below 500°C, the capacities were reduced for all systems except the all-Li electrolyte. This is a consequence of polarization caused by the Li^+-concentration gradients in the multi-cation melts, which is absent for the all-Li melt. The performance with electrolytes based on large cations such as Rb and Cs was noticeably inferior; these had less than half the capacity of the other electrolytes at 500°C and reflects the poor conductivity of these melts.

The capacities at 500°C were greater than the theoretical value of 931 coulombs for the FeS_2 for 1.5 eq mol^{-1} and indicate that parallel discharge processes were taking place, rather than clean consecutive ones; *i.e.*, the primary discharge phase ($Li_3Fe_2S_4$) was being discharged before all of the FeS_2 was consumed. This was clearly evident in earlier work in the postmortem examination of cells discharged under similar conditions (Redey *et al.*, 1987).

5-Cell Battery Tests

The physical and electrical properties of the separator used in the battery are critical for proper functioning.

Physical Properties - The physical properties (*e.g.*, specific heat, heat of fusion) of the electrolyte strongly influence the heat requirements of the battery which must be balanced or optimized for the operating-temperature range. The heat balances used in the evaluation tests are listed in Table 1 with the heat of fusion for the various electrolytes for comparison. (The batteries were balanced so the peak stack temperatures were comparable for the various systems. However, the cooling curves were not identical because of differences in the thermal conductivities.)

[Table 1 here]

The highest heat requirements were for the batteries built with the stamdard and all-Li electrolyte, which had the highest heats of fusion. The final heat balance also will be influenced by the specific heat of the EB material used in the separator and catholyte.

Electrical Properties - The electrical properties of the separator will strongly influence the battery polarization. The electrical resistivities of the various EBs are plotted in Fig. 2 as a function of temperature for the optimum compositions (Redey *et al.*, 1990).

[Figure 2 here]

The EB resistivity for the SNLA low-melting electrolyte is significantly lower than that for the ANL low-melting electrolyte and the standard electrolyte. As expected, the all-Li EB has the lowest overall resistivity. The ohmic contribution of the EB resistivity to the overall cell resistance is intermediate between that of the anode and cathode (Redey *et al.*, 1987).

The cell polarization depends greatly upon the depth of discharge and temperature. At higher temperatures (above 500°C), the bulk of the polarization is associated with the cathode. The cathode polarization shows a maximum near 1.5 eq mol^{-1} of FeS_2, where formation of the so-called "Z-phase" ($Li_3Fe_2S_4$) is maximized (Redey *et al.*, 1987). The Z-phase then discharges to the "X-phase" (Li_2FeS_2). At 400°C, the Z-phase is reported to have a resistivity several orders of magnitude greater than that of FeS_2, while the X-phase is only four times more resistive (Badwal, S.P.S. and Thorn, R.J., 1982). The shape of the cathode polarization-time profile is consistent with the changes in resistivity of the various discharge phases. The magnitude of the resistance "hump" is lessened at higher temperatures.

At temperatures of 450°C and less, the anode contribution to the overall cell polarization dominates for all the electrolytes, except the all-Li. This is a result of severe Li^+-concentration gradients that are generated at the anode-separator interface which are greatest under high-rate discharge.

The electrolyte contribution to battery performance becomes most significant near the end of life, where battery temperatures are lowest and concentration gradients become controlling--assuming there is no limitation of anode or cathode capacities. In the dynamic environment of a battery, the temperature decreases with time because of heat losses. Thus, data generated under isothermal conditions may not necessarily apply to battery conditions.

Performance Data - The relative performances of the three electrolytes in 5-cell $Li(Si)/FeS_2$ batteries are summarized in Figs. 3 and 4 for an activation temperature of -54°C for the standard, the SNLA low-melting, and all-Li electrolytes.

[Figures 3 and 4 here]

As expected, the longest activated life was displayed by the batteries with the low-melting electrolyte (Fig. 3). Surprisingly, the all-Li system performed almost as well as the standard system, though its melting point is over 100°C higher. The kneeing over of the voltage-time curves reflects the onset of electrolyte freezing and is not as sharp for the all-Li system. The conductivity of the all-Li electrolyte near its freezing point is still quite good and accounts for the gentler break in the curve. In contrast, the conductivity of the standard EB drops dramatically at its freezing point (Redey *et al.*, 1990).

The enhanced conductivity of the all-Li EB is shown in the polarization (voltage loss) attendant with each pulse (Fig. 4). The lowest polarization for the first six minutes of discharge was displayed by the all-Li batteries, followed by the low-melting batteries. The performance of the three battery systems at 74°C is shown in Figs. 5 and 6. The batteries with the low-melting electrolyte ran the longest (Fig. 5). The batteries with the standard electrolyte had a somewhat higher voltage than those with the all-Li electrolyte for the first 20 minutes of discharge; this reflects the higher rate of self-discharge for the all-Li system under these discharge conditions.

[Figures 5 and 6 here]

The all-Li system still had the lowest polarization during the pulses for the first 14 minutes of discharge (Fig. 6); *i.e.*, the battery impedance was the lowest during this time for these batteries. The pulse performance (resistance) correlated well with the Li -content of the various electrolytes, as shown in Table 2; *viz.*, the batteries with the lowest resistance used the electrolyte with the highest ionic conductivity.

[Table 2 here]

Test with LLTBs

The SNLA low-melting EB (with 25% MgO) was tested in a LLTB for comparison of performance to data generated with the standard EB (with 35% MgO) used in the original design. The battery was designed with a 50.8-mm-dia. stack of 10 cells; the relative performance is compared in Table 3 at the optimum heat balances for the two systems.

[Table 3 here]

The low-melting electrolyte outperformed the standard electrolyte in the LLTB: it increased the activated life by three minutes for the hot batteries and seven minutes for the cold batteries, yielded comparable or higher minimum voltages during the pulses, and had higher voltages throughout discharge. In addition, it required 6.2% less heat for comparable peak temperatures, thus allowing a saving in weight to be achieved for the same design.

Pulse Battery

The all-Li EB (containing 35% MgO) was tested in a pulse battery for comparison of performance to that with the standard EB (containing 40% MgO). The battery was designed with a 16-mm-dia. stack of 16 cells; the relative performance is compared in Table 4 for an optimum heat balance of 123 cal g^{-1} for a constant resistive load of 12 ohms.

[Table 4 here]

The all-Li pulse batteries had rise times that were 15-25 % shorter than those of the standard pulse batteries because of the much better ionic conductivity of the all-Li electrolyte. This also resulted in large increases in the activated lives and increased the voltage at 3 s by over a volt.

CONCLUSIONS

The performance of the standard LiCl-KCl eutectic electrolyte was compared to that of several low-melting electrolytes and the all-Li LiCl-LiBr-LiF eutectic electrolyte in single cells using the Li(Si)/FeS_2 couple. The all-Li cells have the best overall capacity up to 500°C; at 550°C, some loss in capacity occurs because of the increased rate of self-discharge associated with this electrolyte. The SNLA low-melting LiBr-KBr-LiF eutectic performs better than the ANL low-melting LiCl-LiBr-KBr eutectic; both outperform the standard LiCl-KCl electrolyte at temperatures below 400°C as a result of a larger liquidus range and higher ionic conductivity. Electrolytes based on Cs and Rb halides perform poorly because of low ionic conductivity.

The relative performance of the standard, SNLA low-melting, and the all-Li electrolytes in 5-cell Li(Si)/FeS_2 batteries at activation temperatures of -54°C and 74°C is similar to that observed in the single-cells tests. The all-Li batteries have the lowest internal impedance, followed by the batteries with the low-melting electrolyte; batteries with the SNL low-melting electrolyte exhibit the longest activated lives.

Significant improvements in activated life and pulse performance were realized when the standard electrolyte was replaced in a long-life thermal battery with the SNLA low-melting electrolyte. This electrolyte is ideally suited for used in long-life applications where activated lives in excess of one hour are necessary. The low-melting electrolyte should also be considered for any application where the LiCl-KCl eutectic electrolye would normally be used, because of its overall better performance.

Significant improvements were also obtained when the standard electrolyte was replaced with the all-Li electrolyte in a small pulse battery. The all-Li electrolyte is ideally suited to pulse-battery application where high current densities (hundreds of mA cm^{-1}) and short lives (in the seconds or milliseconds) are involved.

ACKNOWLEDGEMENT

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Searcy, J. Q. (1984), unpublished data.

TABLE 1. HEAT BALANCE USED FOR VARIOUS ELECTROLYTES AND THEIR HEATS OF FUSION

Electrolyte	Battery Heat Balance/cal g^{-1}	Electrolyte Heat of Fusion/cal g^{-1*}
LiCl-KCl eut.	98.6	56.1
LiBr-KBr-LiF eut.	95.4	32.0
LiCl-LiBr-LiF eut.	98.6	70.2

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* Heat output is per total cell mass, including the heat pellet.

** Guidotti and Reinhardt, 1988.

TABLE 2. LITHIUM CONTENT OF THE VARIOUS EBs TESTED IN 5-CELL BATTERIES COMPARED TO PERFORMANCE PARAMETERS

Electrolyte Composition	Electrolyte Li -content/ at %	Battery Activated Life/min	Battery Resistance at 3 Min/ohms
		-54 C	
LiCl-KCl	29.5	13.61	0.347
LiBr-KBr-LiF	33.0	18.42	0.290
LiCl-LiBr-LiF	50.0	15.00	0.243
		74 C	
LiCl-KCl	29.5	20.42	0.297
LiBr-KBr-LiF	33.0	23.08	0.270
LiCl-LiBr-LiF	50.0	19.08	0.247

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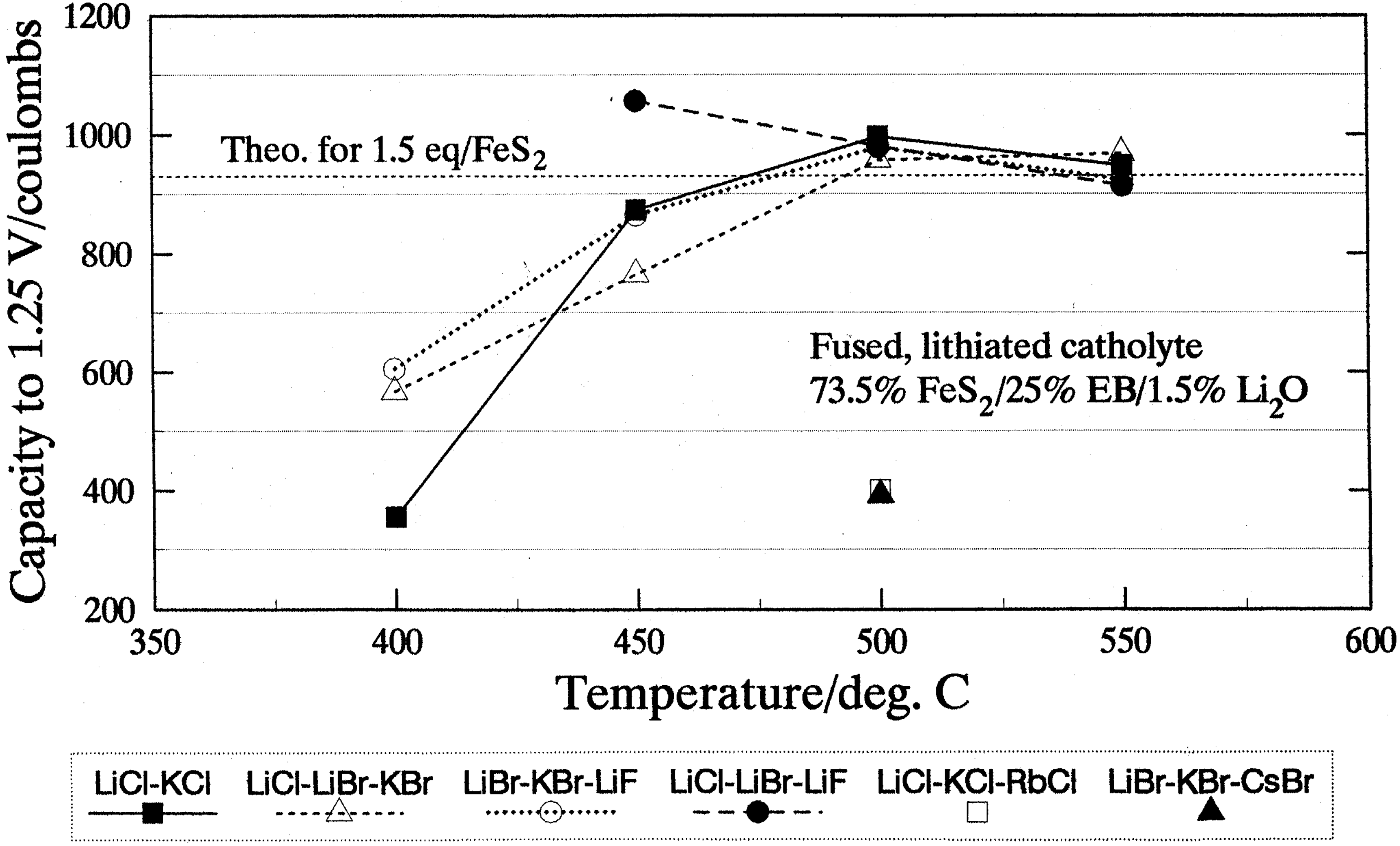
* To 6.25-V cutoff; average of three tests.

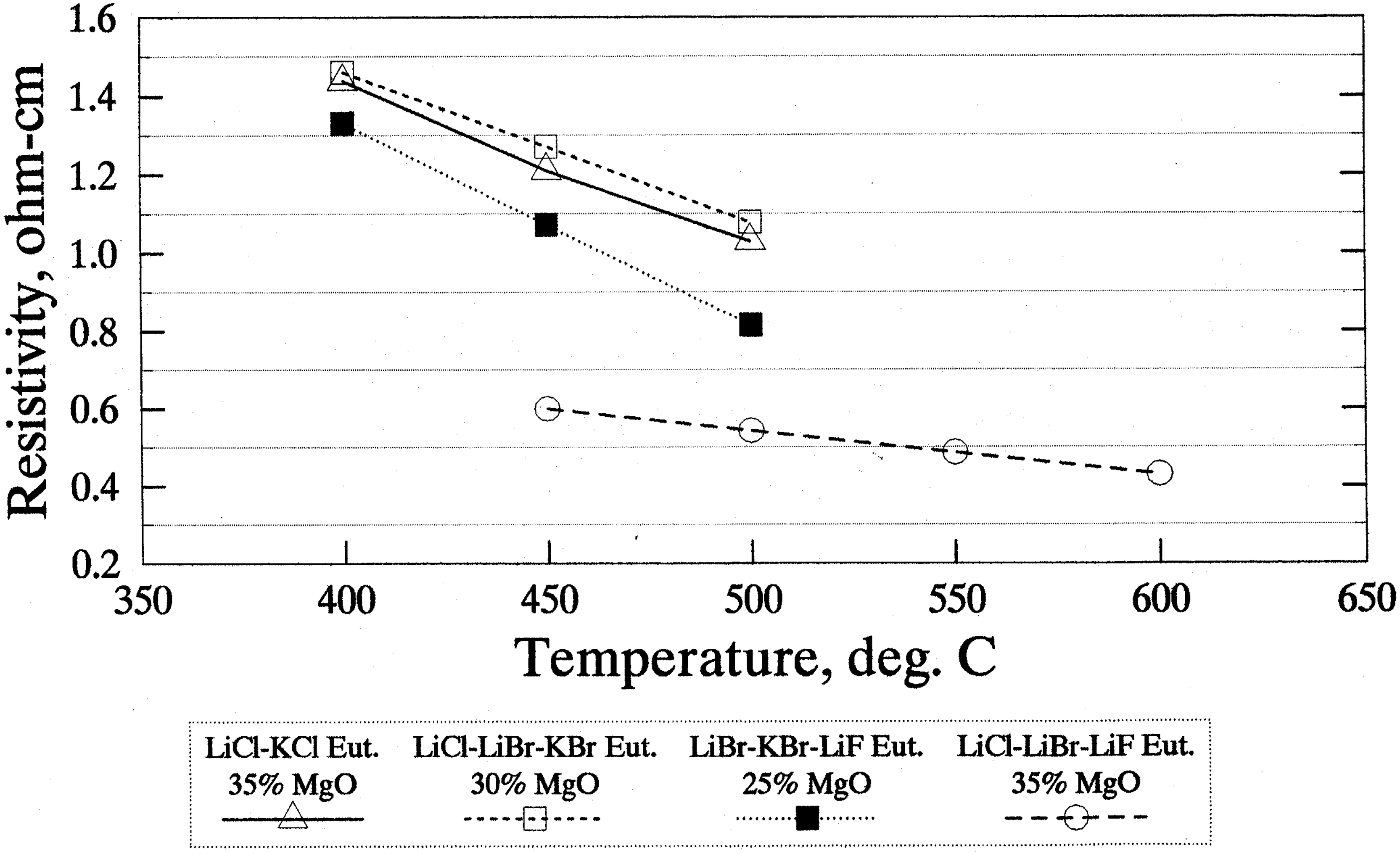
TABLE 3. COMPARISON OF PERFORMANCE OF SNLA LOW-MELTING AND STANDARD ELECTROLYTE IN LONG-LIFE THERMAL BATTERY.

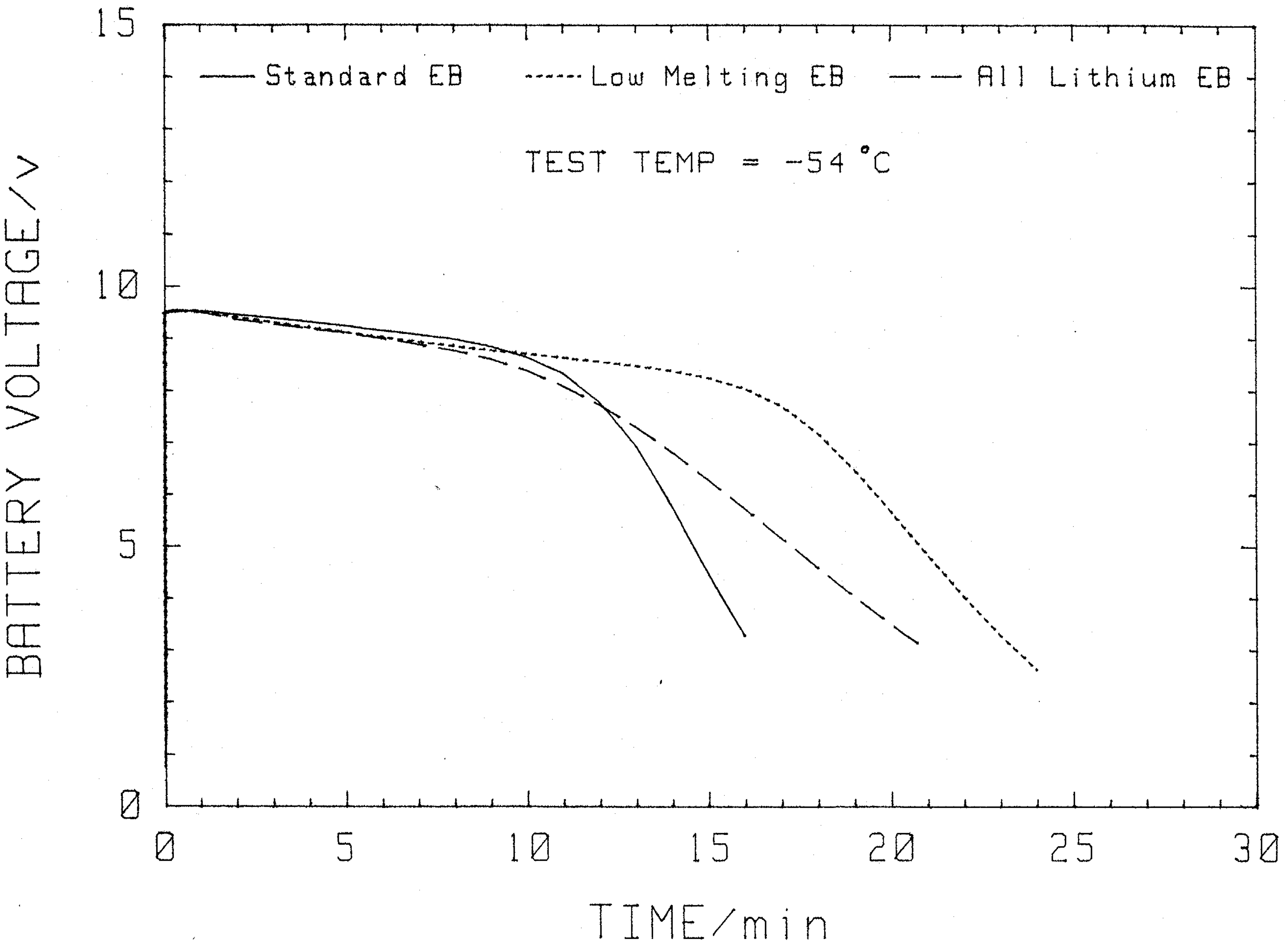
Electrolyte	Activ. Temp./ deg. C	Activated Life/min	Min. Pulse V at 240 s/V	Min. Pulse V at 3580 s/V	Volt. at 3600 s/V
Standard	18	75.2	19.2	16.0	16.2
(92 cal g^{-1})	37	79.5	19.2	15.7	15.8
SNLA low-melting	18	82.4	19.2	16.4	16.7
(88.6 cal g^{-1})	37	82.4	19.2	15.8	16.0

TABLE 4. COMPARISON OF ALL-Li AND STANDARD ELECTROLYTE IN PULSE BATTERY AT A HEAT BALANCE OF 123 CAL G^{-1} .

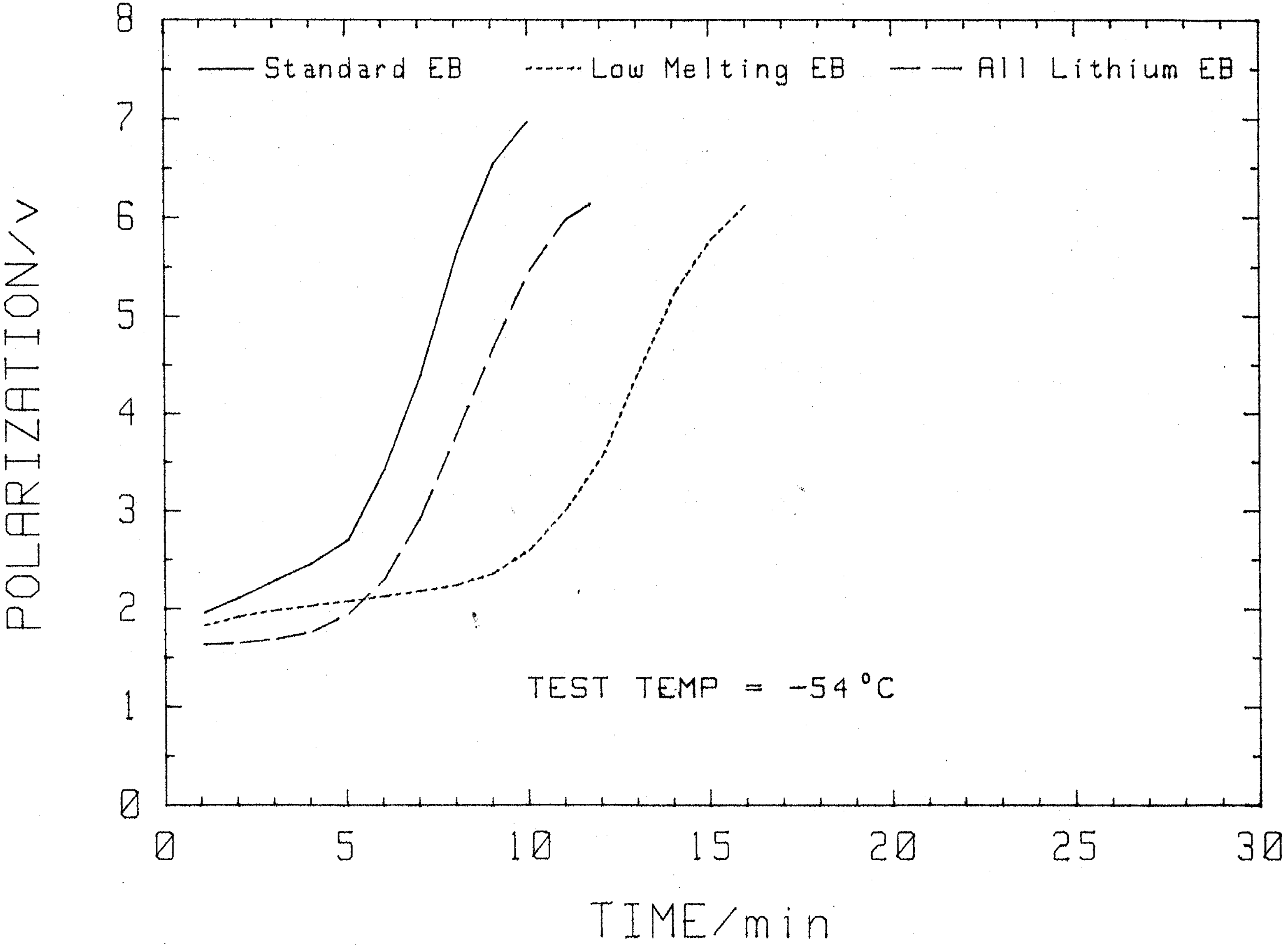
Electrolyte	Temp./ deg. C	Activated Life/s	Voltage at 3 s/V	Rise Time to 26 V/ms
Standard	-54	9.7	26.0	150.0
(40% MgO)	82	11.2	28.0	101.0
All-Li	-54	13.0	27.3	112.3
(35% MgO)	82	19.8	29.4	85.5

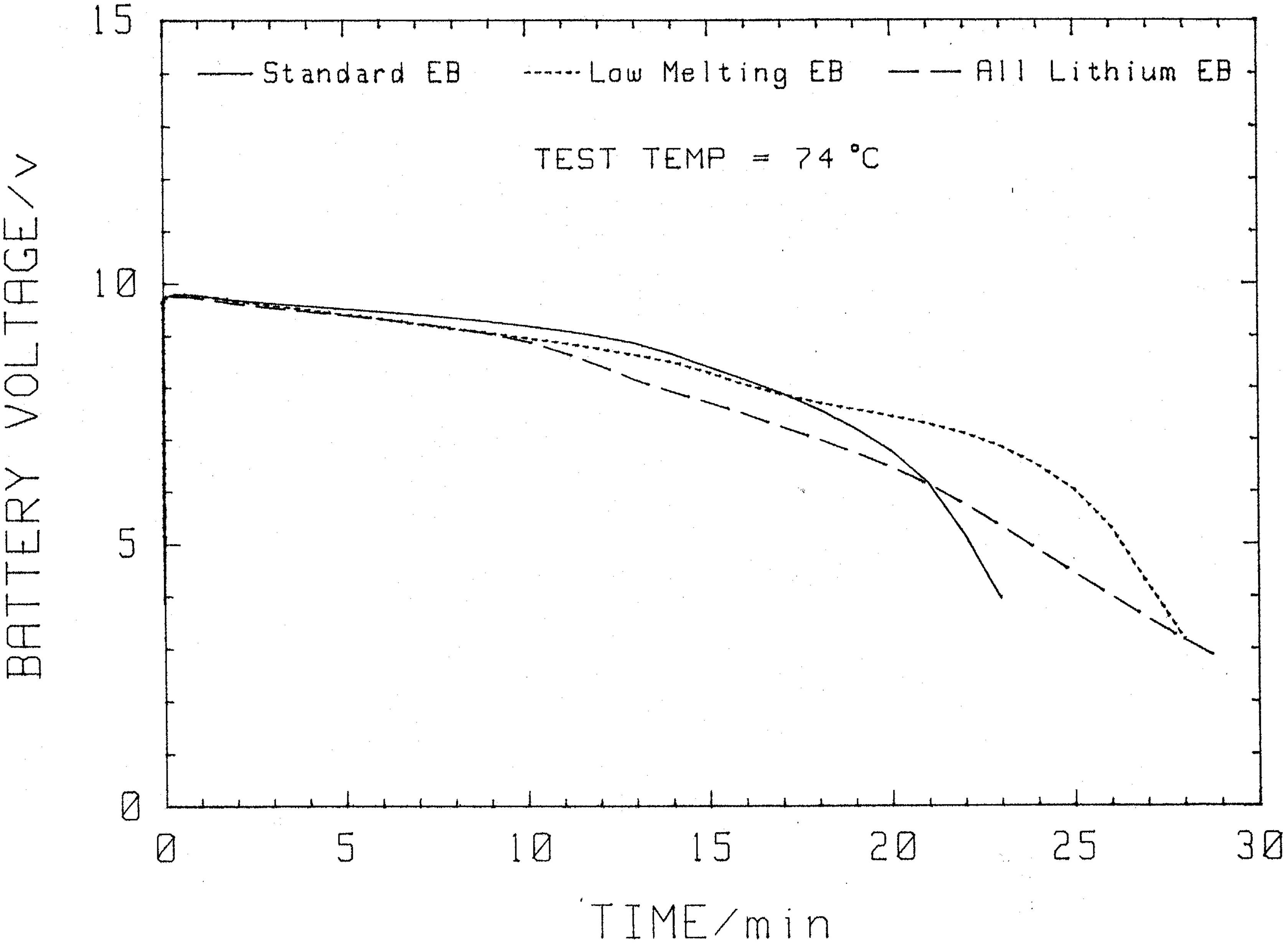

Capacity to 1.25 V/coulombs
1200
1000
800
600
400
200
350
400
450
500
550
600
Temperature/deg. C
Theo. for 1.5 eq/FeS_2
Fused, lithiated catholyte
73.5% FeS_2/25% EB/1.5% Li_2O
LiCl-KCl ■
LiCl-LiBr-KBr △
LiBr-KBr-LiF ⊙
LiCl-LiBr-LiF ●
LiCl-KCl-RbCl □
LiBr-KBr-CsBr ▲

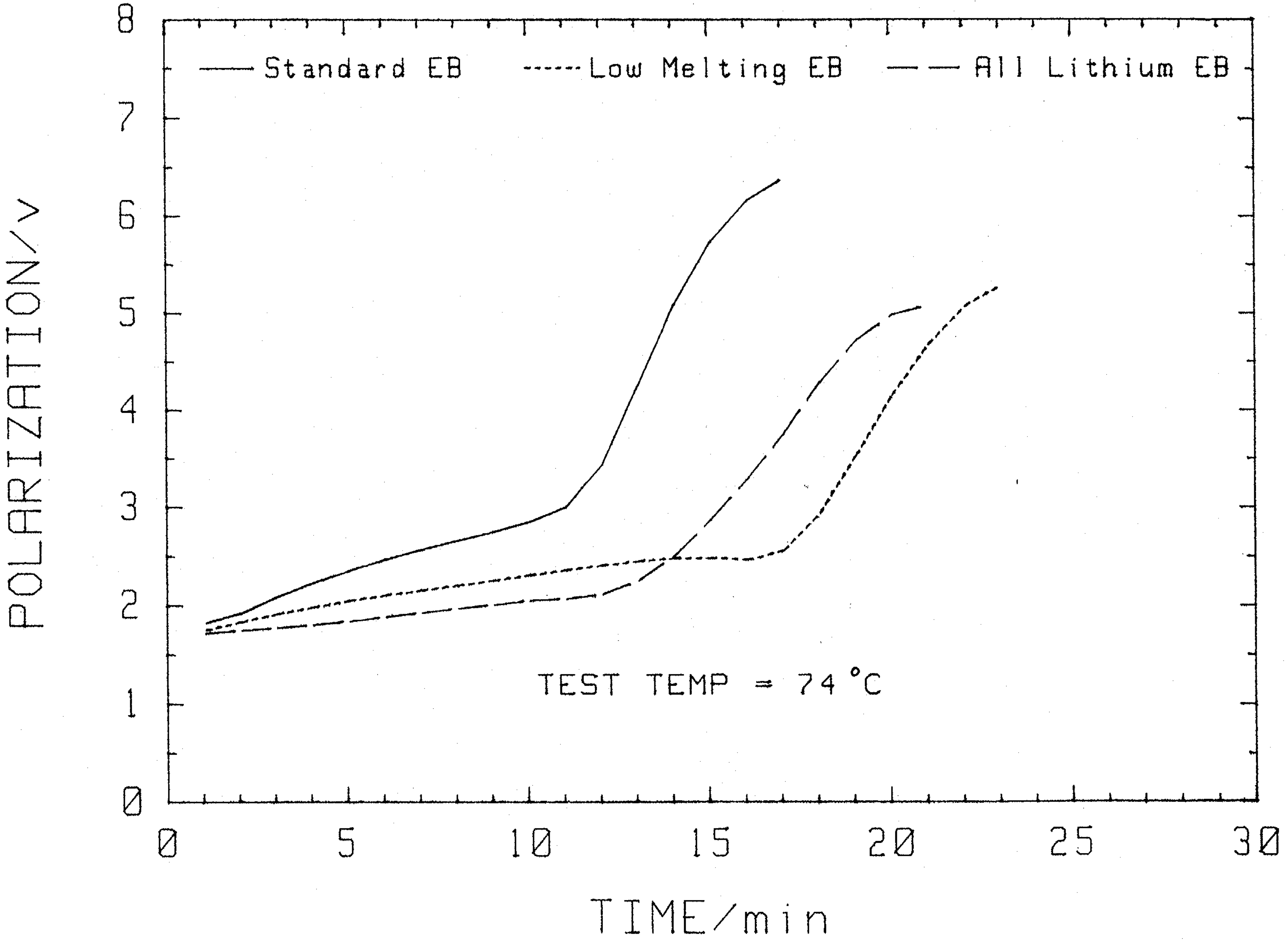

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Resistivity, ohm-cm
350
400
450
500
550
600
650
Temperature, deg. C
LiCl-KCl Eut. 35% MgO
LiCl-LiBr-KBr Eut. 30% MgO
LiBr-KBr-LiF Eut. 25% MgO
LiCl-LiBr-LiF Eut. 35% MgO



15
10
5
0
BATTERY VOLTAGE/V
0
5
10
15
20
25
30
TIME/min
Standard EB
Low Melting EB
All Lithium EB
TEST TEMP = -54 °C


Standard EB
Low Melting EB
All Lithium EB
TEST TEMP = -54 °C
POLARIZATION/V
TIME/min
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
30


Standard EB
Low Melting EB
All Lithium EB
TEST TEMP = 74 °C
BATTERY VOLTAGE/V
15
10
5
0
0
5
10
15
20
25
30
TIME/min


Standard EB
Low Melting EB
All Lithium EB
TEST TEMP = 74 °C
POLARIZATION/V
TIME/min
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
30

ABSTRACT

The main electrolyte used in thermal batteries is the LiCl-KCl eutectic that melts at 352°C. The LiCl-LiBr-LiF eutectic, however, has far superior rate and power capabilities. There are several eutectic electrolytes that have a larger liquidus range and melt at temperatures much lower than that for the LiCl-KCl eutectic. The relative performance of the LiCl-KCl eutectic, the all-Li eutectic, and several low-melting eutectics in Li(Si)/FeS_2 single cells discharged at constant-current under isothermal conditions is discussed, along with that for 5-cell batteries. The results of validation tests with full-sized long-life and pulse thermal batteries are presented.

LEGENDS

Fig. 1. Capacity of Li(Si)/FeS_2 Single Cells as a Function of Temperature and Electrolyte.

Fig. 2. Resistivities of Optimum Electrolyte-Binder Compositions as a Function of Temperature.

Fig. 3. Steady-state Voltage as a Function of Electrolyte for 5-cell Li(Si)/FeS_2 Thermal Batteries Activated at -54°C and Discharged Under a 50-ohm Load (1.05 Ohms Applied Every 5 s Per 60-s Cycle).

Fig. 4. Voltage Loss During 1.05-ohm Pulses as a Function of Electrolyte for 5-cell Li(Si)/FeS_2 Thermal Batteries Activated at -54°C.

Fig. 5. Steady-state Voltage as a Function of Electrolyte for 5-cell Li(Si)/FeS_2 Thermal Batteries Activated at 74°C and Discharged Under a 50-ohm Load (1.05 Ohms Applied Every 5 s Per 60-s Cycle).

Fig. 6. Voltage Loss During 1.05-ohm Pulses as a Function of Electrolyte for 5-cell Li(Si)/FeS_2 Thermal Batteries Activated at 74°C.